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Striking Differences in Properties of Geometric Isomers of $[\text{Ir}(\text{tpy})(\text{ppy})\text{H}]^+$: Experimental and Computational Studies of their Hydricities, Interaction with CO_2 , and Photochemistry

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Abstract: We prepared two geometric isomers of $[\text{Ir}(\text{tpy})(\text{ppy})\text{H}]^+$, previously proposed as a key intermediate in photochemical CO_2 reduction to CO, and characterized their notably different ground- and excited-state interactions with CO_2 and their hydricities using experimental and computational methods. Only one isomer, *C-trans*- $[\text{Ir-H}]^+$, reacts with CO_2 to generate the formate complex in the ground state, consistent with its calculated hydricity. Under photocatalytic conditions in $\text{CH}_3\text{CN}/\text{TEOA}$, a common reactive *C-trans*- $[\text{Ir}]^0$ species, irrespective of the starting isomer or monodentate ligand (e.g., hydride, Cl, etc.), reacts with CO_2 and produces CO with the same quantum yield.

The photochemical reduction of CO_2 to useful chemicals such as CO, formic acid or methanol has gathered significant attention during the last several decades due to problems related to the depletion of fossil fuels and global warming.^[1] Despite the challenges associated with the high thermodynamic and kinetic stability of CO_2 , a number of photocatalytic systems have been investigated with transition metal polypyridyl complexes^[2] as photosensitizers and as catalysts/precatalysts together with sacrificial electron donors. Typical products of photochemical CO_2 reduction are CO and formate, which have been proposed to form via metal-carboxylate and metal-hydride intermediates, respectively, however in some cases proton reduction to H_2 is a competing reaction.

Sato et al. have recently reported an efficient photocatalytic system with $[\text{Ir-Cl}]^+$ ($\text{Ir} = \text{Ir}(\text{tpy})(\text{ppy})$, tpy = 2,2':6',2''-terpyridine, ppy = 2-phenylpyridine) and triethanolamine (TEOA) in CH_3CN that selectively reduces CO_2 to CO under visible light ($410 < \lambda < 750 \text{ nm}$) with a TON of 38 and quantum yield (Φ_{CO}) of 0.13.^[3] This system is twice as efficient as the well-known $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ system under the given conditions.^[3] The proposed catalytic cycle includes the formation of the one-electron-reduced (OER) species, followed by the loss of the coordinated Cl^- and the formation of the hydride species with further reduction. While $[\text{Ir-H}]^+$ was detected by ^1H NMR during the photocatalytic reaction, it does not react with CO_2 in its ground state. Therefore, the further reduced species produced by its photoreduction was considered to react with CO_2 to form a

CO_2 adduct, followed by the removal of CO .^[3] Although the isolation of the hydride complex was mentioned, no synthetic or mechanistic details were provided regarding the reactivity of the hydride.

More recently, Rieger et al. have developed mononuclear $\text{Ir}(\text{III})$ photocatalysts $[\text{Ir}(\text{tpy})(\text{mppy})\text{Cl}]^+$ (mppy = 4-methyl-2-phenylpyridine) and the dinuclear analogues with bis(2-phenylpyridin-4-yl) bridges for photo-induced CO_2 reduction.^[4] They proposed the involvement of five-coordinate $[\text{Ir}(\text{tpy})(\text{mppy})]^{+0}$ without any hydrides. Because the involvement of Ir-hydride intermediates in photochemical CO_2 reduction is not clear, we believe that a more complete understanding of Ir-hydride intermediates is important for the rational development of new catalysts for CO_2 reduction/ CO_2 hydrogenation. Here we have isolated two isomers of $[\text{Ir-H}]^+$, where the hydride is *trans* to either N of ppy (*N-trans*- $[\text{Ir-H}]^+$) or to C of ppy (*C-trans*- $[\text{Ir-H}]^+$) as shown in Scheme 1, and have studied their distinct reactivity in the ground and excited states. We also report on the comparison of the hydricity of the two isomers and its relation to their CO_2 reduction through theoretical and experimental investigations. In fact, the hydricity is an important concept in the reduction of CO_2 beyond CO and formate.^[5,6]

Scheme 1. Geometric isomers of $[\text{Ir}(\text{tpy})(\text{ppy})\text{H}]^+$

Two hydride isomers, *N-trans*- $[\text{Ir-H}]^+$ and *C-trans*- $[\text{Ir-H}]^+$, were prepared by a modification of the published procedures^[7] for $[\text{Ru}(\text{tpy})(\text{ppy})\text{H}]^+$ and are described in detail in the SI. The final yield of *N-trans*- $[\text{Ir-H}]^+$ was low (~10 %) owing to the formation of a hydride bridged iridium dimer, *C-trans*- $[\text{Ir-H-Ir}]^{3+}$, taking place as a side reaction. *C-trans*- $[\text{Ir-H}]^+$ is more difficult to synthesize on a large scale due to its conversion to the more stable *N-trans*- $[\text{Ir-H}]^+$ and the formation of the *C-trans*- $[\text{Ir-H-Ir}]^{3+}$ dimer during the synthesis. The $\mu\text{-H}$ chemical shift was observed at -11.4 ppm (Figure S1), and Ir-H signals for *N-trans*- and *C-trans*- $[\text{Ir-H}]^+$ were found at -19.3 and -7.46 ppm, respectively (Figures S2 and S3). The X-ray structure of *N-trans*- $[\text{Ir-H}](\text{PF}_6)$ has been determined (see Figures S4 and S5) and selected bond distances and angles are summarized together with calculated ones at the M06 level of theory^[8] (see Computational Methods in the SI) for both geometric isomers (Table S2). It should be noted that the calculated Ir-H distance in *C-trans*- $[\text{Ir-H}]^+$ is 0.11 Å longer than that in *N-trans*- $[\text{Ir-H}]^+$ as expected due to the stronger *trans* influence in the former. The hydride isomers exhibit different absorption spectra as shown in Figure 1 and Table 1. The λ_{max} for the MLCT transition occurs at 371 nm ($\epsilon = 6450 \text{ M}^{-1} \text{ cm}^{-1}$) and 385 nm ($\epsilon = 4430 \text{ M}^{-1} \text{ cm}^{-1}$) for *N-trans*- $[\text{Ir-H}]^+$ and *C-trans*- $[\text{Ir-H}]^+$, respectively. Consistent with the large spin-orbit coupling constant of Ir, absorption bands or

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Supporting information for this article is given via a link at the end of the document. CCDC 1415385 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

shoulders also appear to the red of the main peak from 450 to 550 nm for both hydrides due to mixing of excited-state singlet and triplet charge-transfer states.^[9] The calculated UV-vis spectra for *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺ using TDDFT display λ_{max} for the MLCT transition at 366 and 395 nm, respectively, consistent with the experimental spectra (Figure S6). Also, calculations show that the lower absorption bands originate from excitations from Ir-ppy(d- π) based orbitals to tpy. There is strong "ppy" character in the orbital from which excitation occurs.

Figure 1. UV-vis spectra of *N-trans*-[Ir-H]⁺ (black) and *C-trans*-[Ir-H]⁺ (gray) in CH₃CN.

We performed DFT calculations in an attempt to investigate the different reactivity of *N-trans*-[Ir-X]ⁿ⁺ and *C-trans*-[Ir-X]ⁿ⁺ (*n* = 1 with X = H⁻, Cl⁻; *n* = 2 with X = CH₃CN) in the ground state. In the case of Cl⁻ or CH₃CN bound to the Ir center, the *C-trans* isomers are more stable by 8.1 and 6.1 kcal/mol, respectively. Interestingly, *N-trans*-[Ir-H]⁺ is favored by 4.4 kcal/mol compared to *C-trans*-[Ir-H]⁺. As a result, the formation of *N-trans*-[Ir-H]⁺ from the CH₃CN adduct is favored by 10.4 kcal/mol compared to *C-trans*-[Ir-H]⁺, indicating the higher stability of *N-trans*-[Ir-H]⁺ (Scheme S1).

The CO₂ insertion reaction into the Ir-hydride bond to generate a metal-formate complex was investigated for both *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺ isomers. After bubbling CO₂ into the CD₃CN solution of *N-trans*-[Ir-H]⁺, no changes in the ¹H NMR spectrum were observed at RT or 70°C (Figure S7). However, immediate loss of the Ir-H proton peak at -7.46 ppm was observed with *C-trans*-[Ir-H]⁺ while new peaks in the aromatic region (Figure S8) appeared at room temperature. The reactivity of *C-trans*-[Ir-H]⁺ was further confirmed with ¹³CO₂ (a new intense signal at 169.1 ppm with *J*(C,H) = 206 Hz, Figure S9) and ESI-MS (Figure S11), suggesting the generation of a formate species. The drastic difference in the CO₂ reactivity towards ground-state *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺ is possibly due to the difference in their Ir-H bond strength and hydride donor ability, or hydricity (see below).

Next, we examined computationally the reactivity of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺ towards CO₂ and found that the formation of the formate complexes, *N-trans*-[Ir-OCHO]⁺ and *C-trans*-[Ir-OCHO]⁺, by CO₂ insertion into the Ir-H bond is endoergic by 14.6 and 2.0 kcal/mol, respectively. Such a difference in free-energy changes (ΔG_s) for a hydride transfer reaction to CO₂ stems from the greater stabilization of the hydride in *N-trans*-[Ir-H]⁺ compared to other ligands (e.g., CH₃CN) and *C-trans*-[Ir-H]⁺. We also located the transition state (TS) structure for the reaction with *C-trans*-[Ir-H]⁺ (Figure S12), which proceeds with an activation free energy ($\Delta G^\ddagger$) of 14.1 kcal/mol, consistent with the experimental observation of that reaction occurring even at room temperature. Despite all our

efforts, we could not locate a similar TS for *N-trans*-[Ir-H]⁺ as all structures investigated converged to the initial hydride complex, indicating that CO₂ insertion into *N-trans*-[Ir-H]⁺ is not favorable in accord with the endoergic nature of the reaction.

Table 1. Properties of geometric isomers of [Ir-H]⁺.

	<i>N-trans</i> -[Ir-H] ⁺	<i>C-trans</i> -[Ir-H] ⁺
¹ H NMR chemical shift of Ir-H (ppm)	-19.3	-7.46
UV-vis abs.: obsd (nm, M ⁻¹ cm ⁻¹)	371 (6450), 550sh, 530	385sh (4400), 500sh
Calcd MLCT abs. (nm)	366	395
Measured $\Delta G^\circ_{\text{H}^+}$ (kcal/mol)	57	—
Calcd $\Delta G^\circ_{\text{H}^+}$ (kcal/mol)	53.7	43.2
Calcd Ir-H distance (Å)	1.62	1.73
Potentials in CH ₃ CN vs SCE (V)	1.14, -1.30, -1.60	—
Ground-state reactivity toward CO ₂	No	Formation of <i>C-trans</i> -[Ir-OCHO] ⁺
Excited-state lifetime (ns)	176	112
Emission max (nm)	605	—
<i>k_q</i> by TEA (M ⁻¹ s ⁻¹)	1 × 10 ⁸	No quenching, Ir-H cleavage

Cyclic voltammograms of *N-trans*-[Ir-H]⁺ in CH₃CN under Ar or CO₂ are shown in Figure S13. Under Ar, the *N-trans*-[Ir-H]⁺ complex exhibits one reversible reduction of tpy at -1.30 V vs SCE (or -1.70 V vs Fc^{+/0}) followed by a small shoulder at -1.60 V. The oxidation of the iridium metal was observed at potential *E_p* = 1.14 V. Under a CO₂ atmosphere, a catalytic current peak was observed at the first reduction wave (ca. -1.30 V) with slightly increased current compared to that under Ar. A large catalytic current was observed before reaching -1.60 V. This result indicates that *N-trans*-[Ir-H]⁺ also has electrocatalytic ability towards CO₂ reduction, which is similar to what was observed for [Ir(tpy)(ppy)Cl]⁺ by Sato et al.⁹ Experiments were also performed on *C-trans*-[Ir-H]⁺ in acetonitrile, however, we could not obtain reliable data due to its instability and the labile nature of its Ir-H bond.

The hydricities of transition-metal hydrides and their relation to CO₂ reduction activity have been well studied.^[5,6] It is of interest to measure the thermodynamic hydricities of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺ in order to fully understand the CO₂ reduction mechanism. To determine the hydride donor ability of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺, we performed hydride-transfer reactions with an appropriate hydride acceptor of known hydride affinity. The reaction of *N-trans*-[Ir-H]⁺ to hydride acceptors such as the BF₄ salts of tris(*p*-methoxyphenyl)trityl and 4-(acetylamino)-2,2,6,6-tetramethyl-1-oxo-piperidinium (TEMPO⁺) through thermodynamic cycles provides the ground-state hydricity of $\Delta G^\circ_{\text{H}^-} = 57 \pm 4$ kcal/mol in CH₃CN (see the SI). While there exists some ambiguity in the geometric change (i.e., *N-trans*-[Ir-H]⁺ to *C-trans*-[Ir-NCCH₃]²⁺), the observed hydricity of *N-trans*-[Ir-H]⁺ is very similar to that of [CpRe^I(NO)(CO)(CHO)] ($\Delta G^\circ_{\text{H}^-} = 55$ kcal/mol).⁷ The relatively weak ground-state hydricity of *N-trans*-[Ir-H]⁺ explains its stability and lack of reactivity towards CO₂ in the ground state.

Efforts were also made to determine the ground-state hydricity of *C-trans*-[Ir-H]⁺. We encountered difficulty in measuring the heat of reaction of *C-trans*-[Ir-H]⁺ with tris(*p*-methoxyphenyl)-trityl or TEMPO[•] due to the instability of the hydride.

We also performed DFT calculations to predict the hydricity of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-H]⁺, and to do so we calculated hydricities relative to the [Ru^{II}(tpy)(bpy)H]^{+/0}/[Ru^{II}(tpy)(bpy)-(CH₃CN)]²⁺ couple for which the experimental hydricity is known ($\Delta G^{\circ}_{\text{H}^-} = 39$ kcal/mol).^[6] We calculated ($\Delta G^{\circ}_{\text{H}^-} = 53.7$ kcal/mol for *N-trans*-[Ir-H]⁺ which is in good agreement with the experimentally determined value of $\Delta G^{\circ}_{\text{H}^-} = 57$ kcal/mol. Using the same approach, we calculated $\Delta G^{\circ}_{\text{H}^-} = 43.2$ kcal/mol for *C-trans*-[Ir-H]⁺, displaying a similar hydricity to HCOO⁻ (43 kcal/mol) and consistent with the experimental result of CO₂ insertion into its Ir-H bond.

Figure 2. Left: Transient absorption spectra of *N-trans*-[Ir-H]⁺ in the presence of 50 mM TEA at 50 ns (□) and 500 ns (Δ) in CH₃CN. Right: Expanded transient absorption spectrum of the product.

Excitation of *N-trans*-[Ir-H]⁺ with λ_{exc} of 420 nm produces the ³MLCT excited state and the transient spectrum at 50 ns (Figure 2, left panel, black trace(□)), when the hydride is still in contact with the iridium metal atom, which features an absorption at 340 nm ascribed to a $\pi \rightarrow \pi^*$ transition. The excited state spectrum also reveals new transient absorption bands at 410 and 600 nm. The excited state lifetime of 176 ns (Figure S16) is much shorter than those of *C-trans*-[Ir-Cl]⁺ and *C-trans*-[Ir-NCCH₃]²⁺ (2.2 and 2.6 μ s, respectively, Figure S17). The ³MLCT excited state was quenched in the presence of a sacrificial electron donor such as triethylamine (TEA) yielding the one-electron-reduced species of *N-trans*-[Ir-H]⁺ in CH₃CN where the added electron primarily resides in the tpy- π^* -orbitals. The quenching rate constant (k_q) of 1×10^8 M⁻¹ s⁻¹ (Figure S18) is slower than that of *C-trans*-[Ir-Cl]⁺ (3×10^9 M⁻¹ s⁻¹, Figure S19). To identify the product, we carried out Na-Hg reduction of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-NCCH₃]²⁺ in CH₃CN (Figures S20-S21). The spectra of the mono-reduced *N-trans*-[Ir-H]⁺ and the doubly-reduced *C-trans*-[Ir-NCCH₃]²⁺ species are identical indicating the formation of penta-coordinate [Ir]⁰ on the time scale of Na-Hg reduction (10-20 min), presumably by forming 1/2 equiv. of H₂. However, the transient spectrum at 500 ns (Figure 2, right panel) is slightly different from the difference spectrum of *N-trans*-[Ir-H]⁺ and the OER species obtained by Na-Hg reduction (Figure S21) indicating that the Ir-H bond may be intact on this time scale. In fact, the decay kinetics of this reduced species of *N-trans*-[Ir-H]⁺ was not influenced by the presence of CO₂ up to 50 ms (Figure S23). However, as mentioned earlier, the CV under CO₂ exhibits a catalytic current after passing the first reduction potential, indicating that [Ir]⁰ formed by the Ir-H bond cleavage is reactive toward CO₂.

The decay of the excited-state of *C-trans*-[Ir-H]⁺ obeys pseudo-first-order kinetics with a lifetime of about 112 ns (Figure S24). The initial excited-state spectrum of *C-trans*-[Ir-H]⁺ at 50

ns is shown in Figure S25, black trace. No peak at ca. 410 nm was observed for *C-trans*-[Ir-H]⁺. The ³MLCT excited-state could not be quenched with TEA. Furthermore, the bulk photolysis of *C-trans*-[Ir-H]⁺ in CD₃CN monitored by ¹H NMR exhibits the immediate loss of the hydride proton to form the penta-coordinate [Ir]⁰ species (Figure S27). The ³MLCT excitation reduces the electron donor ability of the iridium metal center and enhances the release of the proton as a photoacid. This type of photoinduced excited-state deprotonation has also been observed in other iridium hydride complexes.^[10] It should be noted that *N-trans*-[Ir-H]⁺ was produced with ~40 % yield after a prolonged 10-min bulk photolysis indicating that the protonation of [Ir]⁰ occurs to generate the stable isomer (Figure S27).

Figure 3. Photocatalytic CO formation with 0.5 mM *N-trans*-[Ir-H]⁺ (●) and 0.5 mM *C-trans*-[Ir-H]⁺ (○) in CH₃CN/TEOA (5:1) under CO₂ atmosphere.

Scheme 2. Possible mechanism for photocatalytic CO₂ reduction with [Ir-H]⁺. Unit of ΔG : kcal/mol.

We explored photocatalytic CO₂ reduction using both hydride isomers under visible light irradiation (> 410 nm) in the presence of the sacrificial electron donor TEOA as shown in Figure 3. Both hydrides show similar quantum efficiency (Φ_{CO}) of nearly 13% and a TON of about 45. These results are in good agreement with the efficiency of [Ir-Cl]⁺ in the previous reports.^[3] Small amounts of H₂ and HCOOH were also produced during photocatalytic CO₂ reduction by the hydrides. The similar efficiency of CO formation by both hydrides indicates that the actual photocatalytic reaction occurs through a common penta-coordinate [Ir]⁰ intermediate. We investigated computationally the generation of [Ir]⁰ from both hydride isomers and the mechanism of CO₂ reduction with [Ir]⁰ as the key intermediate. The proposed pathways for CO generation are summarized in

Scheme 1. An interesting feature of the proposed mechanism is that only the *C-trans*-[Ir]⁰ isomer exists in the ground state and is the key reactive species. The detailed theoretical results are described in the SI.

In conclusion, we have investigated using experimental and computational methods the interaction of CO₂ with [Ir–H]⁺ that was previously proposed as the key intermediate. We find that only one isomer, *C-trans*-[Ir–H]⁺, reacts with CO₂ to generate the formate complex at room temperature. Under irradiation, this hydride acts as a photoacid to produce penta-coordinate *C-trans*-[Ir]⁰, which is involved in the photocatalytic reduction of CO₂ to CO. The other hydride isomer, *N-trans*-[Ir–H]⁺, does not react with CO₂ at room temperature or even at higher temperatures to generate the formate complex whereas during the photocatalytic CO₂ reduction cycle with an electron donor, penta-coordinate *C-trans*-[Ir]⁰ (to the vacant site) is formed to generate CO from CO₂. The proposed mechanism for photochemical CO₂ reduction is shown in Scheme 1 (see SI for a detailed description of the proposed mechanism) which features a common reactive *C-trans*-[Ir]⁰ species irrespective of the starting isomer or ligand (e.g., hydride, CH₃CN, etc.) The presence of only one isomer, namely *C-trans*-[Ir]⁰, as a penta-coordinate complex at the formal Ir^I oxidation state is a quite interesting observation and will have profound implications in future ligand design for CO₂ reduction catalysts. In addition to the mechanism, we have also compared the ground-state hydricities of these two isomers. Our evaluation of the hydricities and understanding of mechanism of CO₂ photoreduction should help in further developments in this area. We are currently investigating more details of the CO₂ reaction with [Ir]⁰ and the subsequent reactions.

Experimental Section

The starting complexes [Ir(tpy)Cl₃] and [Ir–Cl]⁺ were prepared according to the previously reported literature procedures.^[3,11] The complexes [Ir–OH₂]²⁺ and [Ir–NCCH₃]²⁺ were prepared by the Cl[–] ligand replacement from [Ir–Cl]⁺ by using water or acetonitrile as the solvent. [Ir–Cl]⁺, [Ir–OH₂]²⁺, and [Ir–NCCH₃]²⁺ were found to have the monodentate ligand *trans* to C of ppy, therefore, we do not specify the geometries thereafter. The synthesis procedure, NMR, ESI-MS, UV-vis and elemental analysis of *N-trans*-[Ir–H](PF₆) and *C-trans*-[Ir–H](PF₆) are summarized in the SI. The detailed procedures and the results of the following experiments are presented in the supporting information: ground- and excited-state chemistry; electrochemistry; reactions with CO₂; X-ray structure of *N-trans*-[Ir–H]⁺; theoretical and experimental determination of the hydricities; and DFT calculations of various Ir species to determine the possible CO₂ reduction mechanism.

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Page No. – Page No.

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Hydricities, Interaction with CO_2 , and
Photochemistry**

Striking Differences of Properties of Geometric Isomers of [Ir(tpy)(ppy)H]⁺: Experimental and Computational Studies on their Hydricities, Interaction with CO₂, and Photochemistry

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Supporting Information

Table of Contents

Experimental Section	S3
Figure S1. ^1H NMR spectra of <i>C-trans</i> - $[\text{Ir-H-Ir}]^{3+}$	S6
Figure S2. ^1H NMR spectra of <i>N-trans</i> - $[\text{Ir-H}]^+$	S7
Figure S3. ^1H NMR spectra of <i>C-trans</i> - $[\text{Ir-H}]^+$	S7
X ray structure of <i>N-trans</i> - $[\text{Ir-H}]^+$	S8
Table S2. Selected experimental and DFT calculated bond lengths and bond angles	S11
Figure S6. Calculated UV-vis absorption spectra for <i>N-trans</i> - $[\text{Ir-H}]^+$ & <i>C-trans</i> - $[\text{Ir-H}]^+$	S12
Figure S7. ^1H NMR spectra of <i>N-trans</i> - $[\text{Ir-H}]^+$ under CO_2 atmosphere	S13
Figure S8. ^1H NMR spectra of <i>C-trans</i> - $[\text{Ir-H}]^+$ under CO_2 atmosphere	S13
Figure S9. ^{13}C NMR spectrum of <i>C-trans</i> - $[\text{Ir-H}]^+$ under $^{13}\text{CO}_2$	S14
Figure S10. HMBC spectrum of <i>C-trans</i> - $[\text{Ir-H}]^+$ under $^{13}\text{CO}_2$	S14
Figure S11. ESI-MS spectrum of <i>C-trans</i> - $[\text{Ir-H}]^+$ under $^{13}\text{CO}_2$	S15
Scheme S1. Relative free energy change for the formation of <i>N-trans</i> - $[\text{Ir-H}]^+$ and <i>C-trans</i> - $[\text{Ir-NCCH}_3]^{2+}$	S15
Figure S12. Optimized transition state structure for hydride transfer from <i>C-trans</i> - $[\text{Ir-H}]^+$ to CO_2	S16
Table S3. Reduction potentials of Ir complexes in CH_3CN	S16
Figure S13. Cyclic voltammogram of <i>N-trans</i> - $[\text{Ir-H}]^+$	S17
Determination of the hydricity of <i>N-trans</i> - $[\text{Ir-H}]^+$	S18
Figure S16. Excited-state decay of <i>N-trans</i> - $[\text{Ir-H}]^+$	S23
Figure S17. Transient absorption spectra and kinetic traces for <i>C-trans</i> - $[\text{Ir-Cl}]^+$ & <i>C-trans</i> - $[\text{Ir-NCCH}_3]^{2+}$	S24
Figure S18. Stern-Volmer plot of <i>N-trans</i> - $[\text{Ir-H}]^+$	S25
Figure S19. Reductive quenching of <i>C-trans</i> - $[\text{Ir-Cl}]^+$ by TEA	S26
Figure S20. Na-Hg reduction of <i>C-trans</i> - $[\text{Ir-NCCH}_3]^{2+}$	S27
Figure S21. Na-Hg reduction of <i>N-trans</i> - $[\text{Ir-H}]^+$ in CH_3CN	S28
Figure S22. Kinetic trace for <i>N-trans</i> - $[\text{Ir-H}]^+$ presence of 50 mM TEA	S29
Figure S23. Kinetic trace for <i>N-trans</i> - $[\text{Ir-H}]^+$ in the presence of 0.24 M TEA under CO_2	S29
Figure S24. Excited state decay of <i>C-trans</i> - $[\text{Ir-H}]^+$	S30
Figure S25. Transient absorption spectra of <i>C-trans</i> - $[\text{Ir-H}]^+$	S30
Figure S26. ^1H NMR spectra for bulk photolysis of <i>N-trans</i> - $[\text{Ir-H}]^+$	S31
Figure S27. ^1H NMR spectra for bulk photolysis of <i>C-trans</i> - $[\text{Ir-H}]^+$	S31
CO_2 Reduction Mechanism	S32
References	S36
Cartesian Coordinates and Electronic Energies of Optimized Structures at M06 Level	S38

1. Experimental Section

Materials. The reagent $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ was purchased from Pressure Chemicals and 2-phenylpyridine (ppy), NaBH_4 , and KPF_6 were purchased from Sigma-Aldrich. The solvents acetonitrile, dichloromethane, methanol, ethylene glycol and diethyl ether were purchased from Sigma-Aldrich. Anhydrous CH_3CN and CD_3CN were further dried over molecular sieves and stored under argon inside a glove box. The starting complexes $[\text{Ir}(\text{tpy})\text{Cl}_3]$ and $[\text{Ir}(\text{tpy})(\text{ppy})\text{Cl}]^+$ ($[\text{Ir}-\text{Cl}]^+$) were prepared according to the previously reported literature procedures.^{1,2} The complexes $[\text{Ir}(\text{tpy})(\text{ppy})(\text{OH}_2)]^{2+}$ ($[\text{Ir}-\text{OH}_2]^{2+}$) and $[\text{Ir}(\text{tpy})(\text{ppy})(\text{NCCH}_3)]^{2+}$ ($[\text{Ir}-\text{NCCH}_3]^{2+}$) were prepared by the Cl^- ligand replacement from $[\text{Ir}-\text{Cl}]^+$ using water or acetonitrile as the solvent. $[\text{Ir}-\text{Cl}]^+$, $[\text{Ir}-\text{OH}_2]^{2+}$, and $[\text{Ir}-\text{NCCH}_3]^{2+}$ were found to have the monodentate ligand *trans* to C of ppy, therefore, we do not specify their geometries thereafter. The synthesis procedure, NMR, ESI-MS, UV-vis and elemental analysis of *N-trans*- $[\text{Ir}-\text{H}](\text{PF}_6)$ and *C-trans*- $[\text{Ir}-\text{H}](\text{PF}_6)$ are summarized below.

Synthesis of Complexes

N-trans- $[\text{Ir}-\text{H}](\text{PF}_6)$: To a methanol solution (20 mL, not recommended to use an anhydrous one) of *C-trans*- $[\text{Ir}-\text{NCCH}_3](\text{PF}_6)_2$ (200 mg, 0.223 mmol), NaBH_4 (17 mg, 0.446 mmol) was added under air. The mixture was stirred for about 5 min under air and then Ar-bubbled for 10 min. NaBH_4 (85 mg, 2.23 mmol) was added again to the solution under Ar and then the resulting green solution was stirred for 4-5 hours. The color of the solution turned red. Solvent was then completely removed. The reddish brown solid was washed well with dichloromethane, the extract was collected, and solvent was removed. The crude material also showed the presence of a hydride-bridged iridium dimer. However, *N-trans*- $[\text{Ir}-\text{H}](\text{PF}_6)$ was purified by using a silica gel flash column with dichloromethane as the eluent in the dark at once. The first pink colored band was collected and the solvent was removed to give the compound in pure form. Yield: 10-15 mg (~ 10%). ¹H-NMR (400 MHz, CD_3CN): δ 8.51 (d, $J = 8.1$ Hz, 2H), 8.32 (d, $J = 8.1$ Hz, 2H), 8.27 (t, $J = 8.0$ Hz, 1H), 8.17 (d, $J = 7.3$ Hz, 1H), 7.99 (ddd, $J = 21.9, 17.7, 8.0$ Hz, 6H), 7.67 (t, $J = 8.0$ Hz, 1H), 7.36-7.22 (m, 4H), 7.19 (d, $J = 5.0$ Hz, 1H), 6.89-6.82 (m, 2H), -19.30 (s, 1H, IrH). Elemental Analysis: calc. for $\text{C}_{26}\text{H}_{20}\text{N}_4\text{IrPF}_6$: C, 43.04; H, 2.78; N, 7.72. Found: C, 43.04; H, 2.80; N, 7.25. ESI-MS analysis: calc. m/z : 581, observed m/z : 581. UV-vis: (CH_3CN) $\lambda_{\text{max}} = 371$ nm ($6450 \text{ M}^{-1}\text{cm}^{-1}$).

***C-trans*-[Ir-H](PF₆):** To a water solution containing an excess amount of NaBH₄ (46 mg, 1.21 mmol) and KPF₆ (55.7 mg, 0.3 mmol), a water: methanol (10:2) solution of [Ir-OH₂]²⁺ (25 mg, 0.03 mmol) was added dropwise at 0°C under Ar atmosphere. Each drop immediately formed orange-yellow powder in the solution. To obtain pure *C-trans*-[Ir-H](PF₆), a quick isolation of the orange-yellow powder from the cold solution is important. The powder was filtered and washed with water and dry-ether. Yield: 18 mg (85%). ¹H-NMR (400 MHz, CD₃CN (Ar bubbled)): (400 MHz, CD₃CN): δ 9.63 (ddd, J = 5.7, 1.4, 0.7 Hz, 1H, H1), 8.50 (d, J = 8.2 Hz, 2H, H17, H19), 8.39 (dd, J = 8.6, 1.2 Hz, 2H, H14, H22), 8.27 (d, J = 8.3 Hz, 1H, H4), 8.20 (td, J = 8.2, 0.9 Hz, 1H, H18), 8.12 (ddd, J = 8.3, 7.6, 1.6 Hz, 1H, H3), 7.98-7.91 (m, 4H, H11, H25, H13, H23), 7.81 (d, J = 7.7 Hz, 1H, H7), 7.47 (ddd, J = 7.6, 5.7, 1.4 Hz, 1H, H2), 7.29 (ddd, J = 7.5, 5.8, 1.4 Hz, 2H, H12, H24), 6.90 (ddd, J = 7.7, 7.5, 1.2 Hz, 1H, H8), 6.72 (ddd, J = 7.5, 7.3, 1.1 Hz, 1H, H9), 5.92 (d, J = 7.3 Hz, 1H, H10), - 7.46 (s, 1H, IrH). Elemental Analysis: calc. for C₂₆H₂₀N₄IrPF₆•0.2KPF₆•0.5CH₃CN: C, 40.68; H, 3.01; N, 7.03. Found: C, 40.33; H, 2.80; N, 6.96. ESI-MS analysis: calc. m/z: 581, observed m/z: 580.3. UV-vis: (CH₃CN) λ_{max} = 385 nm (4430 M⁻¹cm⁻¹).

Instrumentation. UV-vis spectra were measured on an Agilent 8453 spectrophotometer. ¹H and ¹³C NMR spectra were collected on a 400 MHz Bruker UltraShield spectrometer in deuterated acetonitrile (CD₃CN). Chemical shifts in ppm are referenced to the solvent peaks. Electrospray mass spectra (ESI-MS) were measured using a Thermo Finnigan mass spectrometer. Gaseous products such as CO and H₂ were analyzed by gas chromatography (GC) on an Agilent 6890N GC with HP-MOLSIV (30 m × 0.32 mm × 1.5 μm) and GS-CARBON-PLOT (15 m × 0.32 mm × 1.5 μm) columns. CO was quantified via a methanizer using a calibrated FID detector. The products in the solution were analyzed using a Dionex ICS-1600 ion chromatography (IC) instrument. Transient absorption and emission lifetime experiments were performed using a home-built instrument described elsewhere³ where the excitation was provided by an Opotek Vibrant LD 355 II OPO laser (420 nm, 1 mJ per pulse) at 5 Hz. For transient absorption measurements, the sample was probed by a pulsed 150 W Xe arc lamp in a 90° beam geometry arrangement and a Tetronix DPO40332 digital oscilloscope (350 MHz, 2.5GS s⁻¹) was used to digitize the transient signals obtained with a Hamamatsu R928 PMT detector. The sample cuvette was placed in a cell holder equipped with thermostat, and the temperature was maintained at about 25°C. The probe light was filtered through a combination of longpass and shortpass filters to avoid unnecessary irradiation of the sample. For emission lifetime measurements, same setup was used except the sample was not probed with the Xe arc lamp.

Photocatalytic reactions. Photocatalytic reactions were carried out in 10 mL round-bottom flasks at atmospheric pressure containing 4 mL of 5:1 (v/v) MeCN/TEOA solution with an Ir-

hydride (*N-trans*-[Ir-H]⁺ or *C-trans*-[Ir-H]⁺) concentration of 0.5 mM (2 μmol). The solution was purged with CO₂ for 15-20 min and was irradiated with a 150 W Xe lamp combined with a UV cutoff filter and a filter with a cutoff wavelength of 410 nm (42 L) at room temperature. The gaseous products such CO and H₂ were analyzed using a GC equipped with a TCD detector. The solution products were analyzed by IC. The temperature was maintained at 313 K with an eluent of 4.5/0.8 mM sodium carbonate/sodium bicarbonate solutions.

For quantum yield, the incident radiation intensity, I₀, was determined by potassium ferrioxalate actinometry.⁴ The photochemical quantum yield for CO production (Φ_{CO}) was determined according to the following equation:

$$\phi = \frac{[\text{CO}]}{I_0 t} \quad \text{eq. S1}$$

The turnover number (TON) was also calculated by the ratio of concentration of CO produced to the initial concentration of catalyst.

Computational Methods. All geometries were fully optimized at the M06 level of density functional theory⁵ with the SMD continuum solvation model⁶ for acetonitrile as solvent using the Stuttgart [8s7p6d2f | 6s5p3d2f] ECP60MWB contracted pseudopotential basis set⁷ on Ir ([8s7p6d2f | 6s5p3d2f] ECP28MWB basis set for Ru) and the 6-31G(d) basis set on all other atoms.⁸ Non-analytical integrals were evaluated using the integral=grid=ultrafine option as implemented in the Gaussian 09 software package.⁹ The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 cm⁻¹ replaced by 50 cm⁻¹ when computing free energies), and for determining the reactants and products associated with each transition-state structure (by following the normal modes associated with imaginary frequencies). Partition functions were used in the computation of 298 K thermal contributions to free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation.¹⁰ Free-energy contributions were added to single-point M06 electronic energies computed with the SDD basis set on Ir and the 6-311++G(2df,p) basis set on all other atoms to arrive at final, composite free energies.

Solvation effects associated with acetonitrile as solvent were accounted for using the SMD continuum solvation model as stated above. A 1 M standard state was used for all species in solution and the 1 M to 1 M solvation free energy of the proton was taken as -260.2 kcal/mol.¹¹

Time-dependent density functional theory (TDDFT) calculations were performed to predict the UV/visible electronic excitations of relevant structures. The B3LYP density functional,¹² Stuttgart [8s7p6d2f | 6s5p3d2f] ECP60MWB contracted pseudopotential basis set⁷ on Ir and the 6-311+G(d,p) basis set⁸ on all other atoms were used for the TDDFT calculations. Non-equilibrium solvation effects were included via the linear response approximation¹³ in

combination with the SMD aqueous continuum solvation model.⁶

Standard reduction potentials were calculated for various possible redox couples to assess the energetic accessibility of different intermediates at various oxidation states. For a redox reaction of the form

where O and R denote the oxidized and reduced states of the redox couple, respectively, and n is the number of electrons involved in redox reaction, the reduction potential $E_{O|R}^0$ relative to SCE was computed as

$$E_{O|R}^0 = -\frac{\Delta G_{O|R}^0}{nF} - \Delta E_{ref}^0 \quad \text{eq. S3}$$

where $\Delta G_{O|R}^0$ is the free energy change associated with eq. S2 (using Boltzmann statistics for the electron) and ΔE_{ref}^0 is taken as -4.422 V, which is required for the conversion of calculated $E_{O|R}^0$ relative to the vacuum level to $E_{O|R}^0$ versus the saturated calomel electrode (SCE) in acetonitrile.¹⁴

Figure S1. ^1H NMR spectra of $C\text{-trans-}[\text{Ir-H-Ir}]^{3+}$: (400 MHz, CD_3CN) δ 9.13 (d, $J = 5.8$ Hz, 2H), 8.31 (t, $J = 8.2$ Hz, 2H), 8.28 (dd, $J = 8.5, 0.9$ Hz, 2H), 8.22 (ddd, $J = 8.5, 7.6, 1.3$ Hz, 2H), 8.11 (d, $J = 8.2$ Hz, 4H), 8.04 (ddd, $J = 7.5, 7.0, 1.3$ Hz, 4H), 7.98 (d, $J = 7.5$ Hz, 4H), 7.72 (dd, $J = 7.8, 1.0$ Hz, 2H), 7.60 (ddd, $J = 7.6, 5.8, 1.5$ Hz, 2H), 7.65-7.51 (4H, H6''), 7.36 (dd, $J = 7.0, 7.0$ Hz, 4H), 6.90 (ddd, $J = 7.8, 7.6, 0.8$ Hz, 2H), 6.62 (ddd, $J = 7.6, 7.5, 1.2$ Hz, 2H), 5.10 (d, $J = 7.5$ Hz, 2H), -11.44 (s, 1H, μH).

Figure S2. ^1H NMR spectra of *N-trans*- $[\text{Ir-H}]^+$ (400 MHz, CD_3CN): δ 8.51 (d, $J = 8.1$ Hz, 2H), 8.32 (d, $J = 8.1$ Hz, 2H), 8.27 (t, $J = 8.0$ Hz, 1H), 8.17 (d, $J = 7.3$ Hz, 1H), 7.99 (ddd, $J = 21.9$, 17.7, 8.0 Hz, 6H), 7.67 (t, $J = 8.0$ Hz, 1H), 7.36-7.22 (m, 4H), 7.19 (d, $J = 5.0$ Hz, 1H), 6.89-6.82 (m, 2H), -19.30 (s, 1H, Ir-H).

Figure S3. ^1H NMR spectra of *C-trans*- $[\text{Ir-H}]^+$ (400 MHz, CD_3CN): δ 9.63 (ddd, $J = 5.7$, 1.4, 0.7 Hz, 1H), 8.50 (d, $J = 8.2$ Hz, 2H), 8.39 (dd, $J = 8.6$, 1.2 Hz, 2H), 8.27 (d, $J = 8.3$ Hz, 1H), 8.20 (td, $J = 8.2$, 0.9 Hz, 1H), 8.12 (ddd, $J = 8.3$, 7.6, 1.6 Hz, 1H), 7.98-7.91 (4H), 7.81 (d, $J = 7.7$ Hz, 1H), 7.47 (ddd, $J = 7.6$, 5.7, 1.4 Hz, 1H), 7.29 (ddd, $J = 7.5$, 5.8, 1.4 Hz, 2H), 6.90 (ddd, $J = 7.7$, 7.5, 1.2 Hz, 1H), 6.72 (ddd, $J = 7.5$, 7.3, 1.1 Hz, 1H), 5.92 (d, $J = 7.3$ Hz, 1H), -7.46 (s, 1H, Ir-H).

X ray structure of *N-trans*-[Ir–H]⁺.

Collection and Reduction of X-Ray Data. Crystals of *N-trans*-[Ir–H](PF₆) were obtained by slow diffusion of diethyl ether to the NMR sample in CD₃CN. An orange crystal of *N-trans*-[Ir–H](PF₆) used for the X-ray diffraction study contained a small amount of *N-trans*-[Ir–OH](PF₆) that likely was produced during the crystallization of *N-trans*-[Ir–H](PF₆) with a trace amount of H₂O in the CD₃CN. The actual composition is Ir(tpy)(ppy)(X)(PF₆)·0.25NCCD₃, X = H⁺ or OH⁺. A crystal of *N-trans*-[Ir–H](PF₆) was mounted on the end of a glass fiber. Diffraction data were collected at 296K for *N-trans*-[Ir–H](PF₆) with a Bruker Kappa Apex II diffractometer. Space group *P* $\bar{1}$ was used for the solution and refinement of the structure.

Determination and Refinement of the Structure. The structure was solved¹⁹ by Patterson heavy atom methods. In the least-squares refinement,¹⁹ anisotropic temperature parameters were used for all the non-hydrogen atoms except for the acetonitrile of crystallization with partial occupancy. There are two molecules in the asymmetric unit. One molecule is clearly the hydride while the other molecule is a mixture of the hydride and hydroxide as we explain below. Hydrogen atoms were placed at calculated positions and allowed to "ride" on the atom to which they were attached except for the hydride hydrogen atom on Ir(2) which was located on a difference Fourier map and included in a fixed position. The isotropic thermal parameters for the hydrogen atoms were determined from the atom to which they are attached. The data were corrected for absorption using the multi-scan method (SADABS)²⁰. During the refinement of the structure the sixth ligand attached to the Ir(1) was assumed to be the hydride ion but the largest peak in the difference Fourier map was located about 1.8 Å from the iridium atom and it was refined as an oxygen atom with an occupancy factor of 0.40. This peak was introduced into the refinement as a partial oxygen atom making the sixth ligand coordinated to the Ir(1) an hydroxide ion 40% of the time and a hydride 60% of the time. The elongated thermal ellipsoid on O(1) is a result of this position being occupied by a hydride (60%) and a hydroxide (40%).

The *N-trans*-[Ir–H]⁺ complex crystallizes in space group *P* $\bar{1}$ and also features an acetonitrile solvent in the crystal lattice. There are two molecules present in the asymmetric unit. One molecule is clearly the hydride (Figure S4) while the other molecule is a mixture of the hydride (60%) and hydroxide (40%) as shown in ORTEP diagram (Figure S5). The formation of small amount of hydroxide can occur by the presence of water from solvent during crystallization. The hydride ligand is found trans to the nitrogen of ppy. The strong trans effect of the hydrogen ligand tends to lengthen the Ir–N241 bond (2.117(10) Å) of ppy relative to the Ir–N bond of tpy which are roughly 2.03 Å. The Ir–H bond length of 1.66 Å is in accord with the literature value.²¹ The complex also features an N–Ir–H bond angle of 171.1(3)° (Table S2).

Table S1. Crystal data and structure refinement for *N-trans*-[Ir–H]⁺ mixed with 20 % of *N-trans*-[Ir–OH]⁺.

Empirical formula	C _{26.50} H ₂₀ D _{0.75} F ₆ IrN _{4.25} O _{0.20} P
Formula weight	739.11
Color	yellow-orange
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 12.8858(5) Å, α = 99.926(2)° b = 14.6714(6) Å, β = 103.376(2)° c = 14.7986(6) Å, γ = 91.604(2)°
Volume	2674.35(19) Å ³
Z, Calculated density	4, 1.835 Mg/m ³
Absorption coefficient	5.199 mm ⁻¹
F(000)	1425
Crystal size	0.10 × 0.07 × 0.03 mm
Theta range for data collection	2.45 to 25.00 deg.
Limiting indices	–15 ≤ h ≤ 13, –17 ≤ k ≤ 17, –16 ≤ l ≤ 17
Reflections collected / unique	41496 / 9318 [R(int) = 0.1274]
Completeness to theta = 25.00	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5990
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9318 / 0 / 706
Goodness-of-fit on F ²	0.875
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1109
R indices (all data)	R1 = 0.1570, wR2 = 0.1323
Largest diff. peak and hole	1.247 and –1.374 e.Å ⁻³

Figure S4. Structure of *N-trans*-[Ir-H]⁺, with selected label atoms.

Figure S5. The two independent cations in the asymmetric unit of *N-trans*-[Ir-H]⁺, where the sixth ligand is a hydride in one complex and a hydroxide ion (40%) in the other. The thermal ellipsoid of the oxygen is elongated as it represents a hydride (60%) and a hydroxide (40%).

Table S2. Selected experimental and DFT^a calculated bond lengths (Å) and bond angles (°) for *N-trans*-[Ir–H]⁺ and others.

	<i>N-trans</i> -[Ir–H] ⁺	<i>N-trans</i> -[Ir–H] ⁺ <i>calc</i>	<i>C-trans</i> -[Ir–H] ⁺ <i>calc</i>	<i>C-trans</i> -[Ir] ⁰ <i>calc</i>
Ir2-N211	2.027(10)	2.07	2.07	2.05
Ir2-N221	2.002(8)	2.03	1.96	1.93
Ir2-N231	2.022(9)	2.07	2.07	2.05
Ir2-N241	2.117(10)	2.18	2.11	2.13
Ir2-H2	1.667 ^b	1.62	1.73	–
Ir2-C251	2.024(11)	2.04	2.09	2.01
H2-Ir2-N241	171.1(3)	172.7	96.1	–
N221-Ir2-N241	100.7(4)	98.1	174.0	169.2
N221-Ir2-C251	176.7(4)	176.7	95.5	113.6

^a At M06 level⁵; ^b H(2) included in the refinement in a fixed position.

Figure S6. Calculated UV-vis absorption spectra at B3LYP level of theory for *N-trans*-[Ir-H]⁺ (black) and *C-trans*-[Ir-H]⁺ (red). The molecular orbitals associated with electronic excitations with largest contributions to absorptions at λ_{max} are also presented for *N-trans*-[Ir-H]⁺ (upper left corner) and *C-trans*-[Ir-H]⁺ (lower right corner).

Figure S7. ^1H NMR spectra of $N\text{-trans-}[\text{Ir-H}]^+$ in CD_3CN (a) under CO_2 atmosphere at RT (b) under CO_2 atmosphere at 70°C . $N\text{-trans-}[\text{Ir-H}]^+$ does not react with CO_2 .

Figure S8. ^1H NMR spectra of $C\text{-trans-}[\text{Ir-H}]^+$ in CD_3CN (a) under Ar atmosphere at RT (b) under CO_2 atmosphere at RT. $C\text{-trans-}[\text{Ir-H}]^+$ reacts with CO_2 to form $C\text{-trans-}[\text{Ir-OCHO}]^+$.

Figure S9. ^{13}C NMR spectrum of $C\text{-trans-}[\text{Ir-H}]^+$ under $^{13}\text{CO}_2$ in CD_3CN indicating the formation of $C\text{-trans-}[\text{Ir-OCHO}]^+$. The peak at 1.38 and 118.2 ppm corresponds to CD_3CN solvent and at 126 ppm corresponds to $^{13}\text{CO}_2$.

Figure S10. HMBC spectrum of $C\text{-trans-}[\text{Ir-H}]^+$ under $^{13}\text{CO}_2$ in CD_3CN .

Figure S11. ESI-MS spectrum of *C-trans*-[Ir-H]⁺ under ¹³CO₂. The peak at *m/z* = 626.1 corresponding to the iridium formato complex *C-trans*-[Ir-O¹³CHO]⁺.

Scheme S1. Reaction showing the relative free energy change in units of kcal/mol for the formation of *N-trans*-[Ir-H]⁺ and *C-trans*-[Ir-NCCH₃]²⁺ from *C-trans*-[Ir-H]⁺ and *N-trans*-[Ir-NCCH₃]²⁺

Figure S12. Ball and stick model of the optimized transition state structure for hydride transfer from *C-trans*-[Ir-H]⁺ to CO₂. Color code: carbon (gray), nitrogen (blue), oxygen (red), hydrogen (white) and iridium (cyan).

Table S3. Reduction potentials of Ir complexes in CH₃CN vs SCE^a

	Potential, V (ΔE_p /mV)	Ref
<i>N-trans</i> -[Ir-H] ⁺	1.14, -1.30 (93), -1.60 ^b	This work
<i>C-trans</i> -[Ir-Cl] ⁺	1.72, -1.09, -1.35, ^c -1.98 ^b	22
	1.73, -1.04	2
<i>C-trans</i> -[Ir-CH ₃ CN] ²⁺	-0.95 (70), -1.18 ^b , -1.29 ^b	This work

^a Potential were measured in CH₃CN containing 0.5-1.0 mM complex and 0.1 M n-Bu₄NPF₆, vs SCE with a scan rate of 0.1 V/s. ^b Peak potential.

Figure S13. Cyclic voltammogram of $N\text{-trans-}[\text{Ir-H}]^+$ (ca. 0.5 mM) in CH_3CN containing Bu_4NPF_6 (0.1 M) at scanning rate of 100 mV/s at room temperature under Ar atmosphere (a and b) and CO_2 atmosphere (c).

Determination of the hydricity of N -*trans*-[Ir-H]⁺ in acetonitrile

Scheme S2. Thermodynamic cycles relevant to reactions of M–H in acetonitrile

Based on a thermodynamic cycle as depicted by Scheme S2, the hydricity ($\Delta G_{\text{H}^-}^\circ$) of a metal hydride (M–H) is alternatively expressed as a sum of the Gibbs free-energy change associated with the reactions shown in eq. S4.

$$\Delta G_{\text{H}^-}^\circ = \text{BDFE}(\text{MH}) + \Delta G_{\text{M(S)}^\bullet}^\circ + F \left[E^\circ(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet) - E^\circ(\text{H}^\bullet \rightarrow \text{H}^-) \right] \quad \text{eq. S4}$$

By the separation of variables into terms that are independent and dependent on the temperature, T , the $\Delta G_{\text{H}^-}^\circ$ can be divided into enthalpy and entropy terms and simplified to eq. S5 provided the assumption²³⁻²⁵ that the difference between the bond dissociation free energy (BDFE) and the bond dissociation energy (BDE) is equal to an entropy term for $\text{H}^\bullet$ ($-TS^\circ(\text{H}^\bullet)$), where $\Delta H_{\text{rc}}^\circ$ and $\Delta S_{\text{rc}}^\circ$ are the enthalpy and entropy changes, respectively, upon the redox couple of interest. This difference has been thought to be negligible,²³⁻²⁵ and recently it has also been found that the assumptions are inappropriate in the case^{26,27} of reactions involving oxidation-state change on the metal center of first-row transition metal complexes.

$$\begin{aligned} \Delta G_{\text{H}^-}^\circ &= \left[\text{BDE}(\text{MH}) + \Delta H_{\text{M(S)}^\bullet}^\circ - \Delta H_{\text{rc}}^\circ(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet) + \Delta H_{\text{rc}}^\circ(\text{H}^\bullet \rightarrow \text{H}^-) \right] \\ &\quad - T \left[\Delta S_{\text{M(S)}^\bullet}^\circ + S^\circ(\text{H}^\bullet)_{\text{g}} + \Delta_{\text{tr}}^{\text{g} \rightarrow \text{sol}} S^\circ(\text{H}^\bullet) - \Delta S_{\text{rc}}^\circ(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet) + \Delta S_{\text{rc}}^\circ(\text{H}^\bullet \rightarrow \text{H}^-) \right] \\ &= \Delta H_{\text{H}^-}^\circ - T \left[-\Delta S_{\text{rc}}^\circ(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet) + S^\circ(\text{H}^-) \right] \end{aligned} \quad \text{eq. S5}$$

The two quantities $\Delta H_{\text{H}^-}^\circ$ and $\Delta S_{\text{rc}}^\circ$ in eq. S5 are subject to calorimetric and electrochemical measurement, respectively. Because Scheme S3(a) is akin to a half-reaction, it is necessary to deduce $\Delta H_{\text{H}^-}^\circ$ using a full reaction (Scheme S3(b)) of MH with a reference compound, A^+ , for which the BDE of the corresponding reduced form, AH , is known. In this work, we use N -*trans*-[Ir-H]⁺ as the MH and a TEMPO-based cation^{28,29} $\text{TEMPO}^+ = 4$ -(acetylamino)-2,2,6,6-tetramethyl-1-oxo-piperidinium tetrafluoroborate) as the reference compound, A^+ , for which the

BDE(AH) can be estimated as 70 ± 1 kcal/mol from a compilation,³⁰ since the value is not affected by the type of substituent at the 4-position on the TEMPO moiety.

Scheme S3. A thermodynamic cycle for ΔH_{H^-} using a reference compound, A^+ and AH

According to a thermodynamic cycle based on Hess's law, $\Delta H_{\text{H}^-}^\circ$ is described in terms of the reaction heat ($\Delta H_{\text{rxn}}^\circ$), BDE of AH, redox potentials, and the entropy changes upon electron transfer as shown in eq. S6.

$$\Delta H_{\text{H}^-}^\circ = -[-FE^\circ(1) + T\Delta S_{\text{rc}}^\circ(1)] + [-FE^\circ(2) + T\Delta S_{\text{rc}}^\circ(2)] + \text{BDE(AH)} + \Delta H_{\text{rxn}}^\circ \quad \text{eq. S6}$$

Substitution of eq. S6 into eq. S5 yields an equation, eq. S7, allowing the determination of the hydricity in units of Gibbs free energy based on a calorimetric measurement. It is noteworthy that the dependence of eq. S5 on $S^\circ(\text{H}^-)$ is eliminated in eq. S7. Here, we adopt -1.13 V versus Fc^+/Fc ^{24,31} ($E_{\text{Fc}^+/\text{Fc}} = 0.40$ V vs SCE) as the redox potential of the $\text{H}^\bullet/\text{H}^-$ couple in acetonitrile for consistency with previous work.³² The entropy of $\text{H}^\bullet$ in solution ($S^\circ(\text{H}^\bullet)$) is the sum of the entropy of $\text{H}^\bullet$ in the gas phase ($S^\circ(\text{H}^\bullet) = +27.419$ cal/mol·K)^{33,34} and the entropy changes upon solvation of the hydrogen atom into solution ($\Delta_{\text{tr}}S^\circ(\text{H}^\bullet)$), which is reasonably approximated as -11.9 cal/mol·K³⁵ upon the transfer of 1 mol of hydrogen molecules from the gas at 101.325 kPa to the infinitely dilute solution. We also assume that the entropy change ($\Delta S_{\text{M(S)}^\bullet}$) upon the binding of an acetonitrile molecule to $\text{M}^\bullet$ to form $\text{M(S)}^\bullet$ is close to zero because of the acetonitrile being a solvent molecule.

$$\begin{aligned} \Delta G_{\text{H}^-}^\circ = & -F[E(\text{H}^\bullet \rightarrow \text{H}^-) - E(\text{A}^+ \rightarrow \text{A}^\bullet)] + \text{BDE(AH)} \\ & + \Delta H_{\text{rxn}}^\circ + T[-S^\circ(\text{H}^-) - \Delta S_{\text{rc}}^\circ(\text{A}^+ \rightarrow \text{A}^\bullet) + \Delta S_{\text{rc}}^\circ(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet)] \end{aligned} \quad \text{eq. S7}$$

As described in the following subsections, using TEMPO^+ as A^+ and $N\text{-trans-}[\text{Ir-H}]^+$ as MH, ΔH_{rxn} was measured as -43 ± 3 kcal/mol and $\Delta S_{\text{rc}}(\text{A}^+ \rightarrow \text{A}^\bullet)$ is determined to be $+17.7$ cal/mol·K. $\Delta S_{\text{rc}}(\text{M(S)}^+ \rightarrow \text{M(S)}^\bullet)$ was also determined to be $+21.8$ cal/mol·K by approximating the value for $C\text{-trans-}[\text{Ir-NCCH}_3]^{2+}$ to be similar to the value of $N\text{-trans-}[\text{Ir-NCCH}_3]^{2+}$. Then,

the hydricity of *N-trans*-[Ir-H]⁺ in acetonitrile was calculated to be 57 ± 4 kcal/mol at *T* = 298.15 K as shown in eq. S8.

$$\begin{aligned}\Delta G_{\text{H}^-}^{\circ} &= -F[(-1.13) - (+0.32)] + (70 \pm 1) \\ &= (-43 \pm 3) + \frac{T}{1000} \left[-(+15.5) - \frac{0.77}{1000} F + \frac{0.95}{1000} F \right] \\ &= +57 \pm 4 \text{ kcal/mol}\end{aligned}\quad \text{eq. S8}$$

(a) Measurement of the reaction heat ($\Delta H_{\text{rxn}}^{\circ}$) of *N-trans*-[Ir-H]⁺ with TEMPO⁺ in CH₃CN

Figure S14 shows a thermogram acquired by titration of an acetonitrile solution of the PF₆ salt of *N-trans*-[Ir-H]⁺ (0.92 mM) to an acetonitrile solution of the BF₄ salt of TEMPO⁺ (5.0 mM). Each injection of 10 μL of the titrant to the titrand produced heat (1645 ± 10 μJ) and the reaction heat (ΔH_{rxn}) was determined to be -43 ± 3 kcal/mol based on the amount of [Ir-H]⁺ in each injection of the titrant.

Figure S14. Thermogram recorded for 11 titrations (10 μL each) of *N-trans*-[Ir-H](PF₆) (0.92 mM) in dry acetonitrile into TEMPO⁺ (5.0 mM) in dry CH₃CN (0.95 mL) at 25.0 °C.

(b) Measurement of the entropy changes ($\Delta S^\circ_{\text{rc}}$) of *C-trans*-[Ir-NCCH₃]²⁺ and TEMPO⁺ upon one-electron reduction in acetonitrile

$\Delta S^\circ_{\text{rc}}$ can be derived directly from the temperature dependence of half-wave potentials ($E_{1/2}$) by means of electrochemical methods (eq. S9).

$$\Delta S^\circ_{\text{rc}} (A^+ \rightarrow A^\bullet) = F \left(\frac{\partial E^\circ}{\partial T} \right)_p \approx F \left(\frac{\partial E_{1/2}}{\partial T} \right)_p \quad \text{eq. S9}$$

Both *C-trans*-[Ir-NCCH₃]²⁺ and TEMPO⁺ showed reversible one-electron reduction waves in cyclic voltammetry ($E_{1/2} = -1.35$ and $+0.32$ V vs Fc^{+/0}, respectively, at 25°C). Figure S15 shows the temperature dependences of these half-wave potentials ($E_{1/2}$) determined by Osteryoung square wave voltammetry, from which $\Delta S^\circ_{\text{rc}}$ values were determined as $+21.8$ cal/mol·K for -[Ir-NCCH₃]²⁺ and $+17.7$ cal/mol·K for TEMPO⁺.

Figure S15. Temperature dependence of half-wave potentials measured by Osteryoung square wave voltammetry in an $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) acetonitrile solution containing (a) $C\text{-trans-}[\text{Ir-NCCH}_3](\text{PF}_6)_2$ and (b) $\text{TEMPO}^+\text{BF}_4^-$. A carbon disc (diameter = 3 mm) and a Pt wire were used as the working electrode (W.E.) and counter electrode, respectively. The reference electrode consisting of Ag/AgNO_3 in $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) acetonitrile solution was kept at room temperature and isolated from the main compartment by a salt bridge consisting of $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) acetonitrile solution. All measurements were carried out at step height, pulse height, and pulse width of 10 mV, 25 mV, and 50 ms, respectively, corresponding to a scan rate of 0.1 V/s in the case of cyclic voltammetry.

(c) Theoretical Calculations for Hydricities of $C\text{-trans-}[\text{Ir-H}]^+$ and $N\text{-trans-}[\text{Ir-H}]^+$

Density functional theory calculations at the M06 level of theory using the SMD continuum solvation model of acetonitrile were performed to predict the hydricities of $C\text{-trans-}[\text{Ir-H}]^+$ and $N\text{-trans-}[\text{Ir-H}]^+$. Free-energy changes associated with hydride transfer reactions were computed using the $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{H})]^+ / [\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^+$ couple as a reference for which the experimental hydricity is known to be 39.0 kcal/mol³⁶. Using this relative hydricity approach the $\Delta G^\circ_{\text{H-}}$ are assigned for $C\text{-trans-}[\text{Ir-H}]^+$ and $N\text{-trans-}[\text{Ir-H}]^+$. In the case of $N\text{-trans-}[\text{Ir-H}]^+$ two possible values for $\Delta G^\circ_{\text{H-}}$ are computed depending on the final CH_3CN adduct, namely $N\text{-trans-}[\text{Ir-CH}_3\text{CN}]^+$ or $C\text{-trans-}[\text{Ir-CH}_3\text{CN}]^+$.

Figure S16. Excited-state decay of N -*trans*-[Ir-H]⁺ in CH₃CN at room temperature: kinetic trace, fit and time constant at 610 nm.

Figure S17. Kinetic traces observed at 550 nm and transient absorption spectra in CH_3CN : *C-trans*- $[\text{Ir}-\text{Cl}]^+$ (top and bottom at left) and *C-trans*- $[\text{Ir}-\text{NCCH}_3]^{2+}$ (top and bottom at right).

Figure S18. Stern-Volmer plot of *N-trans*-[Ir-H]⁺ in CH₃CN: Quenching of emission with TEA, excitation wavelength 420 nm at room temperature. $k_q = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Figure S19. Reductive quenching of *C-trans*-[Ir-Cl]⁺ by TEA in CH₃CN: (a) Emission kinetic traces at 550 nm; (b) Linear fit of the observed kinetic rate constants vs TEA concentrations; and (c) Transient absorption spectra in the presence of 2.3 mM of TEA, the excited state of *C-trans*-[Ir-Cl]⁺ (black line) and the reduced species (red line).

Figure S20. Na-Hg reduction of *C-trans*-[Ir-NCCH₃]²⁺ in CH₃CN: a) the first reduction step (black to red); b) the second reduction step (black to red); c) the third reduction step (black to red) and d) the fourth reduction step (black to red).

Figure S21. Na-Hg reduction of *N-trans*-[Ir-H]⁺ in CH₃CN: a) the first reduction step (black to red); b) the second reduction step (black to red); and c) the third reduction step (black to red).

Figure S22. Kinetic trace, fit and time constant for *N-trans*-[Ir-H]⁺ at 610 nm in the presence of 50 mM TEA in acetonitrile.

Figure S23. Kinetic trace for *N-trans*-[Ir-H]⁺ at 550 nm in the presence of 0.24 M TEA and 1 atm CO₂ in CH₃CN.

Figure S24. Excited state decay of *C-trans*-[Ir-H]⁺ in CH₃CN at room temperature: kinetic trace fit and time constant at 600 nm.

Figure S25. Left: Transient absorption spectra of *C-trans*-[Ir-H]⁺ -obtained at 50 ns (black), 180 ns (red), 550 ns (blue) after laser excitation ($\lambda_{\text{exc}} = 420$ nm) in dry acetonitrile. Right: Expanded transient absorption spectra of *C-trans*-[Ir-H]⁺ obtained at 550 ns after laser excitation ($\lambda_{\text{exc}} = 420$ nm) in dry acetonitrile.

Figure S26. ^1H NMR spectra of $N\text{-trans-}[\text{Ir-H}]^+$ in CD_3CN (a) under Ar atmosphere before irradiation (b) after 10 min irradiation (c) after 30 min irradiation. The peak at 5.4 ppm corresponds to dichloromethane that was used for column chromatography.

Figure S27. ^1H NMR spectra of $C\text{-trans-}[\text{Ir-H}]^+$ in CD_3CN (a) under Ar atmosphere before irradiation (b) after 1 min irradiation, peak at 4.58 ppm corresponds to H_2 (c) after 10 min irradiation. The peak at -19.3 ppm corresponds to the formation of $N\text{-trans-}[\text{Ir-H}]^+$ isomer.

The Mechanism of CO₂ Reduction

The proposed mechanism for CO₂ reduction by *C-trans*-[Ir-H]⁺ and *N-trans*-[Ir-H]⁺ starts with absorption of light to generate the corresponding singlet excited states, which could relax to lower energy triplet states via intersystem crossing processes. In the triplet excited states, the loss of a proton to generate the *C-trans*-[Ir]⁰ species is very favorable for *C-trans*-[Ir-H]⁺ (pK_a = -6.2) compared to that of *N-trans*-[Ir-H]⁺ (pK_a = -0.4) and the resulting triplet pentacoordinate Ir(I) species are 14.0 kcal/mol more stable for the *C-trans*-[Ir]⁰ isomer than for *N-trans*-[Ir-H]⁰. Therefore, we propose that upon irradiation, *C-trans*-[Ir-H]⁺ behaves as a photoacid and loses a proton to form the penta-coordinate *C-trans*-[Ir]⁰ species whereas *N-trans*-[Ir-H]⁺ is still stable in the excited state and quenched by the sacrificial reductant to generate *N-trans*-[Ir-H]⁰, consistent with the transient absorption spectroscopy results. Further excitation and reduction of *N-trans*-[Ir-H]⁰ with concomitant evolution of H₂ could generate *C-trans*-[Ir]⁰ (Scheme S4). Although both *C-trans*-[Ir]⁰ and *N-trans*-[Ir]⁰ species could exist in the excited state (triplet), only one conformer, *C-trans*-[Ir]⁰ exists in the ground (closed-shell singlet) state, which indicates that both *C-trans*-[Ir-H]⁺ and *N-trans*-[Ir-H]⁺ isomers will form the same penta-coordinate *C-trans*-[Ir]⁰ species upon photo-excitation and reduction steps.

Scheme S4. Proposed pathways for generation of *C-trans*-[Ir]⁰ starting from *C-trans*-[Ir-H]⁺ and *N-trans*-[Ir-H]⁺. Free-energy changes (ΔG) are reported in units of kcal/mol and redox potentials in units of volts vs SCE.

CO₂ binding to *C-trans*-[Ir]⁰ proceeds with a free energy of activation ($\Delta G^\ddagger$) of 15.3 kcal/mol and a free energy change (ΔG) of 13.2 kcal/mol, followed by a very favorable ($\Delta G = -31.6$ kcal/mol) protonation step (Scheme S5). Further protonation and evolution of H₂O to form *C-trans*-[Ir-CO]²⁺ is also exoergic ($\Delta G = -19.7$ kcal/mol). Finally, displacement of CO by CH₃CN generates *C-trans*-[Ir-NCCH₃]²⁺. It should be noted that *C-trans*-[Ir-NCCH₃]²⁺ could be reduced relatively easily (Scheme S6) to generate *C-trans*-[Ir]⁰ and formation of hydride species will be in competition with CO₂ reduction from the *C-trans*-[Ir]⁰ complex.

Scheme S5. Proposed mechanism of CO₂ reduction starting from *C-trans*-[Ir]⁰. Free-energy

changes (ΔG) are reported in units of kcal/mol.

Scheme S6. Generation of *C-trans*-[Ir]⁰ starting from *C-trans*-[Ir-NCCH₃]²⁺. Redox potentials in units of volts vs SCE.

Scheme S8. Calculated reduction potentials and relative free energies of *C-trans*-[Ir] and *N-trans*-[Ir] isomers with different ligands. Free-energy changes (ΔG) are reported in units of

$$\begin{array}{ccc}
 C\text{-}trans\text{-}[\text{Ir-NCCH}_3]^2+ & \xrightarrow{\Delta G = 52.2} & C\text{-}trans\text{-}[\text{Ir-NCCH}_3]^+ \\
 \text{(singlet)} & & \text{(triplet)} \\
 \downarrow \Delta G = 6.1 & & \downarrow \Delta G = 6.7 \\
 N\text{-}trans\text{-}[\text{Ir-NCCH}_3]^2+ & \xrightarrow{\Delta G = 52.7} & N\text{-}trans\text{-}[\text{Ir-NCCH}_3]^+ \\
 \text{(singlet)} & & \text{(triplet)}
 \end{array}$$

$$\begin{array}{ccc} C\text{-trans-}[\textbf{Ir-H}]^+ & \xrightarrow[pK_a = 21.3]{\Delta G = 29.0} & C\text{-trans-}[\textbf{Ir}] + \text{H}^+(\text{soln}) \\ (\text{singlet}) & & (\text{singlet}) \end{array}$$

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Cartesian Coordinates and Electronic Energies of Optimized Structures at the M06 Level of Theory

H₂O (Closed-shell singlet)

E = -76.3820213044 a.u.

8	0.000000	0.000000	0.119947
1	0.000000	0.758255	-0.479789
1	0.000000	-0.758255	-0.479789

CO₂ (Closed-shell singlet)

E = -188.498068375 a.u.

6	0.000000	0.000000	0.000000
8	0.000000	0.000000	1.164844
8	0.000000	0.000000	-1.164844

CO (Closed-shell singlet)

E = -113.248632055 a.u.

6	0.000000	0.000000	-0.649943
8	0.000000	0.000000	0.487457

CH₃CN (Closed-shell singlet)

E = -132.652207924 a.u.

6	0.000000	0.000000	-1.175225
1	0.000000	1.026432	-1.559292
1	-0.888916	-0.513216	-1.559292
1	0.888916	-0.513216	-1.559292
6	0.000000	0.000000	0.277423
7	0.000000	0.000000	1.437812

C-trans-[Ir-Cl]⁺ (Closed-shell singlet)

E = -1784.89333829 a.u.

6	-0.529473	0.575953	3.018219
6	-0.052403	-1.611653	2.340153
6	-0.006232	-2.034118	3.661186
6	-0.225743	-1.114730	4.680546
6	-0.490771	0.208431	4.356437
1	-0.738078	1.599415	2.712309
1	0.195433	-3.076701	3.892574
1	-0.191230	-1.434955	5.718932
1	-0.668729	0.957872	5.122390
6	0.157852	-2.505135	1.188121
6	0.482089	-3.857513	1.211541
6	0.645579	-4.522968	0.000000
1	0.611545	-4.385637	2.152600
6	0.157852	-2.505135	-1.188121
6	0.482089	-3.857513	-1.211541
1	0.904534	-5.578780	0.000000
1	0.611545	-4.385637	-2.152600
6	-0.052403	-1.611653	-2.340153
6	-0.006232	-2.034118	-3.661186
6	-0.529473	0.575953	-3.018219
6	-0.225743	-1.114730	-4.680546
1	0.195433	-3.076701	-3.892574
6	-0.490771	0.208431	-4.356437
1	-0.738078	1.599415	-2.712309
1	-0.191230	-1.434955	-5.718932
1	-0.668729	0.957872	-5.122390
7	-0.316915	-0.304938	2.034603
7	0.022896	-1.886382	0.000000
7	-0.316915	-0.304938	-2.034603
77	-0.376304	0.040342	0.000000
6	1.722744	2.048192	0.000000
6	3.008183	2.601743	0.000000
6	4.123109	1.774387	0.000000
6	3.956768	0.390153	0.000000
6	2.679125	-0.169338	0.000000
1	3.144346	3.682573	0.000000
1	5.121628	2.207501	0.000000
1	4.829898	-0.261783	0.000000
1	2.580095	-1.256885	0.000000
6	0.499708	2.848005	0.000000
6	0.437148	4.241454	0.000000
6	-1.842301	2.730201	0.000000
6	-0.795433	4.874437	0.000000
1	1.353763	4.826050	0.000000
6	-1.958635	4.108679	0.000000
1	-2.710418	2.072427	0.000000

1	-0.849352	5.961098	0.000000
1	-2.943844	4.566690	0.000000
17	-2.835034	-0.548613	0.000000
6	1.542497	0.644724	0.000000
7	-0.647971	2.114596	0.000000

***N-trans*-[Ir-Cl]⁺ (Closed-shell singlet)**

E = -1784.87884473 a.u.

6	-0.456285	0.551754	3.030974
6	-0.010130	-1.637596	2.333727
6	0.101197	-2.053294	3.652818
6	-0.073450	-1.134170	4.681008
6	-0.356800	0.187000	4.366921
1	-0.678402	1.574160	2.732197
1	0.326372	-3.093397	3.874490
1	0.012436	-1.452656	5.717057
1	-0.501346	0.938276	5.138230
6	0.161392	-2.551763	1.185280
6	0.401544	-3.923031	1.214902
6	0.521905	-4.594469	0.000000
1	0.485526	-4.464596	2.153388
6	0.161392	-2.551763	-1.185280
6	0.401544	-3.923031	-1.214902
1	0.708020	-5.665785	0.000000
1	0.485526	-4.464596	-2.153388
6	-0.010130	-1.637596	-2.333727
6	0.101197	-2.053294	-3.652818
6	-0.456285	0.551754	-3.030974
6	-0.073450	-1.134170	-4.681008
1	0.326372	-3.093397	-3.874490
6	-0.356800	0.187000	-4.366921
1	-0.678402	1.574160	-2.732197
1	0.012436	-1.452656	-5.717057
1	-0.501346	0.938276	-5.138230
7	-0.288698	-0.328273	2.036687
7	0.064523	-1.936760	0.000000
7	-0.288698	-0.328273	-2.036687
77	-0.393175	0.052318	0.000000
6	1.642170	2.155134	0.000000
6	2.911333	2.736994	0.000000
6	4.041816	1.938292	0.000000
6	3.899913	0.552380	0.000000
6	2.624198	0.020977	0.000000

1	3.004520	3.819793	0.000000
1	5.030451	2.392108	0.000000
1	4.759257	-0.112207	0.000000
1	2.459541	-1.054593	0.000000
6	0.373760	2.875021	0.000000
6	0.285438	4.272888	0.000000
6	-2.024657	2.708213	0.000000
6	-0.959457	4.885661	0.000000
1	1.185292	4.888152	0.000000
6	-2.112902	4.099189	0.000000
1	-2.940542	2.115168	0.000000
1	-1.033167	5.971849	0.000000
1	-3.092569	4.577517	0.000000
17	-2.700411	-0.640968	0.000000
7	1.525043	0.796471	0.000000
6	-0.784069	2.056958	0.000000

***C-trans*-[Ir-CH₃CN]²⁺ (Closed-shell singlet)**

E = -1457.21298047 a.u.

6	0.557107	-3.039091	0.321091
6	-1.568091	-2.320527	-0.348907
6	-1.982556	-3.633042	-0.518046
6	-1.091423	-4.669200	-0.259906
6	0.195865	-4.370320	0.162441
1	1.553019	-2.751745	0.652463
1	-2.995564	-3.845477	-0.849386
1	-1.405785	-5.701705	-0.390802
1	0.922473	-5.150233	0.371110
6	-2.429384	-1.152244	-0.605056
6	-3.739196	-1.151824	-1.072121
6	-4.377246	0.071474	-1.257457
1	-4.255643	-2.082781	-1.290892
6	-2.415438	1.223533	-0.522230
6	-3.726499	1.271158	-0.983188
1	-5.401040	0.090143	-1.622301
1	-4.234848	2.220406	-1.129518
6	-1.539856	2.360664	-0.187998
6	-1.932259	3.687152	-0.284281
6	0.583443	3.004288	0.559582
6	-1.031900	4.691818	0.054499
1	-2.934975	3.934687	-0.622321
6	0.241979	4.347938	0.483203
1	1.569255	2.682136	0.888988

1	-1.329281	5.735020	-0.018056
1	0.973997	5.102212	0.757095
7	-0.298132	-2.040693	0.077182
7	-1.826848	0.024892	-0.356348
7	-0.279797	2.036029	0.234924
77	0.046065	-0.008149	0.277607
6	2.285889	0.060798	-1.562345
6	2.990859	0.117447	-2.769992
6	2.302754	0.173197	-3.974583
6	0.908978	0.173034	-3.976408
6	0.199198	0.120189	-2.776763
1	4.080462	0.119961	-2.775303
1	2.852641	0.216989	-4.912789
1	0.367093	0.215682	-4.920579
1	-0.891929	0.122136	-2.810840
6	2.932036	-0.004755	-0.253422
6	4.306700	-0.038005	-0.020525
6	2.528751	-0.101056	2.055686
6	4.783395	-0.099753	1.278939
1	4.998885	-0.017512	-0.858478
6	3.881558	-0.130813	2.339888
1	1.779423	-0.126001	2.844072
1	5.854840	-0.124766	1.465360
1	4.214801	-0.179235	3.372662
6	0.871016	0.064517	-1.553243
7	2.065321	-0.039689	0.796045
7	-0.737824	-0.089732	2.304255
6	-1.221300	-0.150509	3.353453
6	-1.816703	-0.227258	4.664164
1	-2.886782	-0.001445	4.598504
1	-1.686258	-1.235802	5.071649
1	-1.336878	0.496306	5.332380

***C-trans*-[Ir-CH₃CN]²⁺ (Triplet)**

E = -1457.12148259 a.u.

6	-0.556625	3.022980	0.490396
6	1.557875	2.334569	-0.342803
6	1.923438	3.677948	-0.507599
6	1.044941	4.680574	-0.160478
6	-0.223357	4.349194	0.353892
1	-1.524906	2.710792	0.877592
1	2.907674	3.914892	-0.905245
1	1.331741	5.722395	-0.282786

1	-0.936616	5.115786	0.642602
6	2.398989	1.206607	-0.645204
6	3.711565	1.202489	-1.110560
6	4.362128	-0.013578	-1.311005
1	4.228061	2.139878	-1.306285
6	2.414740	-1.212235	-0.575513
6	3.721988	-1.230024	-1.033043
1	5.387726	-0.019505	-1.670773
1	4.249702	-2.171511	-1.166839
6	1.577137	-2.337215	-0.212392
6	1.958002	-3.677896	-0.310607
6	-0.525869	-2.995904	0.649883
6	1.085895	-4.672280	0.086545
1	2.943976	-3.924824	-0.696967
6	-0.180436	-4.327236	0.580875
1	-1.497710	-2.672181	1.018120
1	1.382285	-5.716094	0.015796
1	-0.888449	-5.083774	0.906636
7	0.295880	2.029136	0.155167
7	1.794069	-0.003813	-0.429522
7	0.319135	-2.017455	0.264907
77	-0.067605	0.008908	0.209816
6	-2.342079	-0.066052	-1.527718
6	-3.040524	-0.125484	-2.727062
6	-2.340611	-0.172897	-3.930595
6	-0.932856	-0.161004	-3.952996
6	-0.220290	-0.104651	-2.774784
1	-4.128410	-0.137782	-2.744152
1	-2.891735	-0.220071	-4.867448
1	-0.411071	-0.197889	-4.906839
1	0.868660	-0.097186	-2.799056
6	-2.970830	-0.014068	-0.213802
6	-4.339845	0.002223	0.036404
6	-2.514419	0.069505	2.079356
6	-4.790246	0.049831	1.349595
1	-5.049488	-0.020412	-0.786451
6	-3.868027	0.082823	2.388138
1	-1.750150	0.096775	2.853722
1	-5.857345	0.061797	1.558326
1	-4.180733	0.120215	3.427658
6	-0.899712	-0.056438	-1.532257
7	-2.081627	0.022765	0.815003
7	0.825336	0.062707	2.286294
6	1.362135	0.100190	3.310196
6	2.023025	0.147731	4.589729
1	3.088602	-0.073671	4.464680

1	1.910785	1.146575	5.025673
1	1.576639	-0.591739	5.263674

***N-trans*-[Ir-CH₃CN]²⁺ (Closed-shell singlet)**

E = -1457.20220147 a.u.

6	0.534795	-3.035040	0.419227
6	-1.605697	-2.322315	-0.217745
6	-2.024404	-3.638479	-0.342217
6	-1.131562	-4.672362	-0.080657
6	0.166208	-4.368447	0.301918
1	1.537962	-2.742561	0.721767
1	-3.045360	-3.856201	-0.644254
1	-1.453614	-5.706224	-0.178005
1	0.895650	-5.145078	0.512922
6	-2.486589	-1.166615	-0.493636
6	-3.811453	-1.186222	-0.921010
6	-4.448748	0.033923	-1.136368
1	-4.340801	-2.120612	-1.088417
6	-2.466995	1.207588	-0.503293
6	-3.791386	1.245149	-0.931095
1	-5.482500	0.041118	-1.473013
1	-4.305811	2.186411	-1.106349
6	-1.568104	2.350930	-0.233809
6	-1.966447	3.672869	-0.364344
6	0.582307	3.033499	0.402537
6	-1.058141	4.694042	-0.105985
1	-2.983834	3.905287	-0.667483
6	0.234324	4.371873	0.279394
1	1.580501	2.727108	0.707689
1	-1.364327	5.732308	-0.207620
1	0.975363	5.138034	0.488222
7	-0.321037	-2.036904	0.170936
7	-1.885543	0.016366	-0.314299
7	-0.288404	2.047444	0.157621
77	0.068822	0.002611	0.304736
6	2.280519	-0.027464	-1.600533
6	2.935686	-0.050494	-2.832228
6	2.203968	-0.056367	-4.007645
6	0.812551	-0.038849	-3.948348
6	0.206443	-0.018569	-2.707298
1	4.022115	-0.065606	-2.862396
1	2.715381	-0.074505	-4.967486
1	0.200537	-0.041891	-4.845639

1	-0.877156	-0.005583	-2.610574
6	2.925042	-0.018364	-0.291887
6	4.313956	-0.017547	-0.116005
6	2.609597	-0.001074	2.094591
6	4.847120	-0.009943	1.165398
1	4.984485	-0.020835	-0.975053
6	3.993006	-0.002624	2.268670
1	1.966766	0.006690	2.976267
1	5.926389	-0.009216	1.306344
1	4.410021	0.003085	3.275489
7	0.916291	-0.013692	-1.564100
6	2.043499	-0.008191	0.815297
7	-0.624713	0.008958	2.202495
6	-1.064577	0.000844	3.270866
6	-1.601463	-0.013955	4.607882
1	-2.675732	-0.226441	4.573187
1	-1.100255	-0.788870	5.198445
1	-1.441957	0.960579	5.082651

***N-trans*-[Ir-CH₃CN]²⁺ (Triplet)**

E = -1457.11040418 a.u.

6	0.606899	-3.012876	0.378563
6	-1.588912	-2.330663	-0.237393
6	-1.958422	-3.684825	-0.348974
6	-1.046520	-4.681650	-0.103590
6	0.273469	-4.339777	0.264074
1	1.608093	-2.700842	0.668856
1	-2.979439	-3.925550	-0.637639
1	-1.339538	-5.725135	-0.193710
1	1.025154	-5.098637	0.461634
6	-2.452491	-1.223819	-0.509593
6	-3.790557	-1.239417	-0.929509
6	-4.448869	-0.040853	-1.147778
1	-4.307706	-2.184187	-1.084922
6	-2.483139	1.183363	-0.534813
6	-3.799467	1.196141	-0.948209
1	-5.485179	-0.050451	-1.476639
1	-4.329279	2.129891	-1.119560
6	-1.619207	2.331748	-0.275450
6	-2.021845	3.659185	-0.410321
6	0.541963	3.044751	0.337997
6	-1.123549	4.683447	-0.169596
1	-3.044240	3.877945	-0.707932

6	0.183964	4.371189	0.205964
1	1.546090	2.753843	0.636510
1	-1.436011	5.719492	-0.275362
1	0.922171	5.144107	0.399603
7	-0.282788	-2.017120	0.148712
7	-1.853308	-0.003184	-0.346640
7	-0.331106	2.041832	0.112554
77	0.096237	0.006467	0.312904
6	2.311328	-0.009970	-1.570796
6	2.986701	-0.041441	-2.787763
6	2.263523	-0.070649	-3.972595
6	0.875230	-0.067150	-3.925300
6	0.247415	-0.037564	-2.688557
1	4.073169	-0.045638	-2.808301
1	2.783991	-0.096042	-4.926773
1	0.273012	-0.088392	-4.828827
1	-0.836719	-0.035565	-2.596451
6	2.927315	0.021498	-0.252638
6	4.295610	0.045417	-0.024523
6	2.519286	0.059043	2.171775
6	4.767259	0.072461	1.287631
1	5.010276	0.045640	-0.845088
6	3.878321	0.078183	2.383684
1	1.837796	0.065741	3.020876
1	5.839940	0.090779	1.469006
1	4.278745	0.099188	3.395023
7	0.946639	-0.010589	-1.547386
6	1.990984	0.028161	0.852198
7	-0.672290	0.002312	2.189340
6	-1.170778	-0.017672	3.230420
6	-1.780618	-0.044711	4.534350
1	-2.852411	-0.249670	4.435726
1	-1.316562	-0.830186	5.141079
1	-1.641011	0.923646	5.027648

***C-trans*-[Ir-H]⁺ (Closed-shell singlet)**

E = -1325.24478964 a.u.

6	-0.680242	0.556796	3.024807
6	-0.274956	-1.642460	2.340326
6	-0.202114	-2.061803	3.662866
6	-0.370731	-1.136560	4.684470
6	-0.609399	0.193226	4.361235
1	-0.873363	1.583666	2.720613

1	-0.017173	-3.108269	3.891243
1	-0.315404	-1.454079	5.722829
1	-0.743749	0.950174	5.128973
6	-0.099351	-2.537803	1.188487
6	0.224106	-3.890374	1.209776
6	0.380748	-4.559959	0.000000
1	0.365002	-4.414853	2.151394
6	-0.099351	-2.537803	-1.188487
6	0.224106	-3.890374	-1.209776
1	0.637991	-5.616139	0.000000
1	0.365002	-4.414853	-2.151394
6	-0.274956	-1.642460	-2.340326
6	-0.202114	-2.061803	-3.662866
6	-0.680242	0.556796	-3.024807
6	-0.370731	-1.136560	-4.684470
1	-0.017173	-3.108269	-3.891243
6	-0.609399	0.193226	-4.361235
1	-0.873363	1.583666	-2.720613
1	-0.315404	-1.454079	-5.722829
1	-0.743749	0.950174	-5.128973
7	-0.523633	-0.332115	2.035300
7	-0.255272	-1.916288	0.000000
7	-0.523633	-0.332115	-2.035300
77	-0.590321	0.016437	0.000000
6	1.647004	1.964573	0.000000
6	2.946211	2.489070	0.000000
6	4.039570	1.632570	0.000000
6	3.837414	0.252294	0.000000
6	2.543280	-0.268324	0.000000
1	3.113943	3.565884	0.000000
1	5.049244	2.039913	0.000000
1	4.694615	-0.421305	0.000000
1	2.415405	-1.355187	0.000000
6	0.446008	2.802325	0.000000
6	0.439971	4.198869	0.000000
6	-1.897582	2.791036	0.000000
6	-0.761590	4.887264	0.000000
1	1.381241	4.742866	0.000000
6	-1.957076	4.172731	0.000000
1	-2.797426	2.180483	0.000000
1	-0.766995	5.975357	0.000000
1	-2.922221	4.671617	0.000000
6	1.422020	0.568855	0.000000
7	-0.732730	2.117819	0.000000
1	-2.298458	-0.283640	0.000000

***C-trans*-[Ir-H]⁺ (Triplet)**

E = -1325.16734218 a.u.

6	1.187821	2.916993	-0.240030
6	-1.160845	2.650914	0.055408
6	-1.263637	4.032991	0.319698
6	-0.145450	4.831187	0.300813
6	1.120076	4.266958	0.016648
1	2.136008	2.428420	-0.461279
1	-2.239773	4.456691	0.546597
1	-0.235634	5.895090	0.510607
1	2.024140	4.868411	0.000424
6	-2.255098	1.735518	0.075092
6	-3.618709	1.997215	0.321598
6	-4.531073	0.963103	0.295011
1	-3.949745	3.012672	0.529148
6	-2.793391	-0.604916	-0.200086
6	-4.133173	-0.369658	0.027854
1	-5.581323	1.174389	0.483723
1	-4.860528	-1.176391	0.010838
6	-2.148124	-1.895286	-0.469233
6	-2.826612	-3.107247	-0.535913
6	-0.114276	-2.978027	-0.893907
6	-2.120092	-4.273455	-0.791364
1	-3.903244	-3.130582	-0.387314
6	-0.742015	-4.210146	-0.973141
1	0.960333	-2.871169	-1.030158
1	-2.642172	-5.225601	-0.847916
1	-0.152888	-5.100171	-1.175593
7	0.103828	2.116348	-0.237025
7	-1.913380	0.421313	-0.170060
7	-0.795052	-1.849751	-0.651025
77	-0.000083	0.082327	-0.510352
6	2.025562	-0.757359	1.474896
6	2.566586	-1.163146	2.699891
6	1.729891	-1.372266	3.788700
6	0.352467	-1.188184	3.663089
6	-0.198426	-0.797741	2.442706
1	3.639116	-1.323010	2.805695
1	2.151601	-1.692065	4.739706
1	-0.299008	-1.356973	4.519664
1	-1.278434	-0.670312	2.354845
6	2.810798	-0.529551	0.266238
6	4.196670	-0.646317	0.168341

6	2.683653	0.078947	-1.989022
6	4.823019	-0.388930	-1.040180
1	4.777797	-0.931816	1.041616
6	4.055105	-0.017574	-2.140785
1	2.037507	0.372554	-2.813078
1	5.904203	-0.474589	-1.124107
1	4.505941	0.195762	-3.105945
6	0.638849	-0.547528	1.355966
7	2.071698	-0.172397	-0.818113
1	-0.094651	-0.158036	-2.156572

***C-trans*-[Ir-H]⁺ CO₂ Electrophilic Attack Transition State (Closed-shell singlet)**

E = -1513.73944689 a.u.

6	0.979794	2.814337	-1.109056
6	-1.249728	2.577484	-0.441947
6	-1.471160	3.935780	-0.626238
6	-0.429943	4.744357	-1.065392
6	0.813774	4.177002	-1.309336
1	1.932651	2.320214	-1.288657
1	-2.451787	4.359496	-0.425315
1	-0.592576	5.809105	-1.213697
1	1.654662	4.773618	-1.651803
6	-2.276657	1.637211	0.031560
6	-3.592323	1.926802	0.375406
6	-4.403555	0.894656	0.837458
1	-3.982431	2.937256	0.288830
6	-2.589368	-0.648075	0.601527
6	-3.910619	-0.400908	0.959201
1	-5.434443	1.104331	1.111413
1	-4.548258	-1.199937	1.327678
6	-1.869032	-1.929559	0.664940
6	-2.436624	-3.114443	1.113751
6	0.167401	-3.014681	0.271623
6	-1.671360	-4.273957	1.136278
1	-3.471563	-3.131052	1.444850
6	-0.350952	-4.224872	0.708840
1	1.196229	-2.922239	-0.071925
1	-2.106268	-5.206212	1.488135
1	0.281418	-5.108249	0.711688
7	-0.021467	2.030639	-0.690781
7	-1.830716	0.369636	0.145858
7	-0.566409	-1.894786	0.246930
77	0.042421	-0.003186	-0.321046

6	2.225810	0.208835	1.636417
6	2.901258	0.437898	2.841620
6	2.192503	0.823653	3.971928
6	0.808543	0.980218	3.901640
6	0.133006	0.751458	2.702373
1	3.982565	0.315242	2.903939
1	2.718569	1.002416	4.908129
1	0.251097	1.282954	4.787987
1	-0.951878	0.882373	2.676136
6	2.900370	-0.200013	0.404043
6	4.271631	-0.417184	0.264984
6	2.573927	-0.765002	-1.848702
6	4.786726	-0.816135	-0.957704
1	4.929805	-0.274333	1.118272
6	3.924858	-0.996949	-2.036694
1	1.848002	-0.902346	-2.648077
1	5.855174	-0.988832	-1.069020
1	4.287100	-1.314013	-3.010741
6	0.822901	0.362795	1.550535
7	2.073516	-0.373782	-0.663850
1	-0.445872	-0.306874	-2.001090
6	-1.071503	-1.527442	-2.854382
8	-0.111456	-2.066473	-3.310933
8	-2.248689	-1.404665	-2.724231

***C-trans*-[Ir-OCOH]⁺ (Closed-shell singlet)**

E = -1513.76595557 a.u.

6	-0.537266	-3.002851	-0.534008
6	1.567051	-2.307885	0.218647
6	1.981759	-3.625484	0.344125
6	1.102360	-4.652379	0.018832
6	-0.173540	-4.338389	-0.427821
1	-1.526209	-2.705061	-0.877150
1	2.987240	-3.847927	0.691683
1	1.416948	-5.688747	0.113904
1	-0.889793	-5.110690	-0.693432
6	2.423914	-1.148451	0.518694
6	3.736392	-1.158875	0.976120
6	4.377838	0.059510	1.183651
1	4.254258	-2.095163	1.167186
6	2.409845	1.228280	0.488704
6	3.724514	1.264391	0.941410
1	5.404606	0.069772	1.540420

1	4.233048	2.210625	1.106613
6	1.529404	2.372137	0.196170
6	1.929157	3.696950	0.295029
6	-0.615748	3.030270	-0.468364
6	1.020487	4.707939	0.002360
1	2.944645	3.937270	0.598667
6	-0.269237	4.371964	-0.384402
1	-1.613577	2.714870	-0.767552
1	1.322992	5.749569	0.077060
1	-1.008810	5.131517	-0.621188
7	0.304993	-2.011278	-0.221738
7	1.817250	0.034360	0.295970
7	0.255014	2.054630	-0.187662
77	-0.060403	0.019530	-0.295578
6	-2.257511	-0.059314	1.596265
6	-2.941065	-0.098104	2.817394
6	-2.233342	-0.106484	4.012106
6	-0.839745	-0.074466	3.989693
6	-0.151982	-0.037506	2.777086
1	-4.030374	-0.122438	2.842334
1	-2.767212	-0.136516	4.960198
1	-0.281779	-0.078625	4.925714
1	0.939698	-0.012520	2.793612
6	-2.930861	-0.039296	0.297730
6	-4.309596	-0.052675	0.085334
6	-2.564492	0.029962	-2.022114
6	-4.806511	-0.025494	-1.208392
1	-4.989993	-0.082381	0.932672
6	-3.922743	0.016768	-2.284372
1	-1.811979	0.065644	-2.808559
1	-5.881106	-0.036026	-1.378183
1	-4.274800	0.040243	-3.311938
6	-0.840613	-0.030322	1.559596
7	-2.085073	0.001801	-0.768157
8	0.435882	0.150627	-2.415765
6	1.545501	-0.234093	-2.946866
1	2.289049	-0.664411	-2.227838
8	1.834752	-0.165130	-4.132890

N-trans-[Ir-H]⁺ (Closed-shell singlet)

E = -1325.25192018 a.u.

6	-0.645727	0.513796	3.035944
6	-0.237093	-1.679097	2.334144

6	-0.118272	-2.096552	3.652836
6	-0.269228	-1.176890	4.683243
6	-0.535486	0.148671	4.370176
1	-0.857215	1.539120	2.740181
1	0.094771	-3.139751	3.871588
1	-0.177516	-1.496594	5.718437
1	-0.659162	0.902999	5.142355
6	-0.078389	-2.591092	1.185057
6	0.193947	-3.956272	1.213287
6	0.324082	-4.627972	0.000000
1	0.304402	-4.492637	2.152276
6	-0.078389	-2.591092	-1.185057
6	0.193947	-3.956272	-1.213287
1	0.535478	-5.694565	0.000000
1	0.304402	-4.492637	-2.152276
6	-0.237093	-1.679097	-2.334144
6	-0.118272	-2.096552	-3.652836
6	-0.645727	0.513796	-3.035944
6	-0.269228	-1.176890	-4.683243
1	0.094771	-3.139751	-3.871588
6	-0.535486	0.148671	-4.370176
1	-0.857215	1.539120	-2.740181
1	-0.177516	-1.496594	-5.718437
1	-0.659162	0.902999	-5.142355
7	-0.505107	-0.367324	2.036267
7	-0.209825	-1.975348	0.000000
7	-0.505107	-0.367324	-2.036267
77	-0.591056	0.020084	0.000000
6	1.597184	2.079548	0.000000
6	2.871741	2.654191	0.000000
6	3.994651	1.842639	0.000000
6	3.842114	0.457963	0.000000
6	2.556174	-0.054950	0.000000
1	2.981680	3.735591	0.000000
1	4.987498	2.288058	0.000000
1	4.697096	-0.212719	0.000000
1	2.375089	-1.130576	0.000000
6	0.333225	2.823105	0.000000
6	0.291076	4.223870	0.000000
6	-2.070496	2.755859	0.000000
6	-0.927152	4.888686	0.000000
1	1.213101	4.805563	0.000000
6	-2.110115	4.148605	0.000000
1	-3.013516	2.205560	0.000000
1	-0.955708	5.977182	0.000000
1	-3.071449	4.663027	0.000000

1	-2.174360	-0.307851	0.000000
6	-0.857854	2.045535	0.000000
7	1.468756	0.727813	0.000000

***N-trans*-[Ir-H]⁺ (Triplet)**

E = -1325.15977825 a.u.

6	0.649902	3.006145	-0.524440
6	-1.602946	2.381062	-0.193400
6	-1.950553	3.733584	-0.054456
6	-0.983112	4.712889	-0.150833
6	0.347772	4.348549	-0.386658
1	1.666937	2.672036	-0.718675
1	-2.988724	3.997179	0.132546
1	-1.256469	5.760246	-0.041865
1	1.139451	5.087559	-0.468705
6	-2.547191	1.296655	-0.073118
6	-3.947388	1.386741	0.182567
6	-4.662287	0.196151	0.270452
1	-4.436440	2.348776	0.304319
6	-2.654884	-1.079314	-0.111493
6	-4.059946	-1.050417	0.130885
1	-5.734437	0.241537	0.459782
1	-4.636378	-1.967802	0.205433
6	-1.807666	-2.238857	-0.250862
6	-2.267753	-3.559448	-0.132054
6	0.384765	-3.046295	-0.594467
6	-1.386577	-4.615056	-0.248261
1	-3.323178	-3.736867	0.060491
6	-0.029923	-4.360704	-0.482271
1	1.426191	-2.794901	-0.782842
1	-1.746905	-5.637271	-0.154685
1	0.696386	-5.162282	-0.580179
7	-0.284128	2.044818	-0.440451
7	-1.990419	0.083061	-0.209689
7	-0.465109	-2.011351	-0.492779
77	0.048924	-0.001588	-0.597210
6	2.100391	-0.110820	1.584936
6	2.707823	-0.177812	2.838475
6	1.915754	-0.183427	3.978510
6	0.532422	-0.122641	3.852774
6	-0.012500	-0.062238	2.576691
1	3.789992	-0.230562	2.924013
1	2.378646	-0.235915	4.961390

1	-0.119784	-0.124343	4.721730
1	-1.090287	-0.016683	2.418166
6	2.811550	-0.096733	0.304574
6	4.197916	-0.103174	0.207631
6	2.660220	-0.059813	-2.141306
6	4.807798	-0.090369	-1.046312
1	4.823238	-0.112881	1.098568
6	4.038191	-0.071167	-2.220996
1	2.065562	-0.041351	-3.053734
1	5.894143	-0.094833	-1.112243
1	4.534168	-0.062658	-3.189782
1	-0.322762	0.022401	-2.152195
6	1.992244	-0.066761	-0.885373
7	0.749569	-0.057879	1.480984

***N-trans*-[Ir-OCOH]⁺ (Closed-shell singlet)**

E = -1513.75327621 a.u.

6	-0.568979	-3.001095	-0.609836
6	1.546618	-2.338732	0.146252
6	1.943557	-3.664092	0.247907
6	1.053275	-4.677156	-0.090905
6	-0.219993	-4.342197	-0.527761
1	-1.554949	-2.685639	-0.944734
1	2.947102	-3.903732	0.589672
1	1.358036	-5.717969	-0.013659
1	-0.945882	-5.101448	-0.804775
6	2.433309	-1.203899	0.477679
6	3.746138	-1.250351	0.936812
6	4.400547	-0.043701	1.178458
1	4.256191	-2.195497	1.103914
6	2.452423	1.168973	0.513093
6	3.766626	1.179721	0.972811
1	5.426924	-0.057618	1.536897
1	4.290874	2.111318	1.169956
6	1.579836	2.328880	0.234585
6	2.004106	3.643186	0.367137
6	-0.545512	3.052650	-0.431184
6	1.121882	4.682205	0.092769
1	3.022510	3.853957	0.682902
6	-0.171240	4.384108	-0.311170
1	-1.546113	2.765980	-0.747995
1	1.447896	5.714457	0.194483
1	-0.892473	5.164649	-0.536245

7	0.282384	-2.020607	-0.283346
7	1.855840	-0.009084	0.285469
7	0.298348	2.047624	-0.167514
77	-0.090523	0.018398	-0.333479
6	-2.275970	-0.057038	1.606181
6	-2.921408	-0.118303	2.842506
6	-2.181800	-0.164153	4.011842
6	-0.791044	-0.148388	3.940288
6	-0.195820	-0.092372	2.694280
1	-4.007809	-0.131909	2.879639
1	-2.685680	-0.211320	4.974795
1	-0.170893	-0.180093	4.831638
1	0.887292	-0.079145	2.591346
6	-2.936172	0.001398	0.305817
6	-4.327722	0.024657	0.146370
6	-2.647725	0.097096	-2.083059
6	-4.875064	0.080328	-1.127783
1	-4.988939	0.003036	1.012747
6	-4.032236	0.114674	-2.240848
1	-2.001773	0.129074	-2.961343
1	-5.955987	0.098170	-1.256273
1	-4.461965	0.158098	-3.241826
8	0.407281	0.126428	-2.338980
6	1.593695	-0.036951	-2.836204
1	2.394258	-0.267181	-2.094485
8	1.863483	0.045345	-4.022564
7	-0.911346	-0.050088	1.555616
6	-2.066504	0.041734	-0.810703

***C-trans*-[Ir]²⁺ (Closed-shell singlet)**

E = -1324.53061081 a.u.

6	-0.556675	0.590877	3.034804
6	-0.273626	-1.627664	2.343799
6	-0.151506	-2.046448	3.659725
6	-0.238794	-1.109677	4.684574
6	-0.442429	0.226014	4.369781
1	-0.715047	1.625314	2.736790
1	0.014427	-3.096906	3.884465
1	-0.144036	-1.426577	5.720237
1	-0.512081	0.988649	5.140290
6	-0.176286	-2.536584	1.188316
6	0.039901	-3.909178	1.211891
6	0.143180	-4.586449	0.000000

1	0.128296	-4.445422	2.152635
6	-0.176286	-2.536584	-1.188316
6	0.039901	-3.909178	-1.211891
1	0.313647	-5.660068	0.000000
1	0.128296	-4.445422	-2.152635
6	-0.273626	-1.627664	-2.343799
6	-0.151506	-2.046448	-3.659725
6	-0.556675	0.590877	-3.034804
6	-0.238794	-1.109677	-4.684574
1	0.014427	-3.096906	-3.884465
6	-0.442429	0.226014	-4.369781
1	-0.715047	1.625314	-2.736790
1	-0.144036	-1.426577	-5.720237
1	-0.512081	0.988649	-5.140290
7	-0.478305	-0.307369	2.046405
7	-0.283763	-1.911406	0.000000
7	-0.478305	-0.307369	-2.046405
77	-0.580334	0.038801	0.000000
6	1.586149	1.933314	0.000000
6	2.902697	2.405238	0.000000
6	3.965461	1.511776	0.000000
6	3.716833	0.140727	0.000000
6	2.409594	-0.346381	0.000000
1	3.098433	3.476959	0.000000
1	4.988076	1.883601	0.000000
1	4.547981	-0.563324	0.000000
1	2.247161	-1.424272	0.000000
6	0.411651	2.799886	0.000000
6	0.406254	4.193650	0.000000
6	-1.934853	2.770288	0.000000
6	-0.803988	4.870543	0.000000
1	1.345055	4.741677	0.000000
6	-1.998464	4.152296	0.000000
1	-2.827599	2.146386	0.000000
1	-0.817381	5.958377	0.000000
1	-2.963638	4.650665	0.000000
6	1.332808	0.540836	0.000000
7	-0.762499	2.118963	0.000000

N-trans-[Ir]²⁺ (Closed-shell singlet)

E = -1324.49833607 a.u.

6	-0.515037	0.566530	3.046229
6	-0.259254	-1.652804	2.337767

6	-0.134296	-2.076673	3.651755
6	-0.204499	-1.146178	4.683619
6	-0.394610	0.193120	4.378213
1	-0.665702	1.603467	2.753558
1	0.021369	-3.130366	3.869167
1	-0.106726	-1.471149	5.716529
1	-0.450468	0.952639	5.152944
6	-0.171610	-2.575859	1.186125
6	0.018678	-3.953760	1.215417
6	0.108783	-4.629362	0.000000
1	0.096537	-4.495850	2.153780
6	-0.171610	-2.575859	-1.186125
6	0.018678	-3.953760	-1.215417
1	0.258612	-5.706266	0.000000
1	0.096537	-4.495850	-2.153780
6	-0.259254	-1.652804	-2.337767
6	-0.134296	-2.076673	-3.651755
6	-0.515037	0.566530	-3.046229
6	-0.204499	-1.146178	-4.683619
1	0.021369	-3.130366	-3.869167
6	-0.394610	0.193120	-4.378213
1	-0.665702	1.603467	-2.753558
1	-0.106726	-1.471149	-5.716529
1	-0.450468	0.952639	-5.152944
7	-0.454371	-0.325132	2.049610
7	-0.262568	-1.960344	0.000000
7	-0.454371	-0.325132	-2.049610
77	-0.576960	0.065143	0.000000
6	1.559080	2.000353	0.000000
6	2.874451	2.462588	0.000000
6	3.929615	1.567407	0.000000
6	3.664688	0.199738	0.000000
6	2.350886	-0.223756	0.000000
1	3.056562	3.534303	0.000000
1	4.954540	1.930937	0.000000
1	4.460674	-0.539340	0.000000
1	2.098873	-1.280345	0.000000
6	0.359522	2.819499	0.000000
6	0.348557	4.219215	0.000000
6	-2.048334	2.772236	0.000000
6	-0.866815	4.890028	0.000000
1	1.279234	4.786273	0.000000
6	-2.062254	4.166580	0.000000
1	-2.993748	2.225322	0.000000
1	-0.886973	5.978355	0.000000
1	-3.013725	4.697966	0.000000

6	-0.837893	2.073882	0.000000
7	1.323837	0.650091	0.000000

***C-trans*-[Ir-Cl]⁰ (Doublet)**

E = -1457.32513734 a.u.

6	0.495928	-3.036422	0.524856
6	-1.613785	-2.323512	-0.223270
6	-2.028214	-3.649179	-0.342891
6	-1.157515	-4.675681	-0.018438
6	0.129872	-4.365677	0.423485
1	1.487422	-2.740416	0.864182
1	-3.034765	-3.866728	-0.692216
1	-1.476332	-5.711384	-0.110006
1	0.843392	-5.141623	0.686650
6	-2.451267	-1.168424	-0.545324
6	-3.748549	-1.175430	-1.015536
6	-4.374250	0.061961	-1.281391
1	-4.281018	-2.109087	-1.179890
6	-2.390663	1.247260	-0.595192
6	-3.707740	1.258633	-1.075232
1	-5.395652	0.073605	-1.654513
1	-4.203437	2.204227	-1.287722
6	-1.522409	2.356190	-0.335515
6	-1.870464	3.710794	-0.509755
6	0.641521	3.023783	0.361351
6	-0.957048	4.702993	-0.245139
1	-2.871833	3.957923	-0.857306
6	0.336810	4.357026	0.200113
1	1.625194	2.701805	0.702916
1	-1.230644	5.747257	-0.381052
1	1.086716	5.112978	0.415829
7	-0.344047	-2.033489	0.217218
7	-1.819267	0.019861	-0.351970
7	-0.242277	2.036790	0.118248
77	0.047649	0.003591	0.279178
6	2.292293	-0.095931	-1.550376
6	2.995723	-0.152534	-2.759538
6	2.307404	-0.176635	-3.964981
6	0.913104	-0.143554	-3.965138
6	0.205417	-0.089770	-2.765035
1	4.085328	-0.179128	-2.765587
1	2.856035	-0.220399	-4.904142
1	0.370557	-0.160656	-4.910100

1	-0.885718	-0.064676	-2.793329
6	2.941413	-0.060826	-0.241116
6	4.317726	-0.064387	-0.010304
6	2.544134	0.023855	2.065932
6	4.798105	-0.025472	1.288712
1	5.008699	-0.094937	-0.849131
6	3.897798	0.018880	2.350763
1	1.795330	0.060996	2.855053
1	5.870195	-0.028258	1.473872
1	4.233119	0.051043	3.383694
6	0.875559	-0.065790	-1.537067
7	2.075282	-0.015081	0.808168
7	-0.776310	0.081825	2.323553
6	-1.271738	0.130304	3.368388
6	-1.881011	0.191030	4.675072
1	-2.951742	0.400967	4.576650
1	-1.749213	-0.766007	5.191872
1	-1.413160	0.985719	5.266426

***N-trans*-[Ir-Cl]⁰ (Doublet)**

E = -1457.30365968 a.u.

6	-0.609383	3.040348	0.374346
6	1.554554	2.336017	-0.253831
6	1.937048	3.677019	-0.410158
6	1.029079	4.691046	-0.172636
6	-0.274068	4.376308	0.225532
1	-1.606710	2.734392	0.686803
1	2.953369	3.908284	-0.720037
1	1.330888	5.729109	-0.296517
1	-1.016584	5.144862	0.419342
6	2.448075	1.221128	-0.498796
6	3.808343	1.264501	-0.929531
6	4.458744	0.047352	-1.118414
1	4.316615	2.207407	-1.110198
6	2.482343	-1.168127	-0.469830
6	3.842944	-1.182992	-0.901344
1	5.496571	0.058220	-1.451002
1	4.377294	-2.115346	-1.060217
6	1.621197	-2.301889	-0.196854
6	2.041272	-3.634824	-0.322812
6	-0.522274	-3.052166	0.448290
6	1.161902	-4.668237	-0.062486
1	3.063646	-3.844198	-0.628351

6	-0.149723	-4.381233	0.329059
1	-1.527700	-2.767126	0.754518
1	1.492467	-5.699979	-0.163646
1	-0.870460	-5.165785	0.540282
7	0.260154	2.048104	0.150123
7	1.883680	0.020361	-0.302635
7	0.319171	-2.041329	0.200941
77	-0.070690	-0.000161	0.316600
6	-2.264837	-0.051482	-1.608865
6	-2.906880	-0.083041	-2.847687
6	-2.162386	-0.096263	-4.015048
6	-0.771660	-0.078269	-3.940314
6	-0.179291	-0.049478	-2.692172
1	-3.993006	-0.098915	-2.889170
1	-2.663196	-0.120591	-4.980464
1	-0.149929	-0.087221	-4.830998
1	0.902657	-0.035820	-2.578430
6	-2.923799	-0.034347	-0.307012
6	-4.315186	-0.033625	-0.150580
6	-2.641645	-0.001923	2.081233
6	-4.867030	-0.018886	1.122873
1	-4.973299	-0.042342	-1.019458
6	-4.026974	-0.004263	2.237402
1	-2.011028	0.012308	2.972302
1	-5.948271	-0.018246	1.249012
1	-4.457724	0.006876	3.238654
7	-0.901528	-0.036795	-1.557369
6	-2.052841	-0.015877	0.810386
7	0.615625	0.034610	2.209538
6	1.058717	0.060362	3.276736
6	1.601176	0.095654	4.612106
1	2.674193	0.313373	4.570875
1	1.099148	0.874987	5.196059
1	1.449954	-0.873392	5.100700

***C-trans*-[Ir-CH₃CN]⁺ (Doublet)**

E = -1457.32513734 a.u.

6	0.495928	-3.036422	0.524856
6	-1.613785	-2.323512	-0.223270
6	-2.028214	-3.649179	-0.342891
6	-1.157515	-4.675681	-0.018438
6	0.129872	-4.365677	0.423485
1	1.487422	-2.740416	0.864182

1	-3.034765	-3.866728	-0.692216
1	-1.476332	-5.711384	-0.110006
1	0.843392	-5.141623	0.686650
6	-2.451267	-1.168424	-0.545324
6	-3.748549	-1.175430	-1.015536
6	-4.374250	0.061961	-1.281391
1	-4.281018	-2.109087	-1.179890
6	-2.390663	1.247260	-0.595192
6	-3.707740	1.258633	-1.075232
1	-5.395652	0.073605	-1.654513
1	-4.203437	2.204227	-1.287722
6	-1.522409	2.356190	-0.335515
6	-1.870464	3.710794	-0.509755
6	0.641521	3.023783	0.361351
6	-0.957048	4.702993	-0.245139
1	-2.871833	3.957923	-0.857306
6	0.336810	4.357026	0.200113
1	1.625194	2.701805	0.702916
1	-1.230644	5.747257	-0.381052
1	1.086716	5.112978	0.415829
7	-0.344047	-2.033489	0.217218
7	-1.819267	0.019861	-0.351970
7	-0.242277	2.036790	0.118248
77	0.047649	0.003591	0.279178
6	2.292293	-0.095931	-1.550376
6	2.995723	-0.152534	-2.759538
6	2.307404	-0.176635	-3.964981
6	0.913104	-0.143554	-3.965138
6	0.205417	-0.089770	-2.765035
1	4.085328	-0.179128	-2.765587
1	2.856035	-0.220399	-4.904142
1	0.370557	-0.160656	-4.910100
1	-0.885718	-0.064676	-2.793329
6	2.941413	-0.060826	-0.241116
6	4.317726	-0.064387	-0.010304
6	2.544134	0.023855	2.065932
6	4.798105	-0.025472	1.288712
1	5.008699	-0.094937	-0.849131
6	3.897798	0.018880	2.350763
1	1.795330	0.060996	2.855053
1	5.870195	-0.028258	1.473872
1	4.233119	0.051043	3.383694
6	0.875559	-0.065790	-1.537067
7	2.075282	-0.015081	0.808168
7	-0.776310	0.081825	2.323553
6	-1.271738	0.130304	3.368388

6	-1.881011	0.191030	4.675072
1	-2.951742	0.400967	4.576650
1	-1.749213	-0.766007	5.191872
1	-1.413160	0.985719	5.266426

***N-trans*-[Ir-CH₃CN]⁺ (Doublet)**

E = -1457.30365968 a.u.

6	-0.609383	3.040348	0.374346
6	1.554554	2.336017	-0.253831
6	1.937048	3.677019	-0.410158
6	1.029079	4.691046	-0.172636
6	-0.274068	4.376308	0.225532
1	-1.606710	2.734392	0.686803
1	2.953369	3.908284	-0.720037
1	1.330888	5.729109	-0.296517
1	-1.016584	5.144862	0.419342
6	2.448075	1.221128	-0.498796
6	3.808343	1.264501	-0.929531
6	4.458744	0.047352	-1.118414
1	4.316615	2.207407	-1.110198
6	2.482343	-1.168127	-0.469830
6	3.842944	-1.182992	-0.901344
1	5.496571	0.058220	-1.451002
1	4.377294	-2.115346	-1.060217
6	1.621197	-2.301889	-0.196854
6	2.041272	-3.634824	-0.322812
6	-0.522274	-3.052166	0.448290
6	1.161902	-4.668237	-0.062486
1	3.063646	-3.844198	-0.628351
6	-0.149723	-4.381233	0.329059
1	-1.527700	-2.767126	0.754518
1	1.492467	-5.699979	-0.163646
1	-0.870460	-5.165785	0.540282
7	0.260154	2.048104	0.150123
7	1.883680	0.020361	-0.302635
7	0.319171	-2.041329	0.200941
77	-0.070690	-0.000161	0.316600
6	-2.264837	-0.051482	-1.608865
6	-2.906880	-0.083041	-2.847687
6	-2.162386	-0.096263	-4.015048
6	-0.771660	-0.078269	-3.940314
6	-0.179291	-0.049478	-2.692172
1	-3.993006	-0.098915	-2.889170

1	-2.663196	-0.120591	-4.980464
1	-0.149929	-0.087221	-4.830998
1	0.902657	-0.035820	-2.578430
6	-2.923799	-0.034347	-0.307012
6	-4.315186	-0.033625	-0.150580
6	-2.641645	-0.001923	2.081233
6	-4.867030	-0.018886	1.122873
1	-4.973299	-0.042342	-1.019458
6	-4.026974	-0.004263	2.237402
1	-2.011028	0.012308	2.972302
1	-5.948271	-0.018246	1.249012
1	-4.457724	0.006876	3.238654
7	-0.901528	-0.036795	-1.557369
6	-2.052841	-0.015877	0.810386
7	0.615625	0.034610	2.209538
6	1.058717	0.060362	3.276736
6	1.601176	0.095654	4.612106
1	2.674193	0.313373	4.570875
1	1.099148	0.874987	5.196059
1	1.449954	-0.873392	5.100700

***C-trans*-[Ir-H]⁰ (Doublet)**

E = -1325.33832180 a.u.

6	-0.673072	0.559431	3.039890
6	-0.271578	-1.647276	2.324556
6	-0.178285	-2.061404	3.664169
6	-0.334303	-1.143559	4.683934
6	-0.584637	0.198469	4.375058
1	-0.871241	1.588265	2.740484
1	0.015425	-3.108128	3.887156
1	-0.262049	-1.465432	5.721003
1	-0.709879	0.951038	5.148488
6	-0.110937	-2.529558	1.196045
6	0.202129	-3.921490	1.218636
6	0.349782	-4.576033	0.000000
1	0.331738	-4.447926	2.160195
6	-0.110937	-2.529558	-1.196045
6	0.202129	-3.921490	-1.218636
1	0.593562	-5.638322	0.000000
1	0.331738	-4.447926	-2.160195
6	-0.271578	-1.647276	-2.324556
6	-0.178285	-2.061404	-3.664169
6	-0.673072	0.559431	-3.039890

6	-0.334303	-1.143559	-4.683934
1	0.015425	-3.108128	-3.887156
6	-0.584637	0.198469	-4.375058
1	-0.871241	1.588265	-2.740484
1	-0.262049	-1.465432	-5.721003
1	-0.709879	0.951038	-5.148488
7	-0.529010	-0.319201	2.041625
7	-0.257696	-1.917703	0.000000
7	-0.529010	-0.319201	-2.041625
77	-0.596089	0.020999	0.000000
6	1.642275	1.959516	0.000000
6	2.944220	2.478905	0.000000
6	4.034391	1.618801	0.000000
6	3.825495	0.238726	0.000000
6	2.529775	-0.276306	0.000000
1	3.116018	3.555338	0.000000
1	5.045923	2.021913	0.000000
1	4.680156	-0.438451	0.000000
1	2.395674	-1.362419	0.000000
6	0.445583	2.803434	0.000000
6	0.448213	4.200578	0.000000
6	-1.896002	2.807019	0.000000
6	-0.748473	4.897205	0.000000
1	1.393059	4.738577	0.000000
6	-1.948031	4.189331	0.000000
1	-2.800301	2.202736	0.000000
1	-0.747145	5.985394	0.000000
1	-2.910490	4.693668	0.000000
6	1.408685	0.563663	0.000000
7	-0.736816	2.124496	0.000000
1	-2.315111	-0.274138	0.000000

***C-trans*-[Ir-OCOH]⁰ (Doublet)**

E = -1513.87267759 a.u.

6	-0.621737	-3.000012	-0.317724
6	1.538441	-2.294531	0.356284
6	1.895248	-3.642841	0.572869
6	0.989390	-4.648821	0.341296
6	-0.308288	-4.326148	-0.115621
1	-1.608847	-2.696954	-0.667674
1	2.899466	-3.872929	0.924520
1	1.270578	-5.686465	0.509937
1	-1.052681	-5.093817	-0.308319

6	2.405248	-1.175420	0.553913
6	3.733591	-1.157848	1.012296
6	4.399809	0.046658	1.142226
1	4.234618	-2.089908	1.268222
6	2.458361	1.232303	0.385647
6	3.764578	1.270056	0.829501
1	5.427986	0.055753	1.497055
1	4.294421	2.212690	0.941781
6	1.601518	2.371958	0.044356
6	2.017657	3.700580	0.082416
6	-0.535986	3.042546	-0.649973
6	1.130937	4.710338	-0.256191
1	3.037312	3.935484	0.378300
6	-0.170233	4.376827	-0.629956
1	-1.539898	2.729358	-0.933245
1	1.450104	5.749595	-0.228843
1	-0.896365	5.137475	-0.903551
7	0.251980	-1.997705	-0.106196
7	1.828558	0.038424	0.250493
7	0.317438	2.057546	-0.325523
77	-0.059661	0.023635	-0.298475
6	-2.246973	0.101607	1.601143
6	-2.919814	0.161455	2.827734
6	-2.201803	0.231464	4.014257
6	-0.807072	0.244419	3.976333
6	-0.130891	0.187229	2.758750
1	-4.009533	0.156456	2.861551
1	-2.726760	0.277780	4.966913
1	-0.240885	0.300526	4.906158
1	0.961489	0.198728	2.758615
6	-2.932019	0.032305	0.310151
6	-4.313206	-0.007201	0.111642
6	-2.585233	-0.050884	-2.008830
6	-4.821264	-0.066064	-1.176671
1	-4.985351	0.006264	0.966422
6	-3.945598	-0.085598	-2.260582
1	-1.838275	-0.066484	-2.801926
1	-5.897120	-0.096896	-1.336680
1	-4.306045	-0.129802	-3.284775
6	-0.828026	0.113462	1.545494
7	-2.093253	0.003889	-0.761335
8	0.499014	0.012826	-2.437073
6	1.434327	-0.713468	-2.934970
1	1.996066	-1.331851	-2.187177
8	1.749080	-0.782352	-4.118120

***N-trans*-[Ir-H]⁰ (Doublet)**

E = -1325.34460808 a.u.

6	-0.689149	0.529768	3.051295
6	-0.268922	-1.668128	2.318961
6	-0.156652	-2.084583	3.655676
6	-0.313422	-1.175285	4.683669
6	-0.584017	0.163699	4.384536
1	-0.902781	1.557362	2.760229
1	0.053815	-3.129722	3.870922
1	-0.226104	-1.502909	5.717836
1	-0.712859	0.911243	5.162278
6	-0.102773	-2.561448	1.192997
6	0.225251	-3.951294	1.221679
6	0.378117	-4.601586	0.000000
1	0.360396	-4.481392	2.160570
6	-0.102773	-2.561448	-1.192997
6	0.225251	-3.951294	-1.221679
1	0.631748	-5.661840	0.000000
1	0.360396	-4.481392	-2.160570
6	-0.268922	-1.668128	-2.318961
6	-0.156652	-2.084583	-3.655676
6	-0.689149	0.529768	-3.051295
6	-0.313422	-1.175285	-4.683669
1	0.053815	-3.129722	-3.870922
6	-0.584017	0.163699	-4.384536
1	-0.902781	1.557362	-2.760229
1	-0.226104	-1.502909	-5.717836
1	-0.712859	0.911243	-5.162278
7	-0.543193	-0.338118	2.042972
7	-0.255595	-1.960965	0.000000
7	-0.543193	-0.338118	-2.042972
77	-0.620169	0.041963	0.000000
6	1.647740	2.006173	0.000000
6	2.947974	2.521785	0.000000
6	4.033179	1.660368	0.000000
6	3.817477	0.284021	0.000000
6	2.509511	-0.169515	0.000000
1	3.107762	3.597006	0.000000
1	5.045207	2.060551	0.000000
1	4.640991	-0.425134	0.000000
1	2.280204	-1.235943	0.000000
6	0.417348	2.804105	0.000000
6	0.440842	4.205688	0.000000

6	-1.985071	2.849962	0.000000
6	-0.744233	4.927919	0.000000
1	1.388703	4.744763	0.000000
6	-1.960184	4.242755	0.000000
1	-2.953904	2.345527	0.000000
1	-0.722151	6.016677	0.000000
1	-2.897046	4.800997	0.000000
1	-2.218972	-0.240131	0.000000
6	-0.808249	2.077662	0.000000
7	1.458417	0.661259	0.000000

***N-trans*-[Ir-OCOH]⁺ (Doublet)**

E = -1513.85877971 a.u.

6	-0.606071	-2.998094	-0.467495
6	1.553428	-2.297977	0.232203
6	1.913080	-3.654482	0.404085
6	1.015175	-4.657943	0.141291
6	-0.285807	-4.328066	-0.307603
1	-1.592788	-2.690393	-0.813092
1	2.919193	-3.889698	0.747517
1	1.303170	-5.698663	0.277097
1	-1.025921	-5.092832	-0.526777
6	2.429352	-1.194495	0.469650
6	3.762668	-1.200266	0.933888
6	4.421549	-0.001678	1.120408
1	4.267808	-2.140260	1.149852
6	2.484054	1.210576	0.411574
6	3.789559	1.239728	0.865137
1	5.448681	-0.008140	1.479674
1	4.318647	2.174695	1.030703
6	1.611800	2.365292	0.126708
6	2.036291	3.686625	0.223498
6	-0.529835	3.083512	-0.499977
6	1.151225	4.720035	-0.047156
1	3.062778	3.900273	0.511471
6	-0.155769	4.414242	-0.414452
1	-1.538290	2.791036	-0.787005
1	1.479245	5.754234	0.027716
1	-0.882177	5.191399	-0.635982
7	0.256101	-1.992815	-0.220422
7	1.865176	0.030477	0.220310
7	0.319488	2.076911	-0.239398
77	-0.087799	0.036807	-0.346708

6	-2.241016	-0.003691	1.626541
6	-2.859422	-0.038252	2.878296
6	-2.094601	-0.052406	4.032249
6	-0.705545	-0.030773	3.930016
6	-0.137936	0.000093	2.669580
1	-3.944798	-0.055701	2.939505
1	-2.577225	-0.079345	5.006969
1	-0.066373	-0.038870	4.808584
1	0.941820	0.018052	2.533457
6	-2.928111	0.020908	0.338474
6	-4.323288	0.026447	0.210734
6	-2.693803	0.069754	-2.054263
6	-4.900552	0.051195	-1.051322
1	-4.964949	0.013693	1.092346
6	-4.081209	0.072333	-2.183089
1	-2.071603	0.089664	-2.951331
1	-5.984372	0.055172	-1.156213
1	-4.533538	0.092026	-3.175240
8	0.482099	0.169066	-2.342484
6	1.385322	-0.575585	-2.892158
1	1.840312	-1.341202	-2.220252
8	1.744292	-0.492295	-4.057660
7	-0.877864	0.011573	1.546483
6	-2.075626	0.043561	-0.795177

***C-trans*-[Ir]⁺ (Doublet)**

E = -1457.32513734 a.u.

6	0.495928	-3.036422	0.524856
6	-1.613785	-2.323512	-0.223270
6	-2.028214	-3.649179	-0.342891
6	-1.157515	-4.675681	-0.018438
6	0.129872	-4.365677	0.423485
1	1.487422	-2.740416	0.864182
1	-3.034765	-3.866728	-0.692216
1	-1.476332	-5.711384	-0.110006
1	0.843392	-5.141623	0.686650
6	-2.451267	-1.168424	-0.545324
6	-3.748549	-1.175430	-1.015536
6	-4.374250	0.061961	-1.281391
1	-4.281018	-2.109087	-1.179890
6	-2.390663	1.247260	-0.595192
6	-3.707740	1.258633	-1.075232
1	-5.395652	0.073605	-1.654513

1	-4.203437	2.204227	-1.287722
6	-1.522409	2.356190	-0.335515
6	-1.870464	3.710794	-0.509755
6	0.641521	3.023783	0.361351
6	-0.957048	4.702993	-0.245139
1	-2.871833	3.957923	-0.857306
6	0.336810	4.357026	0.200113
1	1.625194	2.701805	0.702916
1	-1.230644	5.747257	-0.381052
1	1.086716	5.112978	0.415829
7	-0.344047	-2.033489	0.217218
7	-1.819267	0.019861	-0.351970
7	-0.242277	2.036790	0.118248
77	0.047649	0.003591	0.279178
6	2.292293	-0.095931	-1.550376
6	2.995723	-0.152534	-2.759538
6	2.307404	-0.176635	-3.964981
6	0.913104	-0.143554	-3.965138
6	0.205417	-0.089770	-2.765035
1	4.085328	-0.179128	-2.765587
1	2.856035	-0.220399	-4.904142
1	0.370557	-0.160656	-4.910100
1	-0.885718	-0.064676	-2.793329
6	2.941413	-0.060826	-0.241116
6	4.317726	-0.064387	-0.010304
6	2.544134	0.023855	2.065932
6	4.798105	-0.025472	1.288712
1	5.008699	-0.094937	-0.849131
6	3.897798	0.018880	2.350763
1	1.795330	0.060996	2.855053
1	5.870195	-0.028258	1.473872
1	4.233119	0.051043	3.383694
6	0.875559	-0.065790	-1.537067
7	2.075282	-0.015081	0.808168
7	-0.776310	0.081825	2.323553
6	-1.271738	0.130304	3.368388
6	-1.881011	0.191030	4.675072
1	-2.951742	0.400967	4.576650
1	-1.749213	-0.766007	5.191872
1	-1.413160	0.985719	5.266426

N-trans-[Ir]⁺ (Doublet)

E = -1457.30365968 a.u.

6	-0.609383	3.040348	0.374346
6	1.554554	2.336017	-0.253831
6	1.937048	3.677019	-0.410158
6	1.029079	4.691046	-0.172636
6	-0.274068	4.376308	0.225532
1	-1.606710	2.734392	0.686803
1	2.953369	3.908284	-0.720037
1	1.330888	5.729109	-0.296517
1	-1.016584	5.144862	0.419342
6	2.448075	1.221128	-0.498796
6	3.808343	1.264501	-0.929531
6	4.458744	0.047352	-1.118414
1	4.316615	2.207407	-1.110198
6	2.482343	-1.168127	-0.469830
6	3.842944	-1.182992	-0.901344
1	5.496571	0.058220	-1.451002
1	4.377294	-2.115346	-1.060217
6	1.621197	-2.301889	-0.196854
6	2.041272	-3.634824	-0.322812
6	-0.522274	-3.052166	0.448290
6	1.161902	-4.668237	-0.062486
1	3.063646	-3.844198	-0.628351
6	-0.149723	-4.381233	0.329059
1	-1.527700	-2.767126	0.754518
1	1.492467	-5.699979	-0.163646
1	-0.870460	-5.165785	0.540282
7	0.260154	2.048104	0.150123
7	1.883680	0.020361	-0.302635
7	0.319171	-2.041329	0.200941
77	-0.070690	-0.000161	0.316600
6	-2.264837	-0.051482	-1.608865
6	-2.906880	-0.083041	-2.847687
6	-2.162386	-0.096263	-4.015048
6	-0.771660	-0.078269	-3.940314
6	-0.179291	-0.049478	-2.692172
1	-3.993006	-0.098915	-2.889170
1	-2.663196	-0.120591	-4.980464
1	-0.149929	-0.087221	-4.830998
1	0.902657	-0.035820	-2.578430
6	-2.923799	-0.034347	-0.307012
6	-4.315186	-0.033625	-0.150580
6	-2.641645	-0.001923	2.081233
6	-4.867030	-0.018886	1.122873
1	-4.973299	-0.042342	-1.019458
6	-4.026974	-0.004263	2.237402
1	-2.011028	0.012308	2.972302

1	-5.948271	-0.018246	1.249012
1	-4.457724	0.006876	3.238654
7	-0.901528	-0.036795	-1.557369
6	-2.052841	-0.015877	0.810386
7	0.615625	0.034610	2.209538
6	1.058717	0.060362	3.276736
6	1.601176	0.095654	4.612106
1	2.674193	0.313373	4.570875
1	1.099148	0.874987	5.196059
1	1.449954	-0.873392	5.100700

***C-trans*-[Ir]⁰ (Closed-shell singlet)**

E = -1324.75644229 a.u.

6	-0.476090	0.509079	3.025620
6	-0.200394	-1.736653	2.336812
6	-0.068496	-2.122070	3.685398
6	-0.143083	-1.187622	4.689108
6	-0.346285	0.167948	4.347771
1	-0.635093	1.541951	2.716504
1	0.099598	-3.172680	3.917074
1	-0.039564	-1.486024	5.730199
1	-0.403927	0.941129	5.110031
6	-0.142422	-2.621752	1.217439
6	0.070271	-3.991361	1.212194
6	0.141814	-4.686650	0.000000
1	0.199498	-4.523229	2.153902
6	-0.142422	-2.621752	-1.217439
6	0.070271	-3.991361	-1.212194
1	0.306375	-5.761596	0.000000
1	0.199498	-4.523229	-2.153902
6	-0.200394	-1.736653	-2.336812
6	-0.068496	-2.122070	-3.685398
6	-0.476090	0.509079	-3.025620
6	-0.143083	-1.187622	-4.689108
1	0.099598	-3.172680	-3.917074
6	-0.346285	0.167948	-4.347771
1	-0.635093	1.541951	-2.716504
1	-0.039564	-1.486024	-5.730199
1	-0.403927	0.941129	-5.110031
7	-0.428775	-0.399389	2.014838
7	-0.363796	-1.970604	0.000000
7	-0.428775	-0.399389	-2.014838
77	-0.441427	-0.042064	0.000000

6	1.423427	2.251152	0.000000
6	2.652654	2.922755	0.000000
6	3.838584	2.199738	0.000000
6	3.799043	0.803479	0.000000
6	2.578310	0.131689	0.000000
1	2.689967	4.012730	0.000000
1	4.794365	2.721160	0.000000
1	4.729216	0.234797	0.000000
1	2.567386	-0.962324	0.000000
6	0.120293	2.907862	0.000000
6	-0.111131	4.284531	0.000000
6	-2.179924	2.500455	0.000000
6	-1.412430	4.760493	0.000000
1	0.727852	4.976902	0.000000
6	-2.471038	3.854242	0.000000
1	-2.965252	1.745758	0.000000
1	-1.602265	5.831994	0.000000
1	-3.505935	4.185668	0.000000
6	1.368420	0.837286	0.000000
7	-0.921941	2.032025	0.000000

***C-trans*-[Ir]⁰ (Triplet)**

E = -1324.74132328 a.u.

6	-0.575639	3.052123	-0.584210
6	1.665834	2.329567	-0.273095
6	2.060689	3.682764	-0.140392
6	1.138453	4.694063	-0.232816
6	-0.226083	4.377853	-0.457286
1	-1.610760	2.754007	-0.757297
1	3.110652	3.907701	0.041575
1	1.451756	5.731393	-0.128083
1	-0.987295	5.149934	-0.531411
6	2.546042	1.213636	-0.179773
6	3.943348	1.221185	0.069661
6	4.605290	0.000250	0.183182
1	4.479823	2.160732	0.180015
6	2.546177	-1.213389	-0.179744
6	3.943478	-1.220771	0.069729
1	5.678119	0.000314	0.377253
1	4.480059	-2.160246	0.180176
6	1.666103	-2.329422	-0.273021
6	2.061117	-3.682558	-0.140201
6	-0.575275	-3.052257	-0.584097

6	1.139001	-4.693974	-0.232534
1	3.111107	-3.907353	0.041784
6	-0.225571	-4.377933	-0.457037
1	-1.610433	-2.754275	-0.757206
1	1.452422	-5.731258	-0.127705
1	-0.986695	-5.150108	-0.531086
7	0.312087	2.040687	-0.514204
7	1.925250	0.000090	-0.332310
7	0.312334	-2.040703	-0.514177
77	-0.028672	-0.000028	-0.555310
6	-2.826207	-0.000065	0.385091
6	-4.221304	0.000051	0.350791
6	-4.875291	-0.000159	-0.871153
6	-4.129827	-0.000446	-2.049288
6	-2.749196	-0.000451	-1.953916
1	-4.787664	0.000325	1.279170
1	-5.962814	-0.000101	-0.907329
1	-4.606167	-0.000629	-3.025922
1	-2.109296	-0.000602	-2.835873
6	-1.986200	0.000010	1.577181
6	-2.481256	-0.000066	2.886483
6	0.276866	0.000208	2.435290
6	-1.605682	0.000037	3.963538
1	-3.556579	-0.000251	3.065628
6	-0.228676	0.000195	3.733736
1	1.357176	0.000307	2.280981
1	-1.992769	-0.000015	4.980887
1	0.461600	0.000291	4.577173
7	-2.113442	-0.000252	-0.772178
6	-0.589208	0.000098	1.334922

***N-trans*-[Ir]⁰ (Triplet)**

E = -1324.75644284 a.u.

6	0.509017	-3.025647	-0.475932
6	-1.736721	-2.336806	-0.200223
6	-2.122142	-3.685381	-0.068266
6	-1.187700	-4.689106	-0.142784
6	0.167874	-4.347788	-0.346049
1	1.541884	-2.716571	-0.635030
1	-3.172756	-3.917047	0.099815
1	-1.486125	-5.730184	-0.039214
1	0.941058	-5.110044	-0.403708
6	-2.621783	-1.217407	-0.142370

6	-3.991448	-1.212200	0.070011
6	-4.686756	0.000000	0.141432
1	-4.523337	-2.153920	0.199039
6	-2.621783	1.217407	-0.142370
6	-3.991448	1.212200	0.070011
1	-5.761750	0.000000	0.305692
1	-4.523337	2.153921	0.199039
6	-1.736720	2.336806	-0.200223
6	-2.122142	3.685381	-0.068266
6	0.509017	3.025647	-0.475931
6	-1.187700	4.689106	-0.142783
1	-3.172756	3.917047	0.099815
6	0.167874	4.347788	-0.346049
1	1.541884	2.716571	-0.635030
1	-1.486125	5.730185	-0.039214
1	0.941058	5.110044	-0.403708
7	-0.399431	-2.014829	-0.428629
7	-1.970614	0.000000	-0.363518
7	-0.399430	2.014829	-0.428629
77	-0.042061	0.000000	-0.441357
6	2.907849	0.000000	0.119982
6	4.284504	0.000000	-0.111571
6	4.760332	0.000000	-1.412914
6	3.853961	0.000000	-2.471435
6	2.500205	0.000000	-2.180191
1	4.976940	0.000000	0.727363
1	5.831814	0.000000	-1.602853
1	4.185277	0.000000	-3.506366
1	1.745441	0.000000	-2.965456
6	2.251321	0.000000	1.423230
6	2.923091	0.000000	2.652368
6	0.132013	0.000000	2.578434
6	2.200228	0.000000	3.838401
1	4.013071	0.000000	2.689552
6	0.803964	0.000000	3.799076
1	-0.961997	0.000000	2.567626
1	2.721781	0.000000	4.794113
1	0.235395	0.000000	4.729318
7	2.031916	0.000000	-0.922166
6	0.837465	0.000000	1.368458

***C-trans*-[Ir]⁰ CO₂ Binding Transition State (Closed-shell singlet)**

E = -1513.25343819 a.u.

6	0.614829	2.990245	-0.347390
6	-1.581858	2.366150	0.214892
6	-1.937272	3.716984	0.331451
6	-0.999817	4.701025	0.099233
6	0.307320	4.329215	-0.248629
1	1.616018	2.652244	-0.611846
1	-2.958206	3.976806	0.603306
1	-1.272119	5.750569	0.186082
1	1.076665	5.072594	-0.440488
6	-2.484867	1.257901	0.414224
6	-3.828878	1.288624	0.755334
6	-4.532738	0.091789	0.909564
1	-4.331050	2.241933	0.910358
6	-2.534497	-1.159678	0.417130
6	-3.879276	-1.132742	0.758404
1	-5.586355	0.113904	1.176643
1	-4.419974	-2.064023	0.917204
6	-1.678227	-2.305559	0.228269
6	-2.090256	-3.639724	0.355860
6	0.495598	-3.026667	-0.309217
6	-1.192757	-4.663783	0.142106
1	-3.122884	-3.854359	0.623501
6	0.132273	-4.350307	-0.197748
1	1.512096	-2.733074	-0.568181
1	-1.508552	-5.700242	0.238596
1	0.871913	-5.127120	-0.373401
7	-0.292697	2.013968	-0.130134
7	-1.879111	0.035915	0.193710
7	-0.372817	-2.010986	-0.111865
77	0.004010	-0.006358	-0.196773
6	2.544772	-0.025804	1.359248
6	3.392156	-0.020652	2.474669
6	2.851626	-0.004493	3.753930
6	1.465196	0.006192	3.920448
6	0.621538	0.002137	2.810241
1	4.475371	-0.028888	2.348826
1	3.508371	-0.000281	4.622344
1	1.040168	0.018234	4.924378
1	-0.462147	0.011452	2.963039
6	3.011058	-0.046469	-0.024631
6	4.344942	-0.065206	-0.435885
6	2.306934	-0.073667	-2.251121
6	4.647654	-0.088386	-1.787388
1	5.139134	-0.062349	0.307325
6	3.610274	-0.094093	-2.717145
1	1.459128	-0.077202	-2.934062

1	5.685104	-0.102876	-2.115236
1	3.801959	-0.113706	-3.786567
6	1.140869	-0.013154	1.510764
7	2.005480	-0.048436	-0.941740
6	-1.302206	0.013935	-2.477965
8	-1.565437	-1.129337	-2.765256
8	-1.400281	1.161817	-2.842497

***C-trans*-[Ir-CO₂]⁰ (Closed-shell singlet)**

E = -1513.26384926 a.u.

6	-0.328009	-3.040042	-0.550007
6	1.788133	-2.255659	0.072695
6	2.264598	-3.560554	0.163200
6	1.415327	-4.620856	-0.113169
6	0.096386	-4.355200	-0.475856
1	-1.348416	-2.780361	-0.826651
1	3.299038	-3.738633	0.447769
1	1.776941	-5.644158	-0.046065
1	-0.602195	-5.156751	-0.700811
6	2.595060	-1.063181	0.323529
6	3.942714	-0.999526	0.650471
6	4.539350	0.250743	0.811221
1	4.525807	-1.909393	0.770626
6	2.445911	1.318315	0.322992
6	3.795716	1.415307	0.649415
1	5.594622	0.315506	1.064688
1	4.265584	2.388025	0.774513
6	1.493591	2.407942	0.131768
6	1.818670	3.758537	0.256411
6	-0.732934	2.965403	-0.333742
6	0.841001	4.720515	0.069392
1	2.838980	4.047861	0.496344
6	-0.460314	4.316776	-0.229763
1	-1.732125	2.600409	-0.566813
1	1.087527	5.776007	0.158725
1	-1.258150	5.038218	-0.384222
7	0.488375	-2.006697	-0.286376
7	1.890078	0.088584	0.178511
7	0.211078	2.024561	-0.163328
77	0.012743	-0.006802	-0.295388
6	-2.307443	-0.167670	1.603234
6	-3.044635	-0.246157	2.793264
6	-2.385166	-0.285109	4.014944

6	-0.990429	-0.246087	4.049580
6	-0.261312	-0.169714	2.862560
1	-4.134573	-0.279451	2.776931
1	-2.956300	-0.346129	4.940171
1	-0.470873	-0.276066	5.008059
1	0.831667	-0.140294	2.919006
6	-2.930338	-0.120518	0.278397
6	-4.307738	-0.096144	0.049650
6	-2.539716	-0.058020	-2.027604
6	-4.795849	-0.045175	-1.245482
1	-4.994117	-0.112281	0.892714
6	-3.895832	-0.030348	-2.306494
1	-1.780698	-0.090890	-2.808527
1	-5.868916	-0.020909	-1.425440
1	-4.231775	-0.000339	-3.339781
6	-0.896079	-0.128120	1.614596
7	-2.059348	-0.090401	-0.770785
6	0.665748	0.106795	-2.385399
8	1.531582	0.978100	-2.617833
8	0.156791	-0.714663	-3.183578

***N-trans*-[Ir-CO₂]⁰ (Closed-shell singlet)**

E = -1784.87884473 a.u.

6	-0.456285	0.551754	3.030974
6	-0.010130	-1.637596	2.333727
6	0.101197	-2.053294	3.652818
6	-0.073450	-1.134170	4.681008
6	-0.356800	0.187000	4.366921
1	-0.678402	1.574160	2.732197
1	0.326372	-3.093397	3.874490
1	0.012436	-1.452656	5.717057
1	-0.501346	0.938276	5.138230
6	0.161392	-2.551763	1.185280
6	0.401544	-3.923031	1.214902
6	0.521905	-4.594469	0.000000
1	0.485526	-4.464596	2.153388
6	0.161392	-2.551763	-1.185280
6	0.401544	-3.923031	-1.214902
1	0.708020	-5.665785	0.000000
1	0.485526	-4.464596	-2.153388
6	-0.010130	-1.637596	-2.333727
6	0.101197	-2.053294	-3.652818
6	-0.456285	0.551754	-3.030974

6	-0.073450	-1.134170	-4.681008
1	0.326372	-3.093397	-3.874490
6	-0.356800	0.187000	-4.366921
1	-0.678402	1.574160	-2.732197
1	0.012436	-1.452656	-5.717057
1	-0.501346	0.938276	-5.138230
7	-0.288698	-0.328273	2.036687
7	0.064523	-1.936760	0.000000
7	-0.288698	-0.328273	-2.036687
77	-0.393175	0.052318	0.000000
6	1.642170	2.155134	0.000000
6	2.911333	2.736994	0.000000
6	4.041816	1.938292	0.000000
6	3.899913	0.552380	0.000000
6	2.624198	0.020977	0.000000
1	3.004520	3.819793	0.000000
1	5.030451	2.392108	0.000000
1	4.759257	-0.112207	0.000000
1	2.459541	-1.054593	0.000000
6	0.373760	2.875021	0.000000
6	0.285438	4.272888	0.000000
6	-2.024657	2.708213	0.000000
6	-0.959457	4.885661	0.000000
1	1.185292	4.888152	0.000000
6	-2.112902	4.099189	0.000000
1	-2.940542	2.115168	0.000000
1	-1.033167	5.971849	0.000000
1	-3.092569	4.577517	0.000000
17	-2.700411	-0.640968	0.000000
7	1.525043	0.796471	0.000000
6	-0.784069	2.056958	0.000000

***C-trans*-[Ir-COOH]⁺ (Closed-shell singlet)**

E = -1513.75386800 a.u.

6	0.552817	3.045957	-0.412274
6	-1.612989	2.341222	0.123149
6	-2.034497	3.658096	0.246854
6	-1.126315	4.688469	0.035411
6	0.185639	4.379487	-0.297913
1	1.567009	2.750673	-0.674320
1	-3.068095	3.876054	0.503155
1	-1.445321	5.723608	0.129695
1	0.926397	5.155112	-0.470841

6	-2.490613	1.177584	0.323390
6	-3.820555	1.179788	0.729338
6	-4.471789	-0.040204	0.888343
1	-4.341253	2.113177	0.927607
6	-2.476851	-1.198242	0.250515
6	-3.807573	-1.240104	0.653235
1	-5.510768	-0.055821	1.207627
1	-4.319227	-2.189289	0.789678
6	-1.587630	-2.337076	-0.021088
6	-1.992816	-3.663967	0.038062
6	0.578805	-2.987890	-0.615321
6	-1.076893	-4.671127	-0.238675
1	-3.019532	-3.907259	0.298790
6	0.227663	-4.329235	-0.570567
1	1.587230	-2.668333	-0.871649
1	-1.383184	-5.713434	-0.195503
1	0.974857	-5.085345	-0.794568
7	-0.317829	2.051348	-0.208427
7	-1.876090	-0.001444	0.096281
7	-0.300112	-2.014053	-0.349892
77	0.033972	0.022114	-0.362271
6	2.087648	-0.095985	1.774765
6	2.685118	-0.161204	3.040667
6	1.892354	-0.194999	4.180207
6	0.503335	-0.164357	4.057485
6	-0.088992	-0.102146	2.795742
1	3.769487	-0.185051	3.146887
1	2.356402	-0.244591	5.163893
1	-0.120383	-0.189956	4.951268
1	-1.181363	-0.081598	2.731660
6	2.862464	-0.046858	0.532727
6	4.256510	-0.077416	0.463366
6	2.749198	0.108382	-1.802618
6	4.893250	-0.017521	-0.764722
1	4.839101	-0.148068	1.378337
6	4.126964	0.081269	-1.922370
1	2.101092	0.210213	-2.670021
1	5.979680	-0.043553	-0.818609
1	4.582474	0.138839	-2.907161
6	0.682395	-0.066119	1.628663
7	2.125557	0.038951	-0.612200
6	-0.412988	0.169902	-2.418573
8	0.084965	0.939799	-3.231453
8	-1.399272	-0.667824	-2.865793
1	-1.518610	-0.471758	-3.820221

***N-trans*-[Ir-COOH]⁺ (Closed-shell singlet)**

E = -1513.76249432 a.u.

6	0.560045	3.044407	-0.471008
6	-1.610146	2.357262	0.067723
6	-2.020065	3.678334	0.181059
6	-1.104614	4.702235	-0.034898
6	0.204525	4.382302	-0.363961
1	1.570081	2.738927	-0.736315
1	-3.052310	3.906765	0.433454
1	-1.417682	5.739902	0.052080
1	0.951674	5.150722	-0.541588
6	-2.515513	1.209234	0.286428
6	-3.846928	1.240306	0.691387
6	-4.508250	0.027592	0.873045
1	-4.362559	2.180150	0.871606
6	-2.527773	-1.163118	0.262475
6	-3.859993	-1.187718	0.667055
1	-5.548089	0.029996	1.190707
1	-4.385543	-2.125415	0.828613
6	-1.635389	-2.315604	0.021739
6	-2.059951	-3.633581	0.114344
6	0.524830	-3.019241	-0.533680
6	-1.158915	-4.664858	-0.124206
1	-3.093144	-3.853739	0.370122
6	0.152995	-4.354266	-0.451435
1	1.539125	-2.723384	-0.793871
1	-1.484398	-5.699992	-0.054985
1	0.890528	-5.127789	-0.646250
7	-0.314728	2.055115	-0.260425
7	-1.925988	0.021716	0.083880
7	-0.337711	-2.021829	-0.306436
77	0.052099	0.012237	-0.398874
6	2.119882	-0.052467	1.782249
6	2.703526	-0.080454	3.052342
6	1.900524	-0.086843	4.180981
6	0.515256	-0.065757	4.038166
6	-0.006676	-0.039518	2.756552
1	3.785388	-0.096900	3.154712
1	2.352901	-0.107992	5.170401
1	-0.149842	-0.069891	4.897408
1	-1.084052	-0.023488	2.588671
6	2.858086	-0.042580	0.515101
6	4.258731	-0.071022	0.472531

6	2.792083	0.007234	-1.887650
6	4.923990	-0.064158	-0.745025
1	4.839621	-0.099382	1.394324
6	4.184455	-0.024740	-1.926999
1	2.241837	0.052287	-2.828220
1	6.012196	-0.088172	-0.773183
1	4.698424	-0.017413	-2.888496
6	-0.387010	0.111145	-2.358364
8	-0.094881	1.013763	-3.127878
7	0.768010	-0.032550	1.662759
6	2.083732	-0.004343	-0.676076
8	-1.108975	-0.944662	-2.844531
1	-1.260608	-0.756068	-3.794284

***C-trans*-[Ir-CO]²⁺ (Closed-shell singlet)**

E = -1437.80323353 a.u.

6	-0.528957	0.603041	3.029832
6	-0.121183	-1.601799	2.344647
6	-0.029088	-2.017039	3.664338
6	-0.188995	-1.086457	4.685501
6	-0.439521	0.240176	4.366901
1	-0.730966	1.627673	2.724961
1	0.162963	-3.061366	3.895038
1	-0.118228	-1.402499	5.723229
1	-0.568798	0.996776	5.135329
6	0.050534	-2.501189	1.190457
6	0.409701	-3.844338	1.212743
6	0.580837	-4.505559	0.000000
1	0.571288	-4.365676	2.152386
6	0.050534	-2.501189	-1.190457
6	0.409701	-3.844338	-1.212743
1	0.868136	-5.553884	0.000000
1	0.571288	-4.365676	-2.152386
6	-0.121183	-1.601799	-2.344647
6	-0.029088	-2.017039	-3.664338
6	-0.528957	0.603041	-3.029832
6	-0.188995	-1.086457	-4.685501
1	0.162963	-3.061366	-3.895038
6	-0.439521	0.240176	-4.366901
1	-0.730966	1.627673	-2.724961
1	-0.118228	-1.402499	-5.723229
1	-0.568798	0.996776	-5.135329
7	-0.376345	-0.291288	2.048817

7	-0.122669	-1.897831	0.000000
7	-0.376345	-0.291288	-2.048817
77	-0.499777	0.057431	0.000000
6	1.797530	1.878211	0.000000
6	3.119684	2.337060	0.000000
6	4.169574	1.428829	0.000000
6	3.903314	0.061790	0.000000
6	2.586991	-0.400605	0.000000
1	3.336354	3.404188	0.000000
1	5.196923	1.787808	0.000000
1	4.725009	-0.653217	0.000000
1	2.417821	-1.478687	0.000000
6	0.643516	2.774964	0.000000
6	0.712214	4.167808	0.000000
6	-1.698972	2.888449	0.000000
6	-0.450791	4.918996	0.000000
1	1.680980	4.659896	0.000000
6	-1.681961	4.269677	0.000000
1	-2.640798	2.346465	0.000000
1	-0.398650	6.005406	0.000000
1	-2.619980	4.817153	0.000000
6	1.517320	0.494663	0.000000
7	-0.569735	2.154687	0.000000
6	-2.469971	-0.220520	0.000000
8	-3.600679	-0.392301	0.000000

[Ru^{II}(tpy)(bpy)(NCCH₃)]²⁺ (Closed-shell singlet)

E = -1464.40555672 a.u.

44	0.044575	0.004773	0.337676
6	0.522095	-3.047114	0.483493
6	-1.593690	-2.335753	-0.195301
6	-2.018077	-3.652112	-0.327982
6	-1.134093	-4.686544	-0.045671
6	0.157215	-4.381285	0.363926
1	1.521149	-2.757776	0.806295
1	-3.033245	-3.868467	-0.650898
1	-1.454637	-5.720711	-0.146694
1	0.880388	-5.159293	0.592697
6	-2.448929	-1.172066	-0.485079
6	-3.765535	-1.192964	-0.935071
6	-4.409504	0.018084	-1.169656
1	-4.283871	-2.133532	-1.103617
6	-2.435497	1.197071	-0.503757

6	-3.751458	1.225338	-0.955419
1	-5.437450	0.021155	-1.523504
1	-4.259052	2.168683	-1.140504
6	-1.568461	2.355551	-0.228354
6	-1.980012	3.674575	-0.374936
6	0.554558	3.053451	0.441617
6	-1.085532	4.703251	-0.104921
1	-2.993549	3.897707	-0.698389
6	0.203070	4.389724	0.306821
1	1.550843	2.758104	0.767400
1	-1.395959	5.739372	-0.216969
1	0.934315	5.162927	0.525998
7	-0.323364	-2.044523	0.215459
7	-1.830138	0.010632	-0.292313
7	-0.301049	2.056260	0.185795
6	2.295013	-0.029566	-1.528513
6	3.003144	-0.056216	-2.726722
6	2.312477	-0.070940	-3.929612
6	0.922628	-0.057914	-3.909837
6	0.273160	-0.032140	-2.686535
1	4.089764	-0.066625	-2.718948
1	2.855289	-0.092129	-4.871486
1	0.339462	-0.067956	-4.826528
1	-0.813964	-0.021660	-2.628218
6	2.931873	-0.012722	-0.208001
6	4.310601	-0.008415	-0.013686
6	2.567728	0.015972	2.088723
6	4.815886	0.007284	1.278083
1	4.985374	-0.016037	-0.865559
6	3.928702	0.019116	2.348890
1	1.838280	0.026266	2.896062
1	5.890211	0.010685	1.445813
1	4.278591	0.031589	3.377599
7	0.935597	-0.018826	-1.518272
7	-0.668884	0.017967	2.235699
6	-1.123591	0.016396	3.301277
6	-1.677983	0.009917	4.633992
1	-2.751868	-0.203708	4.590620
1	-1.186483	-0.760005	5.239360
1	-1.527888	0.986469	5.107989
7	2.070447	0.000643	0.841795

[Ru^{II}(tpy)(bpy)H]⁺ (Closed-shell singlet)

E = -1332.42982027 a.u.

44	-0.651471	-0.009688	0.000000
6	-0.688565	0.496215	3.047726
6	-0.294759	-1.690304	2.341730
6	-0.150563	-2.111489	3.660448
6	-0.283416	-1.192872	4.691752
6	-0.556154	0.135117	4.379468
1	-0.905469	1.523441	2.757905
1	0.070625	-3.154403	3.875365
1	-0.172559	-1.509866	5.726120
1	-0.666244	0.889798	5.153972
6	-0.158082	-2.579455	1.184465
6	0.092020	-3.947518	1.206176
6	0.210875	-4.631315	0.000000
1	0.190570	-4.477400	2.150522
6	-0.158082	-2.579455	-1.184465
6	0.092020	-3.947518	-1.206176
1	0.402391	-5.701528	0.000000
1	0.190570	-4.477400	-2.150522
6	-0.294759	-1.690304	-2.341730
6	-0.150563	-2.111489	-3.660448
6	-0.688565	0.496215	-3.047726
6	-0.283416	-1.192872	-4.691752
1	0.070625	-3.154403	-3.875365
6	-0.556154	0.135117	-4.379468
1	-0.905469	1.523441	-2.757905
1	-0.172559	-1.509866	-5.726120
1	-0.666244	0.889798	-5.153972
7	-0.566305	-0.383520	2.040697
7	-0.293044	-1.932519	0.000000
7	-0.566305	-0.383520	-2.040697
6	1.480015	2.091893	0.000000
6	2.734564	2.700864	0.000000
6	3.874684	1.911127	0.000000
6	3.740127	0.526240	0.000000
6	2.463730	-0.014460	0.000000
1	2.822789	3.783876	0.000000
1	4.859066	2.373578	0.000000
1	4.606582	-0.129953	0.000000
1	2.306325	-1.093522	0.000000
6	0.212961	2.834376	0.000000
6	0.145638	4.226622	0.000000
6	-2.107160	2.691406	0.000000
6	-1.089791	4.854633	0.000000
1	1.057634	4.817609	0.000000
6	-2.238577	4.069797	0.000000

1	-2.978857	2.041340	0.000000
1	-1.154394	5.940191	0.000000
1	-3.230799	4.513511	0.000000
1	-2.283092	-0.329298	0.000000
7	1.357432	0.742940	0.000000
7	-0.912480	2.068608	0.000000