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Synthesis, Structure, and Conformational Dynamics of Rhodium and Iridium Complexes of Dimethylbis(2-pyridyl)borate†

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Abstract

Rhodium(I) and Iridium(I) borate complexes of the structure $[\text{Me}_2\text{B}(\text{2-py})_2]\text{ML}_2$ ($\text{L}_2 = (\text{tBuNC})_2$, $(\text{CO})_2$, $(\text{C}_2\text{H}_4)_2$, cod, dppe) were prepared and structurally characterized (cod = 1,5-cyclooctadiene; dppe = 1,2-diphenylphosphinoethane). Each contains a boat-configured chelate ring that participates in a boat-to-boat ring flip. Computational evidence shows that the ring flip proceeds through a transition state that is near planarity about the chelate ring.

We observe an empirical, quantitative correlation between the barrier of this ring flip and the π acceptor ability of the ancillary ligand groups on the metal. The ring flip barrier correlates weakly to the Tolman and Lever ligand parameterization schemes, apparently because these combine both σ and π effects while we propose that the ring flip barrier is dominated by π bonding. This observation is consistent with metal-ligand π interactions becoming temporarily available only in the near-planar transition state of the chelate ring flip and not the boat-configured ground state. Thus, this is a first-of-class observation of metal-ligand π bonding governing conformational dynamics.

Keywords

Rhodium; Iridium; Inversion Recovery; Back Bonding; Ring Flip

†Honoring John Bercaw, who taught us to find and illuminate the fundamental nature of chemical systems, on the occasion of his 70th birthday.

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Appendix A. Supplementary Material

CCDC 937914 (3a), 937915 (4a), and 937913 (4b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

1. Introduction

Modern organometallic chemistry is enjoying a resurgence of interest in the synthesis, structure, and reactivity of transition metal complexes containing acidic groups, both protic [1] and Lewis acids [2], in the ligand set such as to enable dual-site activation of small molecules. Along these lines, one particular ligand that has enabled the preparation of late metal complexes containing a Lewis acidic boron center is dimethylbis(2-pyridyl)borate. Zinc [3], nickel [3, 4], platinum [5], ruthenium [6], and copper [7] complexes of this ligand have been reported to date, and some of these have enabled new and impressive reactivity, with their applications ranging among C—B bond activation [5c], alcohol oxidation [6a, d], ammonia borane dehydrogenation [6b], alkynyl ene couplings [6c], and photoluminescence [7].

In line with our interest to devise mechanistically novel catalytic systems featuring this ligand and relatives of it [8], we have recently embarked on the exploration of its coordination chemistry with other noble metals [4, 6]. Here we report the syntheses of a family of group 9 (rhodium and iridium) complexes of dimethylbis(2-pyridyl)borate and reveal a very intriguing observation of their conformational dynamics: while complexes of this borate are well-documented to undergo a ring flip of their chelate ring in some circumstances [5, 4] and not others [6a], we observe through the systematic study of these group 9 chelates that the π -symmetry electronics of the complexes' ancillary ligand set have a dramatic and systematic influence on the barrier of this ring flip, thus highlighting a unique example in which metal-ligand π -symmetry interactions control the dynamics of a conformationally fluxional ligand with little regard for the ligand's σ bonding preferences.

2. Results and Discussion

2.1. Syntheses and Structure of Rhodium and Iridium Borate Complexes

The syntheses of rhodium(I) and iridium(I) complexes of dimethylbis(2-pyridyl)borate (**3–7**, Scheme 2) proceeded smoothly from sodium dimethylbis(2-pyridyl)borate ($\text{Na}[(2\text{-py})_2\text{BMe}_2]$) [3] and the corresponding (chloro)metal dimer ($[\text{L}_2\text{MCl}]_2$). The precursors for **3b** and **5ab** were prepared according to literature procedures [9], while **7a** was synthesized by addition of phosphine (dppe) to **6a**.

X-ray structures were obtained for complexes **3a**, **4a**, and **4b**. Table 1 illustrates the boat conformation of the metallocycle in **3a**. In this complex we observe a dihedral angle of $48.9(2)^\circ$ between the metal and pyridine planes and a C9-Rh distance of $3.200 \text{ \AA}$, where C9 is the endo-configured (methyl)boron group. For comparative purposes, Table 1 shows these same metrics for the structures of **4ab**: no significant difference in structure is observed among these complexes.

2.2. Conformational Dynamics

Complexes **3–7** participate in a facile ring flip of their chelate rings, which are boat-configured in the ground state (Scheme 2). In these complexes the borate ligand ($[\text{Me}_2\text{B}(2\text{-py})_2]^-$) contains two nonequivalent methyl groups that provide convenient spectral handles to study the three-dimensional ground state conformations of the complexes, but cursory

inspection of the room temperature ^1H NOESY NMR spectra for these complexes revealed dramatic differences in the rate of the chelate ring flip: we observed that complexes bearing π accepting ancillary ligands tended to participate in a faster ring flip than those with donor groups.

Upon making the original observation, we reasoned that in the boat conformation of the ground state, the ligand's pyridine groups are tilted relative to the metal, so they have little π communication. However, if the ring flip proceeds through a planar transition state, π communication is selectively "turned on" as the bonds rotate through the transition state, thus selectively stabilizing or destabilizing it based on the preferences of the ligand set *trans* to the pyridine groups. Thus, we propose that the modulation in the enthalpic component of the ring flip barrier is primarily describing the π -acceptor ability of the *trans* ligands while sigma bonding enthalpy to the pyridine groups remains largely unaltered throughout the ring flip. Intrigued by this apparently significant impact of metal-ligand backbonding, we measured the ring flip barriers for each member of the analogous series. NMR inversion recovery kinetics provided a very convenient handle to effect such measurements [10].

Experimental values for the energetic barriers for ring flips are shown in Table 2. Generally, those ligands that are π electron acceptors lower the ring flip barrier: the effect is systematic and dramatic. For example, compare rhodium(I) complexes of *tert*-butylisonitrile and the bidentate phosphine dppe (entries 1 and 8): in this pair we see a difference of 9 kcal/mol in the enthalpic ring flip barrier, with the phosphine having the high barrier.

We believe that the observed modulation in the ring flip barriers is largely an electronic effect. For example if steric crowding of the (methyl)boron groups was responsible, a bulky complex should flip faster because of ground state destabilization. By contrast, we observe that the bulkiest ligand (dppe, **7a**, $H^\ddagger = 21.5$ kcal/mol) gives a significantly higher barrier than complexes of CO and *tert*-butylisonitrile ($H^\ddagger = 15.5, 12.3$ kcal/mol), so we perceive that stereoelectronics dominate the barrier. An alternative explanation of the observed behavior that can not be directly eliminated is one based on eclipsing interaction in the transition state of the ring flip: as the chelate ring planarizes, eclipsing in of the pyridine C6-H and C6'-H and the ancillary ligands is greater in the case of the bulky phosphine groups and less in the case of a linear CO or isonitrile. This eclipsing interaction could be contributing significantly to the relative barriers of ring flip.

Complexes exhibit similar ring flip barriers for both Rhodium(I) and Iridium(I) congeners. For example the barriers for complexes of isonitrile (**5ab**), CO (**3ab**), and cyclooctadiene (**4ab**) ligands differ pair-wise by less than 1.5 kcal/mol despite the variation of size and bond strengths [11] between the two metals, suggesting that the energetics of the π -symmetry backbonding is independent of these factors. This observation is consistent with the high homology in geometry of the ground states: for example the average metal-nitrogen bond length is 2.108(3) Å in **4a** and 2.100(2) Å in **4b** and the average metal-carbon bond length to the cod ligand is 2.137(4) Å in **4a** and 2.126(3) Å in **4b**. The bite angle of the borate ligand in **4a** is 85.89(7)° and 86.00(5)° in **4b**, respectively. Furthermore, homology between ring flip barriers for both rhodium(I) and iridium(I) congeners is consistent with a

view that no metal-pyridine bond is cleaved in the ring flip. Accordingly, computational pathways did not involve hemi-dissociation of the borate ligand.

2.3. Computational Modeling

Computational analysis at the DFT/B3LYP level predicts values for the $H^\ddagger$ of the chelate ring flip that are in good agreement with the values obtained experimentally (Table 2, right) [12, 13] This adds value to our observation because, knowing that the calculated values are calibrated to experiment, meaningful values for additional ligands that are not easily prepared can be predicted. Along this line, we determined calculated ligand flip barriers for rhodium complexes of acetonitrile, NH_3 , and AsH_3 (Table 2, entries 2, 6, 7). Ammonia and arsine complexes **9a** and **10a** have ring flip barriers near that of phosphine complex **7a**, which suggests a view that these ligands are similarly poor π acceptors. This seems to contradict our proposal that π -symmetry effects govern modulation of the ring flip barrier, whereas we often think of phosphines as π acceptors [14].

The calculations further enable visualization of the transition state for the ring flipping mechanism, which is concerted in nature and proceeds smoothly through a single transition state. Figure 1 illustrates the transition states for carbonyl and phosphine complexes represented in entries 3 and 8 of Table 2. We see in each that the borate ligand is largely planarized. Moreover, we find that the metal adopts a C2 twist in the transition state, which is accentuated with the more strongly donating phosphine ligand. We are unsure if this C2 twist is more attributable to minimization of eclipsing (steric) interactions or electronic effects. Interestingly, there is little, if any, statistical correlation between the sine of the twist angle and the barrier of the ring flip: plotted against each other, these have a Pearson coefficient [15] of +0.70 (normalized covariance, see supporting information). Optimization of both transition states within C_{2v} symmetry affords structures as second-order saddle points (two imaginary frequencies), allowing us to eliminate these higher symmetry structures from consideration.

2.4. Correlation of Ring Flip Barriers to Known Ligand Parameterization Systems

Transition metal-ligand bonds involve a mix of σ and π components and other influences, thus, a number of empirical ligand parameterization systems have appeared over the last 35 years. These include Tolman's cone angle and electronic parameter (TEP: the symmetric carbonyl stretching frequency of the complex $\text{LNi}(\text{CO})_3$) [16, 17, 18]; Lever's electronic parameter (LEP: the redox potential for reduction of $\text{L}_n\text{Ru}^{\text{III}}$ to $\text{L}_n\text{Ru}^{\text{II}}$) [19]; Odom's amide rotation parameter in $\text{NCr}(\text{Pr}_2\text{N})_2\text{X}$ complexes [20]; and other less-used tools [21, 22, 23, 24, 25, 26]. Interestingly, our measured and calculated ring flip barriers have poor correlation to these systems.

Comparing $H^\ddagger$ values presented here (Table 2) with either the TEP or LEP results in Pearson coefficients [15] of -0.57 (6 points) and -0.29 (8 points), respectively, between our values and the Tolman and Lever parameters (Figure 2). This shows little correlation and, if any relationship exists, it's inverse. For comparison, the TEP and LEP systems have a strong covariance with Pearson coefficient of +0.99 over the same 8 points. We propose that the reason that there is poor correlation between our ring flip enthalpies and Tolman or Lever

parameters is that the latter two regard a combination of both π and σ bonding effects, whereas the ring flipping barrier is dominated by π effects.

By remarkable contrast, these ring flipping energies correlate well with absorption spectroscopic data summarized by Zink for the π - π^* gap (1B_2 - 1A_2 symmetry transitions) of L - $PtCl_3^+$ cations [28]. Comparison of our $H^\ddagger$ values with these absorption data produces a linear correlation with a Pearson score of -0.97 (Figure 3) [29]. This correlation supports the proposal that the ring flip barrier is strongly dependent on π -electronic symmetry interactions.

2.5. Proposed Rationale for Flip Barrier Modulation

We suspect that the origin of the electronic π effect that appears to dominate the ring flip barrier involves minimization of a deleterious filled/filled interaction between occupied orbitals on the pyridine π systems and the metal's d_{xz} and d_{yz} , which is maximized as the ligand planarizes. This interaction is minimized when the d_{xz} and d_{yz} set is lowered by mixing with π^* orbitals on withdrawing ligands. Analogous cases of this type of filled-filled interaction have been concisely explained by Caulton [30] who points out their relevance to rotation barriers for ligands bound to (carbonyl)metal fragments. We believe that the aforementioned twist of the transition is a geometrical manifestation of the filled-filled interaction and ligand-ligand eclipsing.

3. Conclusions

Rhodium(I) and Iridium(I) complexes of dimethylbis(2-pyridyl)borate are easily prepared from air-stable chlorometal precursors and the sodium salt of dimethylbis(2-pyridyl)borate. These complexes undergo a boat-to-boat ring flip for which the barrier is highly dependent on the nature of the ligands *trans* to the chelating pyridine groups. While C—H to ligand eclipsing probably also plays a role, empirical correlation to the metal-ligand π - π^* energy gap leads to a view that π -symmetry electronic interactions dominate the influences that govern the magnitude of the ligand chelate ring flip barrier. The appropriate π -symmetry metal-centered orbitals that might otherwise accept electron density from the pyridine groups in the transition state of the ring flip are occupied, so we believe that a deleterious filled-filled orbital interaction in the transition state of the ring flip is at the basis of this effect. In sum, this system provides a thought-provoking example of π -symmetry bonding and repulsion in the conformational dynamics of group 9 metal chelates.

4. Experimental

4.1. General Procedures

All air and water sensitive procedures were carried out either in a Vacuum Atmosphere glove box under nitrogen (2–10 ppm O_2 for all manipulations) or using standard Schlenk techniques under nitrogen. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. Benzene, toluene, toluene- d_8 , and tetrahydrofuran- d_8 were dried over sodium benzophenone ketyl and distilled prior to use. Hexane, diethyl ether and tetrahydrofuran were obtained from a J. C. Meyer solvent purification system with alumina/copper(II) oxide columns and used without further purification. Organometallic precursors

were purchased from Strem Chemicals and were used as received. Other reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Sonication procedures were conducted with a VWR desktop jewelry cleaner. ^1H and ^{11}B NMR spectra were obtained on a Varian 400-MR spectrometer (400 MHz in ^1H , 128 MHz in ^{11}B , 100 MHz in ^{13}C , 162 MHz in ^{31}P), Varian 500 MHz spectrometer (500 MHz in ^1H , 160 MHz in ^{11}B) or Varian 600 MHz spectrometer (600 MHz in ^1H , 150 MHz in ^{13}C) with chemical shifts reported in units of ppm. All ^1H and ^{13}C chemical shifts are referenced to the residual solvent (relative to TMS). ^{11}B and ^{31}P chemical shifts are referenced to the spectrometer, which is benchmarked within ca. 0.5 ppm. NMR spectra were taken in 8" J-Young tubes (Wilmad or Norell) with Teflon valve plugs. The NMR tubes were shaken vigorously for several minutes with chlorotrimethylsilane then dried under reduced pressure on a Schlenk line prior to use. Melting points were obtained on a mel-temp apparatus. MALDI data is uncalibrated and acquired using anthracene or 2,4-dihydroxybenzoic acid as the matrix. CHN elemental analyses were collected at the University of Illinois at Urbana Champaign at the School of Chemical Sciences Microanalysis Laboratory.

Sodium dimethyldi-2-pyridylborate was synthesized according to literature procedures [3].

4.2. Inversion Recovery Methods and Error Calculation

Inversion recovery data was acquired on a Varian 600 MHz spectrometer (600 MHz in ^1H , 150 MHz in ^{13}C) according to the procedure previously published by our group [10]. Standard error values for the activation parameters, $\sigma(\text{Hq})$ and $\sigma(\text{Sq})$, were calculated according to the equations derived by Girolami et al. [31]. The behavior (methyl)boron signals utilized in the inversion recovery experiments is shown in Figure 4.

4.3. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Rh}(\text{CO})_2$ (3a)

Under N_2 in a dry vial, $[(\text{CO})_2\text{RhCl}]_2$ (58.3 mg, 0.15 mmol) was dissolved in 5 mL of dry diethyl ether. $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (66.0 mg, 0.30 mmol) was added and the reaction solution was stirred at room temperature for 4 hours. Thereafter, a precipitate was allowed to settle and the reaction mixture was filtered through celite. Ether was removed under reduced pressure to give product as a yellow solid, 108.8 mg (0.30 mmol, > 99%).

MP: 125-129 °C with decomposition. ^1H NMR (toluene- d_8 , 400 MHz) δ : 8.16 (d, $J = 5.6$ Hz), 7.74 (d, $J = 7.9$ Hz), 6.89 (td, $J = 7.6, 1.6$ Hz), 6.21 (td, $J = 6.4, 1.6$ Hz), 1.13 (br s), 0.73 (br s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 186.9 (d, $J = 66.9$ Hz), 152.3, 136.2, 129.9, 119.3; ^{13}C NMR (from ^1H - ^{13}C HMBC, toluene- d_8 , 125 MHz, 0 °C) δ : 198.6, 152.6, 136.5, 130.2, 119.7, 23.2, 11.6; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -8.5; MALDI: $m/z = 358.95$ g/mol, calc'd. for $\text{C}_{14}\text{H}_{16}\text{BN}_2\text{O}_2\text{Rh}^+ [\text{M}+\text{H}]^+$: 357.02; FT-IR (thin film / cm^{-1}) $\nu = 2917.6, 2828.4, 2074.0, 2003.4, 1597.0, 1420.7, 1290.1, 1012.5, 755.5$. Anal. Calc'd for $\text{C}_{14}\text{H}_{14}\text{BN}_2\text{O}_2\text{Rh}$: C, 47.23; H, 3.96; N, 7.87. Found: C, 47.17; H, 3.98; N, 7.66.

4.4. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Rh}(\text{cod})$ (4a)

Under N_2 in a dry vial, 3.5 mL dry hexane was added to $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (30.8 mg, 0.14 mmol) and $[(\text{cod})\text{RhCl}]_2$ (34.5 mg, 0.07 mmol). The reaction was briefly (~3 min) sonicated and then stirred at room temperature for 2 hours or until all rhodium was dissolved.

Thereafter, a precipitate was allowed to settle and the reaction mixture was filtered through celite. Hexane was removed under reduced pressure to give product as a yellow solid, 56.6 mg (0.139 mmol, 99%).

MP: 147-149 °C. ^1H NMR (toluene- d_8 , 400 MHz) δ : 8.10 (d, $J = 5.9$ Hz), 7.70 (d, $J = 7.8$), 6.92 (td, $J = 7.6, 1.6$ Hz), 6.30 (td, $J = 6.4, 1.6$ Hz), 3.84-3.76 (m), 2.44-2.35 (m), 1.74 (q, $J = 7.7$ Hz), 1.67 (br s), 1.50 (q, $J = 7.7$ Hz), 0.87 (br s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 148.2, 134.3, 128.5, 119.1, 84.4 (d, $J = 14.9$ Hz), 79.6 (d, $J = 10.6$ Hz), 30.8, 30.63; ^{13}C NMR (from ^1H - ^{13}C HSQC, toluene- d_8 , 100 MHz) δ : 148.5, 134.8, 129.2, 119.6, 84.5, 79.9, 30.8, 30.6, 21.2, 15.0; ^{13}C NMR (from ^1H - ^{13}C HMBC, toluene- d_8 , 100 MHz) δ : 191, 148, 135, 130, 119, 85, 81, 32, 32, 21, 15; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -8.3; MALDI: $m/z = 408.04$ g/mol, calc'd. for $\text{C}_{20}\text{H}_{26}\text{BN}_2\text{Rh}^+ [\text{M}]^+$: 408.12; FT-IR (thin film / cm^{-1}) $\nu = 3017.1, 2912.4, 1590.6, 1453.3, 1287.5, 1003.3, 753.5$. Anal. Calc'd for $\text{C}_{20}\text{H}_{26}\text{BN}_2\text{Rh}$: C, 58.85; H, 6.42; N, 6.86. Found: C, 58.92; H, 6.38; N, 6.96.

4.5. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Rh}(\text{CNTBu})_2$ (5a)

First synthetic step adapted from literature procedure [9a]: Under N_2 in a dry flask, $[(\text{cod})_2\text{RhCl}]_2$ (49.3 mg, 0.10 mmol) was dissolved in 3 mL of dry tetrahydrofuran. *t*-Butylisocyanide (34.9 mg, 47.5 μL , 0.42 mmol) was added by syringe, producing a dark brown solution. The reaction solution was stirred for 2 hours at room temperature. Tetrahydrofuran was then removed under reduced pressure to give a red residue. 3 mL dry tetrahydrofuran and $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (44.0 mg, 0.20 mmol) were added to the flask and the reaction solution was stirred for 2 hours at room temperature to produce an orange solution. Filtration of the reaction mixture through celite and evaporation of the filtrate produced a yellow residue. The residue was triturated with 5 mL dry hexane, sonicated for 20 minutes and filtered to give product as a bright yellow solid, 75.2 mg (0.162 mmol, 81%).

MP: 192-194 °C with decomposition. ^1H NMR (thf- d_8 , 600 MHz, -40 °C) δ : 8.70 (d, $J = 5.7$ Hz), 7.47 (d, $J = 7.9$ Hz), 7.38 (tt, $J = 7.7, 1.3$ Hz), 6.80 (tt, $J = 6.5, 1.3$ Hz), 1.49 (s), 0.66 (s), 0.16 (s); ^{13}C NMR (toluene- d_8 , 150 MHz, -40 °C) δ : 152.7, 134.2, 118.2, 55.6, 30.2; ^{13}C NMR (from ^1H - ^{13}C HMBC, thf- d_8 , 150 MHz, -40 °C) δ : 192.5, 156.7, 154.0, 135.0, 128.9, 119.7, 58.7, 32.2, 20.6, 12.1; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -8.5; MALDI: Parent ion was not observed as a major peak. Three fragments were observed, the latter corresponding to isocyanide hydration in the sample preparation ($m/z = 451.06$ g/mol, calc'd. for $\text{C}_{21}\text{H}_{29}\text{BN}_4\text{Rh}^+ [\text{M}-\text{CH}_3]^+$: 451.15), ($m/z = 473.06$ g/mol, calc'd. for $\text{C}_{21}\text{H}_{29}\text{BN}_4\text{Rh}^+ [\text{M}-\text{CH}_3+\text{Na}]^+$: 474.19), ($m/z = 483.03$ g/mol, calc'd. for $\text{C}_{22}\text{H}_{34}\text{BN}_4\text{ORh}^+ [\text{M}+\text{H}_2\text{O}]^+$: 484.19); FT-IR (thin film / cm^{-1}) $\nu = 2981.6, 2913.0, 2143.6, 2097.1, 1591.5, 1456.9, 1209.1, 755.7$.

4.6. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Rh}(\text{C}_2\text{H}_4)_2$ (6a)

Under N_2 in a dry J. Young tube, $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ (7.8 mg, 0.02 mmol) was dissolved in 750 μL dry toluene- d_8 . $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (8.8 mg, 0.04 mmol) was added and the tube was shaken and allowed to sit at room temperature. The reaction mixture was filtered through celite to give a solution containing $[(\text{py})_2\text{BMe}_2]\text{Rh}(\text{C}_2\text{H}_4)_2$ with a small amount of free

$[(py)_2B(Me)_2]Na$. Toluene- d_8 was removed under reduced pressure to give a solid sample for MALDI and IR.

1H NMR (toluene- d_8 , 400 MHz) δ : 8.01 (d, $J = 5.6$), 7.74 (d, $J = 7.5$ Hz), 6.87 (td, $J = 7.5$, 1.6 Hz), 6.26 (td, $J = 6.4$, 1.7 Hz), 2.75–2.70 (m), 1.69 (br s), 0.84 (br s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 147.0, 134.4, 119.5, 65.5 (d, $J = 11.5$ Hz); ^{13}C NMR (from 1H - ^{13}C HSQC, toluene- d_8 , 100 MHz) δ : 147.0, 134.5, 129.0, 119.9, 65.4, 19.4, 12.8; ^{13}C NMR (from 1H - ^{13}C HMBC, toluene- d_8 , 100 MHz) δ : 191.7, 147.8, 135.9, 130.4, 120.6, 65.7, 19.3, 12.8; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -13.1; FT-IR (thin film / cm^{-1}) $\nu = 3075.0$, 2972.7, 2912.4, 2820.6, 1593.1, 1455.9, 1418.8, 1286.5, 1156.8, 1004.0, 752.8. MALDI: This complex is insufficiently stable to obtain a MALDI, however we were able to detect several ions which we propose to correspond to the complexes formed by exchange of ethylene for solvent, air or water, specifically $[(py)_2B(Me)_2]Rh(toluene-d_8)$ ($m/z = 399.20$ g/mol, calc'd. for $C_{19}H_{14}D_8BN_2Rh^+$ $[M]^+$: 400.14), $[(py)_2B(Me)_2]Rh(O_2)_2$ ($m/z = 363.21$ g/mol, calc'd. for $C_{12}H_{14}BN_2O_4Rh^+$ $[M]^+$: 364.01), and $[(py)_2B(Me)_2]Rh(O_2)(H_2O)$ ($m/z = 349.20$ g/mol, calc'd. for $C_{12}H_{16}BN_2O_3Rh^+$ $[M]^+$: 350.03).

4.7. Synthesis of $[(py)_2B(Me)_2]Ir(CO)_2$ (3b)

First synthetic step adapted from literature procedure [9b]: Under N_2 in a dry flask, $[(coe)_2IrCl]_2$ (44.8 mg, 0.05 mmol) was dissolved in 5 mL of dry benzene. The flask was then evacuated, filled with CO (1 atm) and stirred for 2 hours. The CO was removed and replaced by N_2 and $[(py)_2B(Me)_2]Na$ (22.0 mg, 0.10 mmol) was added. The reaction solution was stirred for overnight at room temperature. Filtration of the reaction mixture and evaporation of the filtrate produced a brown residue. This residue was extracted with a minimal volume of dry hexane (ca. 5–10 mL) and filtered. The hexane solution was concentrated and cooled to give yellow crystals. The supernatant was further concentrated and cooled to give a second crop of yellow crystals with a combined yield of 22.2 mg (0.050 mmol, 50%).

This reaction can also be done in dry acetonitrile (10 mL), with reversed addition of ligand and CO or simultaneous addition of ligand and CO. All methods produce similar yields.

MP: Begins to darken at 85 °C full decomposed by 100 °C. 1H NMR (toluene- d_8 , 400 MHz) δ : 8.27 (d, $J = 5.7$ Hz), 7.75 (d, $J = 7.9$ Hz), 6.84 (td, $J = 7.6$, 1.6 Hz), 6.17 (td, $J = 6.6$, 1.6 Hz), 1.19 (br s), 0.67 (br s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 175.0, 152.9, 136.8, 130.1, 120.1; ^{13}C NMR (from 1H - ^{13}C HMBC, toluene- d_8 , 150 MHz, -20 °C) δ : 194.8, 153.1, 137.0, 130.3, 120.6, 30.1, 11.7; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -8.8; FT-IR (thin film / cm^{-1}) $\nu = 2921.1$, 2830.3, 2064.2, 1984.5, 1599.6, 1460.6, 1460.5, 1266.0, 1113.2, 1033.6, 759.9. Anal. Calc'd for $C_{14}H_{16}BIrN_2O_2$: C, 37.59; H, 3.61; N, 6.26. Found: C, 36.77; H, 2.97; N, 5.98. HR-MS (+ESI): $m/z = 447.0848$ g/mol, calc'd. for $C_{14}H_{15}BIrN_2O_2^+$ $[M+H]^+$: 447.0851 g/mol.

4.8. Synthesis of $[(py)_2B(Me)_2]Ir(cod)$ (4b)

Under N_2 in a dry vial, 3.5 mL dry hexane was added to $[(py)_2B(Me)_2]Na$ (30.8 mg, 0.14 mmol) and $[(cod)IrCl]_2$ (47.0 mg, 0.07 mmol). The reaction solution was briefly (~3 min)

immersed in a desktop sonicator and then stirred at room temperature for 2 hours or until all iridium was dissolved. Thereafter, a precipitate was allowed to settle and the reaction mixture was filtered through celite. Hexane was removed under reduced pressure to give product as an orange solid, 63.8 mg (0.128 mmol, 91%).

MP: 146-151 °C. ^1H NMR (toluene- d_8 , 400 MHz) δ : 8.15 (d, J = 5.9 Hz), 7.85 (d, J = 8.0 Hz), 6.90 (td, J = 7.5, 1.5 Hz), 6.29 (td, J = 6.2, 1.6 Hz), 3.61-3.55 (m), 2.39-2.35 (m), 2.26-2.22 (m), 1.68 (q, J = 8.2 Hz), 1.42 (br s), 1.34 (q, J = 8.2), 0.81 (br s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 148.1, 134.7, 129.6, 119.7, 68.5, 64.1, 31.6, 31.3; ^{13}C NMR (from ^1H - ^{13}C HSQC, toluene- d_8 , 100 MHz) δ : 148, 135, 129, 120, 68, 64, 31, 31, 20, 13; ^{13}C NMR (from ^1H - ^{13}C HMBC, toluene- d_8 , 100 MHz) δ : 190, 148, 134, 130, 120, 68, 64, 32, 32, 21, 14; ^{11}B NMR (toluene- d_8 , 160 MHz) δ : -8.8; MALDI: m/z = 497.96 g/mol, calc'd. for $\text{C}_{20}\text{H}_{26}\text{BIrN}_2^+$ [M] $^+$: 498.18; FT-IR (thin film / cm^{-1}) ν = 2913.2, 2833.8, 1593.7, 1454.1, 1288.5, 1002.3, 754.5. Anal. Calc'd for $\text{C}_{20}\text{H}_{26}\text{BIrN}_2$: C, 48.29; H, 5.27; N, 5.63. Found: C, 48.08; H, 5.08; N, 5.53.

4.9. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Ir}(\text{CNtBu})_2$ (5b)

First synthetic step adapted from literature procedure [9a]: Under N_2 in a dry flask, $[(\text{cod})_2\text{IrCl}]_2$ (47.0 mg, 0.07 mmol) was dissolved in 2.1 mL of dry tetrahydrofuran. *t*-Butylisonitrile (24.4 mg, 33.3 μL , 0.294 mmol) was added by syringe, producing a dark brown solution. The reaction solution was stirred for 2 hours at room temperature. Tetrahydrofuran was then removed under reduced pressure to give a purple or green residue. 2.1 mL dry tetrahydrofuran and $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (30.8 mg, 0.14 mmol) were added to the flask and the reaction solution was stirred for 2 hours at room temperature to produce a yellow-orange solution. Filtration of the reaction mixture through celite and evaporation of the filtrate produced a yellow-brown residue. 5 mL dry hexane was added to the flask, which was then sonicated for 1 hour in an ice bath and filtered to give product as a yellow solid, 51.5 mg (0.093 mmol, 66%). It is important to note that this complex is highly unstable in most solvents, with the exception of tetrahydrofuran.

^1H NMR (thf- d_8 , 600 MHz, -50 °C) δ : 8.80 (d, J = 5.5 Hz), 7.57 (d, J = 8.1 Hz), 7.48 (tt, J = 7.4, 1.5 Hz), 6.88 (tt, J = 6.7, 1.4 Hz), 1.48 (s), 0.59 (s), 0.15 (s); ^{13}C NMR (thf- d_8 , 100 MHz) δ : 154.3, 135.3, 129.2, 119.8, 56.7, 31.5; ^{13}C NMR (from ^1H - ^{13}C HMBC, thf- d_8 , 150 MHz, -50 °C) δ : 197.7, 163.2, 152.7, 133.6, 127.5, 118.4, 55.8, 32.1, 20.7, 10.4; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -13.5; MALDI: m/z = 555.08 g/mol, calc'd. for $\text{C}_{22}\text{H}_{32}\text{BIrN}_4^+$ [M] $^+$: 556.23; FT-IR (thin film / cm^{-1}) ν = 3281.5, 2978.7, 2921.3, 2155.9, 1600.7, 1411.4, 1270.0, 1235.6, 948.1, 764.5.

4.10. Synthesis of $[(\text{py})_2\text{B}(\text{Me})_2]\text{Rh}(\text{dppe})$ (7a)

Under N_2 in a dry flask, $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ (38.9 mg, 0.10 mmol) was dissolved in 4 mL of dry toluene. $[(\text{py})_2\text{B}(\text{Me})_2]\text{Na}$ (44.0 mg, 0.20 mmol) was added to the flask and the reaction solution was stirred for 1 hour at room temperature. A solution of 1,2-bis(diphenylphosphino)ethane (79.7 mg, 0.2 mmol) in 3 mL dry toluene was added dropwise. The reaction solution was stirred for another hour at room temperature and then filtered through celite. Toluene was removed under reduced pressure to give a yellow oil.

The residue was triturated with 5 mL dry hexane, sonicated for 20 minutes and the hexane was removed under reduced pressure to give product as a yellow solid, 137.4 mg (0.197 mmol, 98%).

MP: Decomposes from 85-100 °C with most rapid darkening from 173-177 °C. ^1H NMR (toluene- d_8 , 400 MHz) δ : 8.52, (d, J = 5.0 Hz), 7.96 (t, J = 8.2 Hz), 7.83 (d, J = 7.6 Hz), 7.42-7.38 (m), 7.21-7.14 (m), 6.98-6.92 (m), 6.90 (td, J = 7.5, 1.7 Hz), 6.04 (td, J = 6.6, 1.7 Hz), 2.02-1.94 (m), 1.74-1.64 (m), 1.34 (s), 0.86 (s); ^{13}C NMR (toluene- d_8 , 100 MHz) δ : 152.5, 136.6 (t, J = 16.0 Hz), 134.4 (t, J = 5.8 Hz), 133.5, 133.1 (t, J = 5.3 Hz), 129.8, 129.5, 128.5 (t, J = 4.5 Hz), 128.1 (t, J = 4.5 Hz), 117.7, 30.1 (td, J = 24.9 Hz, 3.0 Hz); ^{13}C NMR (from ^1H - ^{13}C HSQC, toluene- d_8 , 100 MHz) δ : 153, 134, 133, 133, 130, 130, 129, 128, 128, 118, 30, 21, 13; ^{13}C NMR (from ^1H - ^{13}C HMBC, toluene- d_8 , 100 MHz) δ : 193, 153, 137, 135, 134, 133, 131, 130, 129, 129, 128, 118, 31, 21, 13; ^{11}B NMR (toluene- d_8 , 128 MHz) δ : -13.3; ^{31}P NMR (toluene- d_8 , 162 MHz) δ : 70.6 (d, J = 174 Hz); MALDI: m/z = 697.88 g/mol, calc'd. for $\text{C}_{38}\text{H}_{38}\text{BN}_2\text{P}_2\text{Rh}^+ [\text{M}]^+$: 698.17; FT-IR (thin film / cm^{-1}) ν = 3055.2, 2913.4, 1589.2, 1435.6, 1197.1, 1096.9, 1000.1, 743.1, 695.6. Anal. Calc'd for $\text{C}_{38}\text{H}_{38}\text{BN}_2\text{P}_2\text{Rh}$: C, 65.35; H, 5.48; N, 4.01. Found: C, 65.14; H, 5.79; N, 3.80.

4.11. X-ray Crystallographic Data

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Calculated Geometries of the Ring Flip Transition States for (left) **3a** $[(L)Rh(CO)_2]$ and (right) $[(L)Rh(PH_3)_2]$. L = $Me_2B(2-py)_2$ anion.

Figure 2.

Top: Plot of TEP (cm⁻¹) [16, 17, 27] versus $\Delta H^\ddagger$ (kcal/mol). MePPh₂ was used to compare to dppe. Triangles indicate that computational data was used for one or both values. Bottom: Plot of LEP (V) [17, 19] versus $\Delta H^\ddagger$ (kcal/mol). Norbornadiene (nbd) was used to compare to cod. Triangles indicate that computational data was used for one or both values.

Figure 3.

Correlation of 1B_2 - 1A_2 energy difference [28] and $\Delta H^\ddagger$ (kcal/mol). PPh₃ was used to compare to dppe and AsPh₃ was used to compare to AsH₃. Triangles indicate that computational data was used for one or both values.

Figure 4. NMR spectra showing the (methyl)boron signals of **3a** from -30 °C to +40 °C referenced to toluene-*d*₈. Note: complex is crystallized from diethyl ether.

M = Rh, L₂ = (CO)₂ (**3a**, 99%)

cod (**4a**, 99%)

(*t*BuNC)₂ (**5a**, 81%)

(C₂H₄)₂ (**6a**)

dppe (**7a**, 98%) ← dppe, PhMe

M = Ir, L₂ = (CO)₂ (**3b**, 50%)

cod (**4b**, 91%)

(*t*BuNC)₂ (**5b**, 66%)

cod = 1,5-cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane

Scheme 1.

Syntheses of Complexes **3-7**.

Scheme 2.

A Ring Flip of the Chelate Ring Exchanges the Positions of the (Methyl)boron Groups.

Table 1

Structure of Borate-Ligated Complexes.^a

Complex	Dihedral Angle (°) ^b	M-C9 (Å)
3a	48.9(2)	3.200(2)
4a	49.5(2)	3.315(2)
4b	49.7(2)	3.359(2)

^aTop: ORTEP Diagram for Complex **3a**. Ellipsoids are drawn at the 50% probability level. See Table 3 (Experimental Section) for details. Bottom: Tabular data for complexes **3a** and **4ab**.

^bDihedral angles are calculated as an average of four measured torsion angles in the crystal structures.

Table 2Values for Chelate Ring Flip $H^\ddagger$ (kcal/mol) and $S^\ddagger$ (eu) for **3–10**.

Entry	Complex	Experimental		Calculated ^a
		$H^\ddagger$ (kcal/mol)	$S^\ddagger$ (eu)	$H^\ddagger$ (kcal/mol)
1	5a LRh(<i>t</i> BuNC) ₂	12.3(7)	−5.3(21)	14.5 ^b
2	8a LRh(NCMe) ₂	–	–	14.9
3	3a LRh(CO) ₂	15.5(1)	2.8(5)	15.7
4	6a LRh(C ₂ H ₄) ₂	15.9(2)	−6.0(5)	–
5	4a LRh(cod)	16.2(2)	−5.3(5)	17.1
6	9a LRh(NH ₃) ₂	–	–	17.6
7	10a LRh(AsH ₃) ₂	–	–	19.2
8	7a LRh(dppe)	21.5(3)	2.2(8)	19.5 ^c
9	5b LIr(<i>t</i> BuNC) ₂	13.2(3)	0.8(9)	–
10	3b LIr(CO) ₂	14.2(5)	−0.9(16)	–
11	4b LIr(cod)	16.8(8)	3.4(24)	–

^aVide infra (section 2.3) regarding computational studies.^b*t* BuNC modelled as MeNC.^cdppe modelled as (PH₃)₂.

Table 3Crystal data and structure refinement for **3a**, **4a**, and **4b**.

Empirical formula	[(2-py) ₂ B(Me) ₂]Rh(CO ₂)	[(2-py) ₂ B(Me) ₂]Rh(cod)	[(2-py) ₂ B(Me) ₂]Ir(cod)
Compound Number	3a	4a	4b
CCDC Deposition Number	CCDC 937914	CCDC 937915	CCDC 937913
Formula weight	355.99	408.15	497.44
Chemical Formula	C ₁₄ H ₁₄ BN ₂ O ₂ Rh	C ₂₀ H ₂₆ BN ₂ Rh	C ₂₀ H ₂₆ BIrN ₂
Crystal Habit	Prism	Prism	Prism
Crystal size	0.35 × 0.47 × 0.50 mm ³	0.24 × 0.25 × 0.38 mm ³	0.143 × 0.22 × 0.25 mm ³
Crystal color	Clear/yellow	Clear/yellow	Clear/yellow
Data Collection			
Wavelength	0.71073 Å MoKα	0.71073 Å MoKα	0.71073 Å MoKα
Data Collection Temperature	100(2) K	143(2) K	100(2) K
Unit cell dimensions	a = 9.343(2) Å	a = 10.3908(5) Å	a = 10.3674(3) Å
	α = 90°	α = 90°	α = 90°
	b = 11.129(3) Å	b = 11.3411(6) Å	b = 11.3096(3) Å
	β = 106.030(3)°	β = 96.549(1)°	β = 96.360(1)°
	c = 14.519(3) Å	c = 15.4163(8) Å	c = 15.3893(5) Å
	γ = 90°	γ = 90°	γ = 90°
Volume	1451.0(6) Å ³	1804.85(16) Å ³	1793.31(9) Å ³
Z	4	4	4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/n	P 21/n
Density (calculated)	1.630 g/cm ³	1.502 g/cm ³	1.842 g/cm ³
F(000)	712	840	968
q range for data collection	2.27 to 30.70°	2.23 to 27.51°	2.24 to 30.54°
Index ranges	−13 h 12	−13 h 13	−14 h 14
	−15 k 15	−14 k 13	−16 k 16
	−20 l 20	−15 l 20	−21 l 21
Reflections collected	26000	10620	43335
Independent reflections	4407 [R _{int} = 0.0445]	4036 [R _{int} = 0.0496]	5450 [R _{int} = 0.0229]
Absorption coefficient	1.177 mm ^{−1}	0.949 mm ^{−1}	7.447 mm ^{−1}
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.6848 and 0.5911		0.4160 and 2570
Structure solution and Refinement			
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 1990)
Structure solution method	Direct methods	Direct methods	Direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 1997)	SHELXTL XT 2013/1 (Bruker AXS)
Structure refinement program	SHELXL 2012-4 (Sheldrick, 2012)	SHELXL 2012-4 (Sheldrick, 2012)	SHELXTL XT 2013/2 (Bruker AXS)
Refinement method	Full matrix least-squares on F ²	Full matrix least-squares on F ²	Full matrix least-squares on F ²

Function minimized	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4407 / 0 / 183	4036 / 0 / 219	5450 / 0 / 219
Goodness-of-fit on F2	1.018	1.080	1.077
Final R indices I>2σ(I)	R1 = 0.0247 wR2 = 0.0644	R1 = 0.0361 wR2 = 0.0859	R1 = 0.0126 wR2 = 0.0282
R indices (all data)	R1 = 0.0272 wR2 = 0.0676	R1 = 0.0400 wR2 = 0.0889	R1 = 0.0141 wR2 = 0.0285
Weighting scheme	w = $1/[\sigma^2(F_o^2) + (0.0366P^2 + 1.2011P)]$ where $P = (F_o^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.4245P]$ where $P = (F_o^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.0101P)^2 + 1.3986P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.634 and -1.248 e.Å ⁻³	1.112 and -0.859 e.Å ⁻³	0.682 and -0.596 e.Å ⁻³
R.M.S. deviation from mean	0.090 e.Å ⁻³	0.100 e.Å ⁻³	0.079 e.Å ⁻³