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Synthesis of Iridaboratranes Bearing Phosphine-Tethered Borane: Reversible CO/PR₃ (R = Me, OMe, OEt) Substitution Reactions Induced by a σ -Electron-Acceptor Borane Ligand

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Supporting Information

ABSTRACT: The iridaboratrane $[\{o-(Ph_2P)C_6H_4\}_3B]IrH(CO)$ (1-Ir), bearing phosphine-tethered borane, was synthesized via phosphine ligand exchange between the tris(triphenylphosphine) carbonyl hydride $IrH(CO)(PPh_3)_3$ (2-Ir) and the tris(phosphine)borane $\{o-(Ph_2P)C_6H_4\}_3B$ (3). 1-Ir was fully characterized on the basis of its ¹H, ¹¹B, and ³¹P NMR spectra, X-ray diffraction analysis, and elemental analysis. Density functional theory calculations revealed the important properties of the σ -acceptor borane ligand that led to its unique electron distribution in 1-Ir. The



borane ligand extracts a significant amount of electron density from the iridium center, but the iridium center maintains an electron density similar to that of the boron-free compound **2-Ir** by decreasing π back-donation from Ir to CO and strengthening the donation from the phosphorus atom (or by weakening the d_{metal}- σ^*_{P-R} interaction). The properties of the borane ligand can promote the reversible CO/PR₃ (R = Me, OMe, OEt) substitution reaction.

■ INTRODUCTION

The unique properties of σ -electron-acceptor (Z-type) borane ligands have been identified.¹⁻⁷ One of these is the flexibility of the metal-boron interaction in response to the Lewis basicity of the metal center. Hence, complexes containing a Z-type ligand are potentially allowed to access the multielectron state and are therefore expected to promote multielectron redox reactions. Peters and Moret recently demonstrated the usefulness of this property and reported dinitrogen activation using a trigonalbipyramidal {o-(i-Pr)₂PC₆H₄}₃BFe scaffold.^{7b} Another useful property is the strong trans effect induced by electron positive borane,^{2i,1} which can promote the formation of coordinatively unsaturated complexes that exhibit high reactivity. A few studies of the trans effect of σ -acceptor borane in a hydrotris(2-methyl-1imidazolyl)borate or similar derivative system have been conducted to date. Hill et al. reported that the σ -acceptor borane ligand appears to exhibit a pronounced trans effect as a σ boryl ligand, even though the M–B bond character in the σ -boryl ligand is very different from that in the σ -acceptor borane ligand; the σ -boryl ligand has a conventional one-electron covalent bond, and the σ -acceptor borane ligand exhibits a two-centertwo-electron dative interaction.⁸ Additionally, Hill et al. have synthesized the ruthenaboratrane $[Ru(CO)(PPh_3){B(mt)_3}]$ (mt = methimazolyl) and found that the phosphine ligand trans to the borane ligand is labile and readily and reversibly replaced by CO.²¹ However, in their imidazolyl-based borane systems, the presence of the base-stabilized boryl tautomer may not be negligible (Scheme 1).²ⁱ The phosphine-borane system developed by Bourissou et al. seems to be a more appropriate system for discussion of the properties of the σ -acceptor borane ligand because of the absence of such a tautomer.^{5,1f}

Scheme 1. Tautomerization in the Imidazolyl-Based Borane Systems (R = Me, *i*-Pr, *t*-Bu)



We focused on the triphosphine–borane (TPB) rhodium complexes [$\{o-(Ph_2P)C_6H_4\}_3B$]RhH(CO) (**1-Rh**) with a framework similar to that of the well-known RhH(CO)(PPh_3)_3 (**2-Rh**) and obtained important information regarding the properties of the σ -acceptor borane ligand from direct comparison of these complexes (Chart 1).⁹ Additionally, density functional

Chart 1. TPB Complex 1-M (M = Rh, Ir) and Its Related Borane-Free Complex 2-M



theory (DFT) calculations using 1-Rh and borane-free 2-Rh revealed some unique properties of the Z-type borane ligand.

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Specifically, incorporation of the borane ligand does not change the electron density of the metal center, even though the borane extracts the electron density from the metal center. Additionally, the carbonyl ligand trans to the borane ligand appears to accept relatively less electron density through π back-donation. The electronic deviation induced by the σ -borane ligand seemingly results in the rare CO dissociation of neutral Rh(I) complexes.

As an extension of our continuing work in this field, we attempted to synthesize the iridium complex [$\{o-(Ph_2P)-C_6H_4\}_3B$]IrH(CO) (**1-Ir**), bearing phosphine-tethered borane 3, because direct comparison of the TPB complex **1-Ir** and borane-free **2-Ir** can provide valuable information regarding a Z-type ligand in the same way as for the corresponding Rh system. Furthermore, Hill et al. recently reported that the bond dissociation energy for Ir \rightarrow BR₃ was greater than that for Rh \rightarrow BR₃ in an imidazolyl-based system.^{2m} Hence, the replacement of Rh with Ir is expected to induce the prominent functions of a Z-type ligand owing to the relatively strong Ir \rightarrow B interaction.

RESULTS AND DISCUSSION

An iridium complex with carbonyl, hydride, and phosphinetethered borane ligands, $[{o-(Ph_2P)C_6H_4}_3B]IrH(CO)$ (1-Ir), was synthesized in a manner similar to that used to prepare 1-**Rh**.⁹ The reaction of IrH(CO)(PPh_3)₃ (2-Ir) with { $o-(Ph_2P)-C_6H_4$ }_3B (3) at 100 °C in toluene produced 1-Ir in moderate yield (eq 1).



Although we could not obtain single crystals of 1-Ir suitable for X-ray diffraction analysis by using common organic solvents, the addition of an equivalent amount of 18-crown-6 to a THF solution of 1-Ir resulted in the formation of crystals sufficient for X-ray diffraction. Figure 1 shows the molecular structure of 1-Ir. The iridium adapts a pseudo-octahedral structure. The Ir-B distance (2.326 Å) is comparable to the sum of the covalent radii of iridium and boron $(2.23 \text{ Å})^{10}$ and slightly shorter than the Rh–B distance in 1-Rh (2.370 Å). Because the covalent radii for rhodium (134 pm)¹⁰ and iridium (136 pm)¹⁰ are similar, the iridium in 1-Ir apparently donates more electrons to the boron than does the rhodium in 1-Rh. The geometric deviation from planarity in boron is slightly larger in 1-Ir than in 1-Rh (1-Ir, $\sum (C-B-C) = 330.9^{\circ}$; 1-Rh, $\sum (C-B-C) = 332.5^{\circ}$), which is consistent with the relatively stronger $Ir \rightarrow B$ interaction. The Ir-CO bond distance increases from 2-Ir $(1.887 \text{ Å})^{11}$ to 1-Ir (1.941 Å). The same trend was observed for the Rh system. However, the extent of M-CO elongation is smaller for the Ir system than for the Rh system, suggesting that the π backdonation from M to CO still remains to a greater extent for 1-Ir than for **1-Rh**. This relatively strong π back-donation for the Ir



Figure 1. Molecular structure of **1-Ir** with thermal ellipsoids at the 40% probability level. The hydrogen atoms and phenyl groups (except for ipso carbon) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–CO = 1.941(14), Ir1–P1 = 2.309(2), Ir1–P2 = 2.349(3), Ir1–P3 = 2.321(3), Ir1–B1 = 2.326(11); $\sum (C-B-C) 330.9$.

complex is also supported by the ν (CO) values of the IR spectra. Specifically, the $\Delta \nu$ (CO) values for Ir complexes (1920 cm⁻¹ $(\mathbf{\hat{2}}$ -Ir) \rightarrow 1972 cm⁻¹ (1-Ir)) are smaller than those for Rh complexes (1918 cm⁻¹ (2-Rh) \rightarrow 1994 cm⁻¹ (1-Rh)). The apparent discrepancy between the strong $Ir \rightarrow B$ interaction and the strong Ir-CO π back-donation in comparison with the corresponding Rh complex will be discussed later. Two phenylene groups trans to each other are found to be unequal in the solid state and in solution. The phenylene group bearing the C2 atom nearly lies on the plane defined by B1-Ir1-P1, and the torsion angle of C2–B1–Ir1–P1 is 6.2°. In contrast, another phenylene group bearing the C38 atom shows a significant deviation over the plane defined by B1–Ir1–P3, giving a large C38-B1-Ir1-P3 torsion angle (41.8°). Three signals were observed in the ³¹P{¹H} NMR spectrum, indicating that this unsymmetrical situation was maintained even in solution.

The ${}^{31}P{}^{1}H}$ NMR spectrum of 1-Ir recorded at 20 °C exhibited a slightly broad single resonance (Figure 2). When the temperature was lowered to -40 °C, the signal split into two mutually coupled signals at 25.3 and 26.4 ppm with an intensity ratio of 2:1. Further measurement at lower temperatures showed that the resonance at higher magnetic field gradually broadened again. These findings appear to indicate that the two phosphine ligands located at trans positions to each other differ at low temperatures, owing to the rigid framework ligated by the *o*-phenylene.

DFT calculations¹² were carried out to shed more light on the nature of the Ir \rightarrow B interaction. The actual experimental systems **1-Ir** and **2-Ir** were computed using the hybrid functional B3PW91.¹³ The calculated structures for **1-Ir** and **2-Ir** were in excellent agreement with the experimental data (see the Supporting Information, STable 15), and the frontier molecular orbitals revealed three-center B-Ir-L interactions (L = CO). These interactions involve the d_z² orbital of Ir, the p orbital of boron, and the molecular orbital of CO, with bonding iridium–boron and antibonding iridium–carbon interactions in the highest occupied molecular orbital (HOMO) and an antibonding iridium–boron interaction in the LUMO+1 (Figure 3). Similar three-center–four-electron interactions have been reported in a 2-mercapto-1-R-imidazolyl-tethered (R = Me, *t*Bu) borane system independently by Hill et al.²ⁱ and Parkin et al.^{3b}

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Figure 2. Variable-temperature ${}^{31}P{}^{1}H$ NMR spectra (163 MHz, toluene- d_8) of 1-Ir.



Figure 3. HOMO $(left)^{15}$ and LUMO+1 (right) of 1-Ir. Hydrogen atoms are omitted for clarity.

as well as in a phosphine–borane system by Bourrisou et al.^{5b} The contribution of the HOMO strengthens the Ir–B bond and weakens the Ir–CO bond, which seems to be the origin of the trans influence of the σ -acceptor borane ligand in **1-Ir**.¹⁴

Natural population analysis data¹⁶ together with ν (CO) data for 1-3 are summarized in Table 1. A comparison of 1-Ir, 2-Ir, and 3 revealed unique features of the σ -acceptor borane ligand. The natural charge on boron is lower in 1-Ir (0.37) than in 3 (0.88) and in 1-Rh (0.43), indicating the presence of a relatively strong Ir \rightarrow B interaction. However, q_{Ir} (-1.67) is equal to that of boron-free 2-Ir (-1.67), irrespective of the Ir \rightarrow B interaction. This singular phenomenon has been observed in the corresponding Rh system and can be explained by natural charges in the phosphorus atom (q_p) and CO fragment (q_{CO}) . The incorporation of the boron consequently results in the increase of q_{CO} and q_{P} , and the Ir center seems to retain the same electron density by decreasing π back-donation to CO and strengthening electron donation from the phosphorus ligand (or weakening the $d_{metal} - \sigma^*_{P-R}$ interaction). The amounts of electron transfer of CO and phosphorus atoms were estimated on the basis of differences in the charges of the CO (Δq_{CO}) and phosphorus atoms ($\Delta(\sum q_P)$) between the (TPB)M (M = Rh, Ir) complexes 1 and the related boron-free complexes 2. While $\Delta q_{
m CO}$ is smaller in Ir than in Rh, $\Delta(\sum q_{
m P})$ is slightly larger in Ir

Table 1. NBO Atomic Charges (q_M (M = Ir, Rh), q_{CO} , q_P , and q_B) and ν (CO) (cm⁻¹)

| | P P P C O 1-Ir | P P C C 2-lr | P PP | B Rh H CO H H | PRhP PC C 2-Rh |
|--------------------------|-------------------------------|--------------------------|-------|------------------------------|--------------------------|
| | 3 | 1-Ir | 2-Ir | 1-Rh ⁹ | 2-Rh ⁹ |
| $q_{ m Rh}$ | | -1.67 | -1.67 | -1.56 | -1.54 |
| $q_{ m B}$ | 0.88 | 0.37 | | 0.43 | |
| $q_{ m P}$ | | 1.41 | 1.29 | 1.35 | 1.25 |
| | | 1.42 | 1.29 | 1.36 | 1.24 |
| | | 1.35 | 1.30 | 1.29 | 1.26 |
| $\sum q_{ m P}$ | | 4.18 | 3.88 | 4.00 | 3.75 |
| $\Delta(\sum q_{\rm P})$ | | 0.30 | | 0.25 | |
| 9co | | 0.26 | 0.18 | 0.28 | 0.18 |
| $\Delta q_{ m CO}$ | | 0.08 | | 0.10 | |
| $\nu(CO)$ | | 1972 | 1920 | 1994 | 1919 |

than in Rh. The smaller value of Δq_{CO} in Ir the system is consistent with the results of the CO stretching frequencies.

Natural localized molecular orbital (NLMO) analyses¹⁶ of **1-Rh** and **1-Ir** also supported the relatively strong Ir–B interaction (Table 2). The metal–boron interaction reflects more on

Table 2. Hybridization of the NLMO Involving the Metal (Rh or Ir) and Boron Atoms and NLMO/NPA Bond $\rm Orders^{17}$

| | 1-Rh | 1-Ir |
|------------------------------|-------|-------|
| NLMO $d(M) \rightarrow p(B)$ | | |
| % d(M) | 76.21 | 58.50 |
| % p(B) | 19.14 | 30.59 |
| donor NBO d(M) | | |
| % s(M) | 0.23 | 3.62 |
| % p(M) | 8.14 | 24.12 |
| % d(M) | 91.62 | 72.26 |
| acceptor NBO p(B) | | |
| % s(B) | 18.80 | 19.98 |
| % p(B) | 81.19 | 80.01 |
| M–B bond order | 0.571 | 0.667 |

the 2s orbital character of the boron in 1-Ir (19.98%) than in 1-Rh (18.80%), and the NLMO/NPA bond order¹⁷ between M and B in 1-Ir (0.667) is also larger than that between Rh and B in 2-Rh (0.571).

The coordination of the borane ligand reflects the Brønsted basicity of the complex. To estimate the Brønsted basicity of 1-Ir, we examined the reactions of 1-Ir with several protonic acid or hydrido reagents. However, these reactions gave several uncharacterized products, and the basicity of 1-Ir was hardly estimated. Previously, we reported the synthesis of anionic rhodium complexes, $[{o-(Ph_2P)C_6H_4}_3BRh(CO)][K(18$ crown-6)] (4) and $[Rh(CO)(PPh_3)_3][K(18-crown-6)]$ (5), which were obtained from the reaction of the corresponding neutral complexes 1-Rh and 2-Rh with KH in the presence of 18-crown-6.9 In this study, we found that the reverse reactions, namely reactions of these anionic complexes with 1 equiv of H_2O , resulted in the quantitative formation of the corresponding neutral complexes; there exist perfect equilibria between the neutral complex and the corresponding anionic complex. These equilibrium reactions enabled us to compare the Brønsted basicities of 1-Rh and 2-Rh. When the reaction of 1-Rh with

1 equiv of 5 was monitored by ³¹P NMR spectroscopy, the quantitative formation of 2-Rh and 4 was observed (eq 2). The reverse reaction, namely, the reaction of 2-Rh with 4, did not form 1-Rh and 5. These results strongly imply that the coordination of the borane ligand decreases the Brønsted basicity of the complex. It is also acceptable that the reduction of steric repulsion in 1-Rh is a driving force of the one-way reaction.



We have recently reported preparation of the cationic silyl, germyl, and stannyl iridium(III) complexes $[\{(o-Ph_2PC_6H_4)\}_3$ -EIr(H)(CO)][BF₄] (6, E = Si; 7, E = Ge; 8, E = Sn), whose cationic parts are isoeletronic and isostructural with 1-Ir. Complexes 6–8 were deprotonated by 3 equiv of triethylamine (NEt₃) to afford the corresponding neutral complexes $\{(o-Ph_2PC_6H_4)\}_3$ EIr(CO).¹⁸ In this study, abstraction of one hydride from $[Ir(H)_2(CO)(PPh_3)_3][BF_4]$ (9) was also found to occur by 3 equiv of NEt₃ to give 2-Ir, quantitatively, while 1-Ir did not react with 3 equiv of NEt₃. These results show that 1-Ir is more basic than 6–9 despite the strong Ir→B interaction (Chart 2). It is also possible that the constrained tetradentate frameworks influence the Brønsted basicity of the complexes.

The electronic deviation of 1-Ir from the related boron-free complex 2-Ir is also expected to influence the reactivity of the iridaboratrane. Substitution of a carbonyl ligand with a phosphine ligand is one of the fundamental reactions in organometallic chemistry¹⁹ and seems to be an appropriate reaction for a better understanding of a new system. We previously reported that the CO/PMe₃ substitution reaction of 1-Rh was induced by the strong trans-labilizing effect and σ -electron-acceptor properties of the borane ligand (eq 3).⁹ To check the limitations of the CO/PR₃ substitution reaction for 1-Rh and 1-Ir, we here examined the reaction of 1-Rh with PR₃ (R = Et, Ph, OMe, OEt, O(*i*-Pr)) and those of 1-Ir with PR₃ (R = Me, OMe, OEt).





Similar to the reaction of 1-Rh with PMe₃, the reactions with $P(OR)_3$ (R = Me, Et) gave the corresponding hydrido phosphite complexes. When the reaction of 1-Rh with 3 equiv of $P(OR)_3$ (R = Me, Et) was monitored by ¹H and ³¹P NMR spectroscopy, the reaction was complete within 2 h. In comparison, the reaction with 3 equiv of PMe₃ under the same conditions afforded a 40:60 mixture of 1-Rh and 10a-Rh and took place relatively slowly. These results indicate that the less bulky phosphorus compounds lead to smooth formation of the phosphine or phosphite complexes and that steric hindrance is more important to the substitution reactions than the basicity of a phosphorus ligand. In fact, 1-Rh did not react with the relatively large phosphine PR_3 (R = Et, Ph) and phosphite $P(OR)_3$ (R = *i*-Pr) under mild conditions, and elevating the reaction temperature resulted in the formation of a mixture of unidentified products. These results implied that the vacant site generated by carbonyl dissociation is not large enough to accept a relatively large phosphine or phosphite ligand.

The newly synthesized compounds **10b-Rh** and **10c-Rh** were unambiguously characterized on the basis of elemental analysis as well as ¹H, ¹¹B, and ³¹P NMR spectroscopic data, which were similar to those of the trimethylphosphine analogue **10a-Rh**. The solid-state structures of **10b-Rh** and **10c-Rh** were confirmed by X-ray diffraction studies (see below).

The TPB iridium complex 1-Ir also reacted with PR₃ (R = Me, OMe, OEt) to afford the corresponding phosphine and phosphite complexes [$\{o-(Ph_2P)C_6H_4\}_3B$]IrH(PR₃) (10a-Ir, R = Me; 10b-Ir, R = OMe; 10c-Ir, R = OEt) via the elimination of the carbonyl ligand (eq 4). Complexes 10a-Ir and 10b-Ir were fully characterized on the basis of ¹H, ¹¹B, and ³¹P NMR spectra and elemental analysis. The reaction with 20 equiv of trimethyl phosphite gradually proceeded even at ambient temperature, and the reaction at 60 °C was complete within 36 h. These reactions were reversible, and exposure of 10-Ir to CO immediately generated 1-Ir almost quantitatively.







Figure 4. Molecular structures of hydrido phosphine and hydrido phosphite complexes **10b-Rh**, **10c-Rh**, **10a-Ir**, and **10b-Ir**. Hydrogen atoms (except for hydride) and phenyl groups (except for ipso carbon) are omitted for clarity. C2 and C3 in **10b-Ir** show the disorder in the crystal (C2:C2b = C3:C3b = 55:45).

Table 3. Structural Parameters for 10a-Rh, 10b-Rh, 10c-Rh, 10a-Ir, and 10b-Ir



| | M = Rh | | M = Ir | | |
|----------------------|---------------------|------------|------------|------------|------------|
| | 10a-Rh ⁹ | 10b-Rh | 10c-Rh | 10a-Ir | 10b-Ir |
| M–B1 (Å) | 2.354(4) | 2.343(6) | 2.351(4) | 2.336(6) | 2.338 |
| \sum (C-B-C) (deg) | 330.8 | 330.0 | 331.6 | 327.5 | 328.6 |
| $M-PR_3$ (Å) | 2.4077(11) | 2.3128(18) | 2.3083(11) | 2.3719(14) | 2.2776(19) |
| $M-PPh_2$ (Å) | 2.3463(10) | 2.2951(17) | 2.3126(11) | 2.2984(13) | 2.297(2) |
| | 2.3033(11) | 2.3451(17) | 2.3454(11) | 2.3339(13) | 2.3388(19) |
| | 2.3002(11) | 2.3017(16) | 2.2934(10) | 2.3018(14) | 2.3087(19) |

It should be noted that **1-Ir** undergoes a CO/PR₃ exchange reaction, because iridium generally has a tendency to form extremely strong Ir–CO bonds. For example, the Ir–CO bond dissociation energy (BDE) in Ir(CO){P(*i*-Pr)₃}₂Cl was estimated to be 72 kcal/mol, which is much greater than that for any previously reported M–CO BDE.²⁰ Indeed, to the best of our knowledge there are no examples of neutral monocarbonyl iridium(I) complexes bearing triphosphine ligands that dissociate the CO ligand in not only a square-planar system but also a trigonal-bipyramidal system.²¹ Therefore, CO dissociation can be apparently attributed to the properties of the σ -borane ligand, although steric factors also probably contribute to the lability of the CO ligand in **1-Ir**.

The crystal structures of the hydrido phosphine and hydrido phosphite complexes **10b-Rh**, **10c-Rh**, **10a-Ir**, and **10b-Ir** are shown in Figure 4. The molecular frameworks of these structures are similar to those of the hydrido carbonyl complexes **1-Rh** and **1-Ir**. The M–B distances of **10** range from 2.336 to 2.354 Å, which are similar to those of **1** (Table 3). These findings indicate the presence of a M→B interaction. The boron pyramidalization observed in **10** ($\sum(C-B-C) = 327.5-331.6^{\circ}$) was greater than that observed in **1**, probably owing to enhancement of the Lewis basicity of the metal center derived from the better σ -donating ability of these phosphorus ligands. The M–PR₃ (M = Rh, Ir; R = Me, OMe, OEt) distances are longer in phosphine complex **10a** than in phosphite complexes **10b,c**. This is likely a result of the

steric repulsion between the Ph₂P groups in the TPB ligand and PR₃, although the effect of π back-donation through a $d_{metal}-\sigma^*_{P-R}$ interaction cannot be ruled out.

To gain greater insight into the mechanisms involved in the substitution reactions of a carbonyl ligand, kinetic studies were carried out. The reactions of **1-Rh** and **1-Ir** with P(OMe)₃ produced the phosphite complexes **10b-Rh** and **10b-Ir**, respectively, with no observed intermediate species. The disappearance of **1-Rh** and **1-Ir** was monitored by ³¹P NMR spectroscopy, and first-order reactions were found to occur in the carbonyl complexes. The rate constant of the reaction of **1-Ir** was smaller than that of **1-Rh** by a factor of about $1/50\ 000$. The enthalpy of activation (**1-Rh**, $\Delta H^{\ddagger} = 17.9 \pm 0.4\ \text{kcal}\ \text{mol}^{-1}$; **1-Ir**, $\Delta H^{\ddagger} = 25.2 \pm 0.9\ \text{kcal}\ \text{mol}^{-1}$) is the dominant factor determining the rate constant, which can likely be attributed to the relatively strong Ir–CO bond (Table 4). Furthermore, the small negative value of entropy

Table 4. Enthalpy and Entropy of Activation and the Rate Constant for the Reaction with $P(OMe)_3$ at 70 °C

| complex | ΔH^{\ddagger} (kcal mol ⁻¹) | ΔS^{\ddagger} (eu) | $k_{ m obsd}$ at 70 °C (s ⁻¹) | | |
|--|---|----------------------------|---|--|--|
| 1-Rh | 17.9 ± 0.4 | -3.5 ± 1.6 | 4.92 ^{<i>a</i>} | | |
| 1-Ir | 25.2 ± 0.9 | -3.8 ± 2.6 | 9.90×10^{-5} | | |
| ^a Value calculated by artrapolation | | | | | |

"Value calculated by extrapolation.

(1-Rh, $\Delta S^{\ddagger} = -3.5 \pm 1.6$ eu; 1-Ir, $\Delta S^{\ddagger} = -3.8 \pm 2.6$ eu) implies a dissociative interchange mechanism. This hypothesis is supported by the dependence of the rate constant on the strengthening M–CO bond as well as the absence of a detected intermediate. On the basis of these results, we conclude that the rate-determining step involved CO dissociation and that the σ -acceptor and trans-labilizing abilities of the σ -borane ligand undoubtedly weakened the Ir–CO bond and led to unprecedented CO dissociation in 1-Ir.

SUMMARY

We report here the synthesis of new iridaboratranes, in which the iridium donates its electron density to the borane through an interaction of the d_{z^2} orbital of the Ir center and the p orbital of the boron. Structural analysis and DFT calculations indicated that the metal \rightarrow boron interaction in **1-Ir** is stronger than that observed in the corresponding Rh system. The Brønsted basicity of 1 was strongly reflected by the coordination of the borane ligand, and 1 exhibited a Brønsted basicity lower than that for the related borane-free complex 2 and higher than those for the cationic complexes 6–9. Furthermore, the σ -acceptor borane of the phosphine-borane system exhibited a strong transinfluencing ability similar to that of an imidazolyl-based system, as well as significant elongation of the Ir-CO bond trans to the boron. The electronic and structural deviation induced by the $Ir \rightarrow B$ interaction caused an unexpected reversible CO/PR₃ substitution reaction of 1-Ir. Kinetic studies strongly suggested that the CO/PR₃ substitution reaction proceeded via a dissociative interchange mechanism, and the σ -acceptor and trans effects of the borane ligand undoubtedly contributed to weakening of the Ir-CO bond. Neutral monocarbonyl iridium-(I) complexes lead to almost no dissociation of the carbonyl ligand due to the strong Ir(I)-CO bond, which is known to have an extremely high dissociation energy. In fact, the catalytic mechanism including Ir(I)-CO dissociation is recognized as unreasonable.¹⁹ The low CO dissociation property of Ir(I) complexes appears to be one of the reasons that IrH(CO)- $(PPh_3)_3$ rarely exhibits high catalytic activity in comparison with the Rh analogue $RhH(CO)(PPh_3)_3$. We are currently investigating a new catalytic process that takes full advantage of this feasible CO dissociation.

EXPERIMENTAL SECTION

General Procedures. The compounds described below were handled under a dinitrogen atmosphere, and air and water were removed completely using Schlenk techniques. [$\{o-(Ph_2P)C_6H_4\}_3B$]-RhH(CO) (**1-Rh**),⁹ RhH(CO)(PPh_3)_3 (**2-Rh**),²² IrH(CO)(PPh_3)_3 (**2-Ir**),²³ { $o-(Ph_2P)C_6H_4\}_3B$ (**3**),⁹ and [Ir(H)₂(CO)(PPh_3)_3][BF₄] (**9**)²⁴ were prepared as previously described. Benzene- d_{6} , toluene- d_{8} , THF- d_{8} , diethyl ether, and benzene were dried over sodium benzophenone ketyl and distilled under a dinitrogen atmosphere. Tetrahydrofuran, hexane, and toluene were purified using a two-column solid-state purification system. Chloroform-d, dichloromethane- d_2 , and dichloromethane were dried over P2O5 and stored over 4 Å molecular sieves. The other reagents used in this study were purchased from commercial sources and used without further purification. The ¹H, ¹¹B, and ³¹P NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer. ¹H NMR data were analyzed with reference to the residual peaks of the solvent, and ¹¹B and ³¹P NMR chemical shifts were referenced to external BF₃·Et₂O and 85% H₃PO₄ samples, respectively. IR spectra were recorded on a Perkin-Elmer FTIR-Spectrum One spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer.

Preparation of IrH(CO)[B{o-C₆H₄(PPh₂)}₃] (1-Ir). A 50 mL Schlenk tube was filled with 3 (254 mg, 0.320 mmol), 2-Ir (208 mg, 206 mmol), and toluene (4 mL). The reaction mixture was stirred at 100 °C.

After 24 h, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was extracted with diethyl ether (20 mL) and the extract then filtered through a column packed with Celite. After the volatile materials were removed, washing the residual solid with hexane (3 mL × 2) and cold diethyl ether (2 mL × 1) afforded **1-Ir** as a pale yellow solid (132 mg, 130 mmol, 63%). ¹H NMR (400 MHz, toluene- d_8 , -80 °C): δ -9.64 (dt, $J_{P-H} = 103.2$, $J_{P-H} = 16.4$, 1H, Ir–H), 6.45-6.88 (m, 30H, Ar), 7.39 (m, 3H, Ar), 7.86 (m, 6H, Ar), 8.28–8.51 (m, 3H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆, 20 °C): δ 25.4 (s). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ -7.2. Anal. Found for C₅₅H₄₃P₃OBIr: C, 65.07; H, 4.55. Calcd: C, 65.03; H, 4.27. IR (KBr): 1972 cm⁻¹.

Reaction of 1-Rh with [Rh(CO)(PPh₃)₃][K(18-crown-6)] (5). An NMR sample tube equipped with a Teflon Seal-cock was filled with **1-Rh** (5.9 mg, 0.0064 mmol) and THF- d_8 (0.4 mL). To the solution was added **5** (7.8 mg, 0.0064 mmol) in THF, and then the reaction was carried out at ambient temperature for 24 h. The quantitative formation of **2-Rh** and [{o(Ph₂P)C₆H₄}₃BRh(CO)][K(18-crown-6)] (4) was confirmed by ³¹P NMR spectroscopy.

Reaction of [Ir(H)₂(\hat{CO})(PPh₃)₃][BF₄] (9) with NEt₃. An NMR sample tube was filled with 9 (5.9 mg, 0.0054 mmol), THF- d_8 (0.45 mL), and triethylphosphine oxide (2 mg) as an internal standard. To the solution was added NEt₃ (2.3 μ L, 0.016 mmol), and then the reaction was carried out at ambient temperature for 15 h. The solution gradually turned from colorless to yellow, and the quantitative formation of 2-Ir was confirmed by ³¹P NMR spectroscopy.

Preparation of RhH{P(OMe)₃**[B{o-C**₆**H**₄(**PPh**₂)**}**₃**] (10b-Rh).** A 50 mL Schlenk tube was filled with 1-Rh (137.1 mg, 0.148 mmol), P(OMe)₃ (50 μL, 0.423 mmol), and toluene (3 mL). The reaction mixture was stirred at room temperature for 15 h, after which the solvent was removed under reduced pressure. Washing the residual solid with hexane (2 mL × 2) afforded **10b-Rh** as a pale yellow solid (127.4 mg, 0.121 mmol, 82%). ¹H NMR (400 MHz, C₆D₆): δ –9.63 (m, 1H, Rh–H), 2.94 (d, *J*_{P-H} = 10.8 Hz, 9H, P(OMe)₃), 6.78–6.89 (m, 18H, Ar), 7.00–7.05 (m, 6H, Ar), 7.13–7.22 (m, 6H, Ar), 7.39–7.43 (m, 9H, Ar), 7.82–7.84 (m, 3H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆, 20 °C): δ –51.2 (dd, *J*_{P-Rh} = 130.0 Hz, *J*_{P-P} = 19.2 Hz, PPh₂), 144.3 (dq, *J*_{P-Rh} = 147.1 Hz, *J*_{P-P} = 19.2 Hz, P(OMe)₃). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ –7.5. Anal. Found for C₅₇H₅₂O₃P₄BRh: C, 66.65; H, 4.77. Calcd: C, 66.95; H, 5.13.

Preparation of RhH{P(OEt)₃}[B{o-C₆H₄(PPh₂)}₃] (10c-Rh). A 50 mL Schlenk tube was filled with 1-Rh (92.4 mg, 0.0997 mmol), P(OEt)₃ (50 μL, 0.292 mmol), and toluene (3 mL). The reaction mixture was stirred at room temperature for 15 h, after which the solvent was removed under reduced pressure. Washing the residual solid with hexane (2 mL × 2) afforded 10c-Rh as a pale yellow solid (86.3 mg, 0.0790 mmol, 79%). ¹H NMR (400 MHz, CD₂Cl₂): δ –9.90 (m, 1H, Rh–H), 0.84 (t, *J*_{H–H} = 6.4 Hz, 9H, P(OCH₂CH₃)₃), 3.49 (m, 6H, P(OCH₂CH₃)₃), 6.57–7.72 (m, 42H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆, 20 °C): δ 51.3 (dd, *J*_{P–Rh} = 128.6 Hz, *J*_{P–P} = 18.5 Hz, PPh₂), 158.0 (dq, *J*_{P–Rh} = 136.0 Hz, *J*_{P–P} = 18.5 Hz, P(OEt)₃). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ –7.6. Anal. Found for C₆₀H₅₈O₃P₄BRh: C, 67.74; H, 5.57. Calcd: C, 67.68; H, 5.49.

Preparation of IrH(PMe₃)[B(o-C₆H₄(PPh₂)]₃] (10a-Ir). A 50 mL Schlenk tube was filled with 1-Ir (59.1 mg, 0.0582 mmol), a 1 M toluene solution of PMe₃ (0.50 mL, 0.50 mmol), and toluene (4 mL). The reaction mixture was stirred at 80 °C. After 12 h, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Washing the residual solid with hexane (3 mL × 2) afforded 10a-Ir as a pale yellow solid (52.9 mg, 0.0497 mmol, 85%). ¹H NMR (400 MHz, C₆D₆): δ –11.68 (br s, 1H, Ir–H), 0.90 (d, *J*_{P–H} = 6.8 Hz, 9H, PMe₃), 6.77–7.05 (m, 30H, Ar), 7.39–7.42 (m, 3H, Ar), 7.74–7.78 (m, 3H, Ar), 7.89–7.92 (m, 3H, Ar), 8.27–8.33 (m, 3H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆, 20 °C): δ –66.6 (br s, *w*_{1/2} = 48.2 Hz, PMe₃), 23.8 (br s, *w*_{1/2} = 40.6 Hz, PPh₂). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ –7.4. Anal. Found for C₅₇H₅₂P₄BIr: C, 64.17; H, 4.87. Calcd: C, 64.35; H, 4.93.

Preparation of $IrH{P(OMe)_3}[B{o-C_6H_4(PPh_2)}_3]$ (10b-Ir). A 50 mL Schlenk tube was filled with 1-Ir (48.5 mg, 0.0477 mmol), P(OMe)_3 (50 μ L, 0.423 mmol), and toluene (4 mL). The reaction

mixture was stirred at 80 °C. After 12 h, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Washing the residual solid with hexane (3 mL × 2) afforded **10b-Ir** as a pale yellow solid (46.7 mg, 0.0420 mmol, 88%). ¹H NMR (400 MHz, CD₂Cl₂): δ –11.67 (dtd, *J*_{P-H} = 82.0 Hz, *J*_{P-H} = 15.2 Hz, *J*_{P-H} = 3.6 Hz, 1H, Ir–H), 4.07 (d, *J*_{P-H} = 7.2 Hz, 9H, P(OMe)₃), 6.62–6.64 (m, 3H, Ar); 6.79–7.09 (m, 21H, Ar), 7.13–7.25 (m, 9H, Ar), 7.42–7.45 (m, 6H, Ar), 7.76–7.79 (m, 3H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆, 20 °C): δ 23.8 (m, PPh₂), 24.9 (m, PPh₂), 111.4 (m, P(OMe)₃). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ –7.2. Anal. Found for C₅₇H₅₂O₃P₄BIr: C, 61.27; H, 5.03. Calcd: C, 61.57; H, 4.71.

Preparation of IrH{P(OEt)₃}[B{o-C₆H₄(PPh₂)}₃] (10c-Ir). A 50 mL Schlenk tube was filled with 1-Ir (43.7 mg, 0.0430 mmol), P(OEt)₃ (50 μL, 0.292 mmol), and toluene (4 mL). The reaction mixture was stirred at 80 °C. After 12 h, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Washing the residual solid with hexane (3 mL × 2) afforded 10c-Ir as a pale yellow solid (43.4 mg, 0.0376 mmol, 87%). ¹H NMR (400 MHz, C₆D₆): δ –11.68 (dtd, *J*_{P-H} = 69.6 Hz, *J*_{P-H} = 15.6 Hz, *J*_{P-H} = 3.6 Hz, 1H, Ir–H), 0.83 (t, *J*_{H-H} = 7.0 Hz, 9H, P(OCH₂CH₃)₃), 3.53 (qd, *J*_{H-H} = 7.0 Hz, *J*_{P-H} = 6.2 Hz, 6H, P(OCH₂CH₃)₃), 6.62–7.45 (m, 30H, Ar), 7.72–7.92 (m, 9H, Ar), 8.24–8.28 (m, 3H, Ar). ³¹P{¹H} NMR (163 MHz, C₆D₆); 20 °C): δ 22.0 (m, PPh₂), 24.7 (m, PPh₂), 106.0 (m, P(OEt)₃). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 20 °C): δ –7.2. Anal. Found for C₆₀H₅₈O₃P₄BIr: C, 62.18; H, 5.01. Calcd: C, 62.45; H, 5.07.

Reaction of 10b-Ir with CO. A 50 mL Schlenk tube was filled with **10b-Ir** (34.9 mg, 0.0314 mmol) and toluene (5 mL). After the tube was evacuated at -196 °C using a high-vacuum line, 1 atm of CO (2.0 mmol) was transferred into the tube. The reaction mixture was then stirred at 60 °C. After 3 h, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Washing the residual solid with hexane (3 mL × 2) afforded **1-Ir** as a pale yellow solid (30.1 mg, 0.0296 mmol, 94%).

Kinetic Study of the Reactions of MH(CO)[B{o-C₆H₄(PPh₂)}₃] (1-Rh, M = Rh; 1-Ir, M = Ir) with Trimethyl Phosphite. A Schlenk tube was charged with 1-Rh (55.0 mg, 0.0594 mmol), toluene- d_8 (1.6 mL), and triphenylphosphine (15.0 mg) as an internal standard. The solution was divided evenly into four NMR sample tubes. The NMR probe was cooled at the appropriate temperature (-30, -20, -15, -15)and -10 °C), and 20 equiv of trimethyl phosphite (35 μ L, 0.30 mmol) was introduced into the tube at -78 °C. The sample was then shaken and placed in the spectrometer. Data collection with an automated acquisition program began immediately after the sample was placed in the probe. The rate constants were calculated on the basis of the time conversion of [1-Rh]. The obtained rate constants are given in STable 1 (see the Supporting Information). The temperature dependence of the rate constants yielded the following activation parameters: ΔH^{\ddagger} = $17.9 \pm 0.4 \text{ kcal mol}^{-1} \text{ and } \Delta S^{\ddagger} = -3.5 \pm 1.6 \text{ cal mol}^{-1} \text{ K}^{-1}$. The rate constants for the reaction of 1-Ir with trimethyl phosphite were similarly estimated at the appropriate temperatures (70, 75, 80, and 90 °C) using 60.0 mg of 1-Ir (0.0591 mmol) instead of 1-Rh. The obtained rate constants are given in STable 2 (see the Supporting Information). The temperature dependence of the rate constants yielded the following activation parameters: $\Delta H^{\ddagger} = 25.2 \pm 0.9$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -3.8 \pm$ 2.6 cal mol⁻¹ K⁻¹.

Structural Determination by X-ray Diffraction. Suitable single crystals of 2-Ir, 10b-Rh, 10c-Rh, 10a-Ir, and 10b-Ir were obtained from slow diffusion of *n*-hexane into CH₂Cl₂ solutions of the corresponding complexes. Single crystals of 1-Ir were also obtained as described above. The single crystals were mounted onto a CryoLoop with Paratone oil, and X-ray diffraction experiments were carried out using a Rigaku/MSC Mercury CCD diffractometer with a graphite-monochromated Mo K α radiation source ($\lambda = 0.71069$ Å) at 200 K. Cell refinement and data reduction were carried out using the CrystalClear program.²⁵ The intensity data were corrected for Lorentz--polarization effects and empirical absorption. The structures were determined by direct methods (SIR 97). All non-hydrogen atoms were found on the basis of a difference Fourier synthesis and were refined anisotropically. Refinement using the SHELXL-97 package²⁶ was carried out by leastsquares methods based on F^2 with all measured reflection data. The

crystal data and results of the analyses are given in STables 3-14 (Supporting Information).

Density Functional Theory (DFT) Calculations. DFT calculations were carried out at the B3PW91¹³ level in conjunction with the Stuttgart/Dresden ECP and associated with triple- ξ SDD basis sets.²⁷ For C, H, B, O, and P, 6-31G(d) basis sets were employed. All calculations were performed without symmetry constraints, utilizing the Gaussian09 program.²⁸ The molecular structures were drawn using the GaussView version 4.1.2 program.²⁹ Cartesian coordinates are given in STables 16 and 17 (Supporting Information).

ASSOCIATED CONTENT

Supporting Information

Tables of atomic coordinates and parameters, bond lengths and angles, torsion angles, and structure refinement details, ORTEP drawings, and CIF files for 1-Ir, 2-Ir, 10b-Rh, 10c-Rh, 10a-Ir, and 10b-Ir and tables of Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) We could not find the structural data for **2-Ir** via the Cambridge Structural database (version 5.32); therefore, the structure was determined by X-ray diffraction analysis (the details are given in the Supporting Information).

(12) Density functional theory (DFT) calculations were carried out at the B3PW91 level¹³ in conjunction with the Stuttgart/Dresden ECP²⁷ and associated with triple- ξ basis sets for Rh and Ir. For H, C, B, O, and P, 6-31G(d) was employed. The optimized geometries, shown in SFigure 15, reproduced the key features of 1-Ir and 2-Ir well, with a maximum deviation of only 0.0319 Å in the Ir–P1 distance in 2-Ir being observed (the details are given in the Supporting Information).

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(14) Owen recently suggested two factors that contribute to strong trans labilization of a σ -acceptor borane in a d⁸ octahedral system.^{1f} One is the electropositive nature of the boron atom. The other dominating factor is similar orbital energies between the square-based pyramidal and boron-stabilized octahedral, suggesting there is no significant gain or loss in energy for a ligand to occupy the site trans to boron. However, the Ir–CO interaction in **1-Ir** still appears to be considerably strong, and the kinetic studies of the CO/P(OMe)₃ substitution reaction do not support the formation of an intermediate generated by a dissociation mechanism. Therefore, there seems to be no positive information that supports his suggestion. We will continue our research, keeping his suggestion in mind.

(15) The HOMO apparently involves the small contribution of the bonding interaction between the d_z^2 torus and the molecular orbital of CO, but the antibonding (σ^*) interaction between the two-bladed propeller of the d_z^2 orbital and the lone pair on the carbon in CO appears to be the main component.

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(21) Although the silvl group of $[\{\sigma-(Ph_2P)C_6H_4\}_3SiIr(H)(CO)]$ [BF₄] (5) considerably weakens the Ir–CO bond trans to the Si atom in the solid state (Ir–CO distance 1.965 Å), the CO/P(OMe)₃ substitution reaction of 5 does not proceed under conditions (at 60 °C) similar to those of 1-Ir. Therefore, the σ -acceptor borane ligand appears to promote the CO elimination more strongly than the silvl group.

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