ORGANOMETALLICS

Boron Functionalization and Unusual B–C Bond Activation in Rhodium(III) and Iridium(III) Complexes with Diphenylbis(pyrazolylborate) Ligands (Ph₂Bp)

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Supporting Information

ABSTRACT: The Rh(III) and Ir(III) pentamethylcyclopentadienyl compounds $[M(Cp^*)(\kappa^2-Ph_2Bp)Cl]$ (M = Rh, 1; M = Ir, 4) were readily prepared from interaction of the salt K[Ph_2Bp] (Ph_2Bp = diphenylbis(pyrazolyl)borate) and the $[M(Cp^*)Cl_2]_2$ dimer precursors in dichloromethane under anhydrous conditions. When the same reactions were carried out in non-anhydrous conditions by using acetonitrile as solvent, we observed, in the case of Rh, both B–N bond hydrolysis and Rh–C(Ph) bond activation with the formation of the hydroxy(pyrazolyl)borate complex [Rh(Cp*)(Ph){ κ^2 -(pz)(OH)BPh_2] (2). In contrast, in the case of Ir only B–N hydrolysis was observed and the ionic species [Ir(Cp*)(Hpz){ κ^2 -(pz)(OH)BPh_2]Cl (5) was obtained, upon coordination of the liberated Hpz. Additionally, by reaction of 1 with AgClO₄ in acetonitrile, the ionic [Rh(Cp*)-(Ph){ κ^2 -(pz)(OH)B(OH)]ClO₄ (3) was isolated. Complexes 1–3 and 5 have been structurally characterized by X-ray crystallography. Spectral studies have been



performed for all species, together with a computational DFT modeling investigation. A decomposition mechanism for the diphenylbis(pyrazolyl)borate ligand in the different complexes is proposed.

INTRODUCTION

The dimeric chloro-bridged complexes $[\{M(\eta^5-Cp^*)(\mu-Cl)-Cl\}_2]$ (M = Rh, Ir) have been extensively used as starting materials for a wide number of organometallic complexes that have found applications in several fields.¹ These complexes undergo a rich variety of chemistry through chloro bridge cleavage reactions, leading to the formation of interesting neutral and cationic mononuclear complexes.² In addition, rhodium(III) and iridium(III) complexes containing scorpionate ligands³ have recently attracted considerable attention because of their ability to activate the aliphatic and aromatic C–H bonds of hydrocarbons and other substrates.⁴

Bis(pyrazolyl)borate ligands (Bp') are versatile anionic chelating ligands widely used in coordination chemistry, able to yield stable complexes with all metals across the periodic table in both low and high oxidation states. In some cases, however, the nucleophilicity of the B–H bond and the latent Lewis acidity of the boron center allowed important functionalization of the BH₂ moiety⁵ as a consequence of hydrolysis or alcoholysis reactions, yielding hydroxy- and alkoxy(pyrazolyl)borate complexes, mainly when Rh or Ir acceptors have been employed.⁶

We have previously reported that η^5 -pentamethylcyclopentadienyl rhodium(III) containing the unsubstituted bis-(pyrazolyl)borate ligand Bp provided the formation of

 $[Rh(Cp^*)(\kappa^2-Bp)Cl]$ in high yield. At variance with this, two different compounds, monomeric [IrCp*Cl₂(pzH)] and the binuclear $[Ir(Cp^*)Cl]_2(\mu Cl)(\mu - pz)$, are generated from the reaction of $[Ir(Cp^*)Cl_2]_2$ with K[Bp].⁷ From the reaction of the analogous diphenyl-substituted ligand Ph₂Bp with $[Rh_2Cl_2(LL)_2]$ (LL = cyclooctadiene, norbornadiene, or 2CO) formation of the corresponding[Rh(LL)(Ph₂Bp)] derivatives is observed, for which spectroscopic data showed that the $C_{2\nu}$ symmetry of the Ph₂Bp group was preserved in the complexes.⁸ Thompson prepared the complex [Ir(N,C2'-(2-ptolylpyridine))2(Ph2Bp)] in good yields, provided that the complex is chloride-free prior to the addition of the Ph2Bp ligand.9 A report describing Mo(II) and W(II) derivatives containing the Ph₂Bp ligand showed the intrinsic instability of B-N bonds, which readily undergo an hydrolytic cleavage with formation of the new (OH)(pz)BPh₂ ligand acting as a chelating O,N-donor.¹⁰

As an extension of our works on scorpionates containing Rh(III) and Ir(III),¹¹ we have undertaken a systematic study of the reactions of the dimers $[M(Cp^*)Cl_2]_2$ (M = Rh, Ir) with the diphenylbis(pyrazolyl)borate K[Ph₂Bp] ligand. In addition to the previously observed B–N hydrolysis, here we report also

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on the unexpected B–C activation, with consequent transfer of one phenyl substituent from the Ph_2Bp moiety to the Rh(III) center.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and reagents were of reagent grade quality and were used as received without further purification. The potassium salt of the scorpionate ligand K[Ph₂Bp] was synthesized as previously reported.³ Dichloromethane was freshly distilled from CaH₂. Acetonitrile was used without previous distillation. The samples were dried in vacuo to constant weight (20 °C, ~0.1 Torr). Elemental analyses were carried out in house with a Fisons Instruments 1108 CHNSO elemental analyzer. IR spectra were recorded from 4000 to 600 cm⁻¹ with a Perkin-Elmer Spectrum 100 FT-IR instrument. ¹H and ¹³C NMR spectra were recorded on a 400 Mercury Plus Varian instrument operating at room temperature (400 MHz for ¹H and 100 MHz for ¹³C). ¹H and ¹³C chemical shifts (δ) are reported in parts per million (ppm) from SiMe₄ (¹H and ¹³C calibration by internal deuterium solvent lock). Peak multiplicities are abbreviated as follows: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. Melting points are uncorrected and were taken on an STMP3 Stuart Scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_{M} , reported as Ω^{-1} cm² mol⁻¹) of acetonitrile solutions of the complexes were taken with a Crison CDTM 522 conductimeter at room temperature.

Syntheses of Complexes. [Rh(Cp*)(Ph₂Bp)Cl] (1). To a dichloromethane solution (10 mL) of [Rh(Cp*)Cl₂]₂ (0.618 g, 1.00 mmol) was added K[Ph₂Bp] (0.676 g, 2.00 mmol) at -10 °C. The mixture was stirred for 1 h, while the temperature was raised to 0 °C, and then was filtered to remove KCl. The solution was dried under vacuum, and the orange residue obtained was recrystallized from 1/1 CH₂Cl₂/light petroleum (40-60 °C) and shown to be compound 1 (0.334 g, 0.568 mmol, yield 88%). Anal. Calcd for C₂₉H₃₄BClN₄Rh, C, 59.26; H, 5.83; N, 9.53. Found: C, 58.96; H, 5.68; N, 9.60. IR (cm⁻¹): 3112 w, 3037 w. 1564 m, 1526 w ν(C=C, C=N). ¹H NMR (CDCl₃, 293 K): δ 1.26 (s, 15H, CH₃ Cp*), 6.32 (t, 2H, H4 pz), 6.62 (dd, 2H, Ph), 6.95 (dbr, 2H, Ph), 7.10-7.18 (m, 6H, Ph), 7.22 (d, 2H, H5 pz), 7.48 (d, 2H, H3 pz). ¹³C NMR (CDCl₃, 293 K): δ 8.9 (s, CH₃ Cp^{*}), 95.6 (d, C Cp^{*}, $J(^{103}\text{Rh}-^{13}\text{C}) = 7.9 \text{ Hz}), 105.9 \text{ (s, C4 pz)}, 126.1, 126.9, 127.4, 127.5,$ 128.5, 132.2, 139.3 (s, Ph), 135.8 (s, C5 pz), 143.6 (s, C3 pz). $\Lambda_{\rm M}$ (CH₃CN, 10⁻³ M): 1.3 Ω^{-1} cm² mol⁻¹. After 1 h the conductivity of the CH₃CN solution increases to 25.3 Ω^{-1} cm² mol⁻¹. After 1 day the conductivity of the acetonitrile solution reaches the value 71.3 Ω^{-1} cm² mol⁻¹

[Rh(Cp*)(Ph){(pz)(OH)BPh₂}] (2). To a stirred acetonitrile solution (20 mL) of [Cp*RhCl₂]₂ (0.618 g, 1.0 mmol) was added 0.676 g (2.0 mmol) of Kpz₂BPh₂. The red solution was stirred for 10 min, giving an orange solution, and the solvent was then removed under reduced pressure. The resulting orange solid was vigorously stirred with 20 mL of chloroform at room temperature for 1 h and then the solution was slowly evaporated. Yellow-orange crystals of 2 were obtained in 40% yield. Anal. Calcd for C32H37BN2ORh: C, 66.34; H, 6.44; N, 4.84. Found: C, 66.11; H, 6.28; N, 4.91. IR (cm⁻¹): 3221 br ν (O–H), 3123 w, 3060 w ν(C-H), 1737 m ν(O-H), 1596 w, 1564 w ν(C∸C, C⁻⁻N). ¹H NMR (CDCl₃, 293 K): δ 1.27 (s, 15H, CH₃ Cp*), 3.40 (br, 1H, H-OB), 6.34 (t, 1H, H4 pz), 6.68-7.08 (m, 11H, Ph), 7.17-7.24 (m, 5H, Ph and H5 pz), 7.67 (d, 1H, H3 pz). 13 C NMR (CDCl₃, 293 K): δ 8.9 (s, CH₃ Cp*), 95.19 (d, C Cp*, $J(^{103}\text{Rh}-^{13}\text{C}) = 8.0$ Hz), 105.92 (s, C4, pz), 126.1, 126.9, 127.1, 127.5, 128.5, 132.2, 139.3 (s, Ph), 135.8 (s, C5 pz), 143.6 (s, C3 pz). $\Lambda_{\rm M}$ (CH₃CN, 10⁻³ M): 3.2 Ω ⁻¹ cm² mol⁻¹

 $[Rh(Cp*)(Ph){pzB(OH)_2}]ClO_4$ (3). A 0.103 g amount of AgClO₄ (0.05 mmol) was added to a CH₃CN (7 mL) solution/suspension of 1 (0.293 g, 0.05 mmol) under N₂. After 48 h at room temperature a colorless precipitate formed, which was filtered off and shown to be AgCl. The clear orange solution obtained was evaporated under vacuum and the residue washed with light petroleum and shown to be compound 3 (0.091 g, 0.015 mmol, yield 31%). It was recrystallized from CH₂Cl₂/light petroleum (40–60 °C). Mp: 240 °C dec. Anal.

Calcd for C₂₃H₃₆BClN₂O₆Rh: C, 47.16; H, 6.20; N, 4.78. Found: C, 47.32; H, 6.12; N, 4.68. IR (cm⁻¹): 3221 m ν(O–H), 3123 w, 3060 w νν(C–H), 1656m ν(O–H), 1564m, 1524w, 1509w ν(C–C, C–N), 1074 s ν(ClO₄). ¹H NMR (CDCl₃, 293 K): δ 1.67 (s, 15H, CH₃ Cp^{*}), 6.74 (t, 1H, H4 pz), 6.80–7.18 (m, 5H, Ph), 7.91 (d, 1H, H5 pz), 7.95 (d, 1H, H3 pz), 11.20 (br, 1H, H-OB), 12.0 (br, 1H, H-OB). ¹³C NMR (CDCl₃, 293 K): δ 9.0 (s, CH₃ Cp^{*}), 97.3 (d, C Cp^{*}, $J(^{103}Rh^{-13}C) = 7.8$ Hz), 111.5 (s, C4 pz), 123.5, 128.2, 136.0 (s, Ph), 131.3 (s, C5 pz), 143.4 (s, C3 pz). Λ_M (CH₃CN, 10⁻³ M): 134.6 Ω⁻¹ cm² mol⁻¹.

 $[lr(Cp^*)(Ph_2Bp)Cl]$ (4). To a dichloromethane solution (10 mL) of [Cp*IrCl₂]₂ (0.398 g, 0.50 mmol) was added K[Ph₂Bp] (0.338 g, 1.00 mmol) at -10 °C. The mixture was stirred for 1 h, while the temperature was raised to 0 °C, and then was filtered to remove KCl. The solution was dried under vacuum, and the orange residue obtained was recrystallized from 1 1 CH₂Cl₂/light petroleum (40-60 °C) and shown to be compound 4 (0.541 g, 0.800 mmol, yield 80%). Anal. Calcd for C₂₉H₃₄BClN₄Ir: C, 51.44; H, 5.06; N, 8.27. Found: C, 51.33; H, 5.00; N, 8.12. IR (cm⁻¹): 3194 w, 3116 w, 3056 w, 1602 m, 1566 m, 1543 w ν (C \div C, C \div N). ¹H NMR (CDCl₃, 293 K): δ 1.78 (s, 15H, CH₃ Cp*), 6.78-6.95 (m, 6H, Ph and H4 pz), 7.04 (m, 2H, Ph), 7.09 (d, 2H, H5 pz), 7.28 (m, 4H, Ph), 7.88 (d, 2H, H3 pz). ¹³C NMR (CDCl₃, 293 K): δ 8.7 (s, CH₃ Cp*), 88.6 (s, C Cp*), 104.16 (s, C4 pz), 122.2, 126.5, 127.5, 127.9, 128.2 (s, Ph), 137.3 (s, C5 pz), 139.1 (s, C3 pz). $\Lambda_{\rm m}$ (CH₃CN, 10⁻³ M): 1.2 Ω^{-1} cm² mol⁻¹. After 1 h the conductivity of the CH_3CN solution increases to 16.1 $\Omega^{-1}\mbox{ cm}^2\mbox{ mol}^{-1}.$ After 1 day the conductivity of the acetonitrile solution reaches the value 65.5 Ω^{-1} cm² mol⁻¹

[lr(Cp*){(pz)(OH)BPh₂(pzH)}]Cl (5). To a stirred acetonitrile solution (20 mL) of $[\bar{C}p*IrCl_2]_2$ (0.398 g, 0.5 mmol) was added 0.338 g (1.0 mmol) of K[Ph₂Bp]. The red solution was stirred for 10 min, giving an orange solution, and the solvent was then removed under reduced pressure. The resulting orange solid was vigorously stirred with 20 mL of chloroform at room temperature for 1 h and then the solution was slowly evaporated. Yellow-orange crystals of 5 were obtained in 15% yield. Anal. Calcd for C32H44BClIrN4O: C, 51.99; H, 6.00; N, 7.58. Found: C, 52.11; H, 5.89; N, 7.40. IR (cm⁻¹): 3200 br ν (O–H), 3123 w, 3060 w ν (C–H), 1641 m ν (O–H), 1597 w, 1567 w ν(C⁻⁻C, C⁻⁻N). ¹H NMR (CDCl₃, 293 K): δ 1.55 (s, 15H, CH₃ Cp*), 2.60 (br, 1H, H-OB), 6.37 (t, 1H, H4 pzH), 6.40 (t, 1H, H4 pz), 6.70-7.10 (m, 6H, Ph), 7.20-7.45 (m, 4H, Ph), 7.60 (d, 1H, H5 pzH), 7.79 (d, 1H, H5 pz), 7.85 (d, 1H, H3 pzH), 8.02 (d, 1H, H3 pz).¹³C NMR (CDCl₃, 293 K): δ 9.3 (s, CH₃ Cp*), 87.7 (s, C Cp*), 106.6 (C4 pz), 122.2, 127.2, 128.3, 133.2, 139.7 (s, Ph), 137.5 (s, C5 pz), 141.8 (s, C3 pz). $\Lambda_{\rm m}$ (CH₃CN, 10⁻³ M): 126.1 Ω^{-1} cm² mol⁻¹.

X-ray Crystallography. The X-ray intensity data for 1.H₂O, 2, 3, and 5 were measured on a Bruker SMART Apex II diffractometer equipped with a CCD area detector using a graphite-monochromated Mo K α radiation source (λ = 0.71073 Å). Čell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by $0.3^{\circ} \omega$ steps. The software SMART¹² was used for collecting frames of data, indexing reflections, and determination of lattice parameters. The collected frames were then processed for integration by SAINT¹² software, and an empirical absorption correction was applied with SADABS.¹³ The structures were solved by direct methods (SIR 97)¹⁴ and subsequent Fourier syntheses and refined by full-matrix leastsquares calculations on \dot{F}^2 (SHELXTL),¹⁵ attributing anisotropic thermal parameters to the non-hydrogen atoms. All hydrogen atoms were located in the Fourier map. The aromatic and methyl hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters $U(H) = 1.2[U_{eq}(C)]$ or $U(H) = 1.3[U_{eq}(C)]$, respectively, and allowed to ride on their carrier carbons, whereas the hydroxy H atoms in 2, 3, and 5 were located in the Fourier map and refined isotropically $(U(H) = 1.2[U_{eq}(O)])$. Complex 1·H₂O was found to crystallize with one water molecule of crystallization. In 3 three oxygens of the ClO_4^- were found to be disordered over two positions with occupation factors of 0.57 and 0.43% for the major and



minor components, respectively. Crystal data and details of the data collection for $1 \cdot H_2O$, 2, 3, and 5 are reported in Table S1 (Supporting Information) and relevant bond distances and angles in Table S2 (Supporting Information).

Computational Details. The B3LYP exchange-correlation functional,¹⁶ as implemented in the GAUSSIAN03 program package,¹⁷ is used for all DFT calculations. All geometry optimizations have been performed in vacuo and in solution with a LANL2DZ basis set for all atoms, along with a LANL 2^{18-21} pseudopotential for Rh and Ir centers. Solvation effects and solution free energies are evaluated from a single-point energy calculation with the 6-31G^{*22} basis set for C, H, B, N, and O atoms and LANL2DZ for Rh and Ir centers, by the conductor-like polarizable continuum model (C-PCM)²³⁻²⁸ on the geometries optimized in solution. As in the experimental conditions, calculations in solution were performed in acetonitrile. Vibrational frequency analysis was performed on the geometries optimized in vacuo. The evaluation of Gibbs free energy was calculated by following a procedure similar to that employed for the evaluation of absolute pK_a 's.²⁹⁻³¹ Following a thermodynamic cycle, the Gibbs free energy in solution of species i (G_{solv}^i) is defined as $G_{solv}^i = G_{vac}^i + \Delta G_{solv}$, where $G_{
m vac}^{
m i}$ is the free energy of the species in vacuo and $\Delta G_{
m solv}$ is the free energy of salvation. G_{vac}^{i} is computed at the geometry optimized in vacuo, followed by frequency calculations to take into account the vibrational contribution to the total partition function. The translational and rotation contributions were evaluated by standard statistical mechanics (particle in a box and rigid rotor models). ΔG_{solv} was directly calculated by a C-PCM single-point calculation together with a reference calculation in vacuo.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of **Complexes.** The compound $[Rh(Cp^*)(Ph_2Bp)Cl]$ (1; Cp* = C_5Me_5) is readily obtained from a 1:1 interaction of the potassium salt of ligand K[Ph₂Bp] with the dimer [Rh(Cp*)-Cl₂]₂ in anhydrous dichloromethane, under an atmosphere of N_2 (Scheme 1). The complex is air stable in the solid state but sensitive to moisture in chlorinated solution. However, under an inert atmosphere the solution is indefinitely stable. NMR data for 1 suggest an η^5 -Cp* coordination due to a doublet observed in the ¹³C{¹H} NMR spectrum at δ 95.6 (¹J(C-Rh) = 7.9 Hz). The nonelectrolytic nature of 1 has been confirmed by conductivity measurements in acetonitrile; however, on prolonged standing of the solution in contact with air, a progressive increase of conductivity has been observed, in accordance with partial displacement of chloride from Rh and substitution with acetonitrile or water from moisture.

When the same reaction was carried out for longer periods under non-anhydrous conditions by using acetonitrile as solvent, the complex $[Rh(Cp^*)(Ph){\kappa^2-(pz)(OH)BPh_2}]$ (2) was obtained, where the chelating ligand bears one hydroxyl group in place of one pyrazolyl ring and, unexpectedly, a phenyl group is directly bonded to the metal center (Scheme 1).

The source of Ph is the decomposition of a second molecule of the Ph₂Bp ligand. Accordingly, the yield of **2** is only 40%. In solution an additional amount of not clearly identifiable byproducts based on pz and OH is found. In the ¹H NMR spectrum of **2** the resonance due to the hydroxyl group bonded to the boron atom appears at δ 3.40. The signals due to the phenyl group directly bonded to Rh and those on B fall in the ranges 6.80–7.08 and 7.17–7.24 ppm.

To further develop the potential reactivity of $[Rh(Cp^*)-(Ph_2B)Cl]$ (1), containing the chelating coordinated Ph_2Bp , we have performed the reaction of 1 with $AgClO_4$ in acetonitrile: a colorless precipitate immediately appeared, which was filtered off and shown to be AgCl. From evaporation under vacuum of the clear orange solution a residue was obtained and shown to be the ionic $[Rh(Cp^*)(Ph)\{\kappa^2-(pz)(OH)B(OH)\}]ClO_4$ (3). 3 is a very unusual borane complex, in which the rhodium bears a phenyl ring and is coordinated by a pyrazolyl and a hydroxyl group from the pzB(OH)₂ ligand, clearly formed in situ during the reaction (Scheme 2), through both B–N and B–C breaking.



We can reasonably hypothesize that the origin of Ph and of $pzB(OH)_2$ coordinated to 3 is due to the presence of the Lewis acidic reagent AgClO₄ and to water traces within the reaction mixture. The IR spectrum of 3 shows absorptions at 3221 and 1737 cm⁻¹ due to ν (O–H) and γ (O–H) modes and typical strong absorptions due to ClO₄ in the anionic form centered at 1074 cm^{-1.32} The ionic nature of 3 has also been confirmed by

conductivity measurements in acetonitrile that give a value typical of 1:1 electrolytes. The ¹H NMR spectrum of **3** shows resonances due to Ph bonded to the Rh atom in the range 6.80–7.18 ppm, whereas the two hydroxyl groups on the boron atom are magnetically different and afford two resonances of equal intensity at 11.20 and 12.00 ppm. Tricoordinate borane species are in general strong Lewis acids, requiring the donation of an extra electron pair to complete the octet of valence electrons. The relevant fact that boron in **3** maintains a trigonal-planar sp² hybridization seems to indicate a weak Lewis acidity of the borane moiety. In the literature only a report on an analogous free borane has been found,³³ in which however the pyrazole is C-bonded to boron (Scheme 3).





C-bonded pyrazolyl dihydroxoborane N-bonded pyrazolyl dihydroxoborane

In order to give further insight into the possible catalytic role of rhodium in the degradation of the starting $(Ph_2Bpz_2)^$ ligand, we have extended our studies toward analogous iridium(III) compounds. By interaction of $[Ir(Cp^*)Cl_2]_2$ with $K[Ph_{2}Bp]$ under the same reaction conditions employed for 1, the compound $[Ir(Cp^*)(Ph_2Bp)Cl]$ (4) was obtained (Scheme 4). This derivative is sufficiently air-stable in the solid state but is sensitive to moisture in chlorinated solution. The spectroscopic data are in accordance with the proposed formulation and need no further comment. However, when the same reaction was carried out for longer periods under nonanhydrous conditions by using acetonitrile as solvent, the different compound $[Ir(Cp^*){\kappa^2-(pz)(OH)BPh_2(pzH)}]Cl$ (5) was isolated, containing the same chelating $(pz)(OH)BPh_2$ ligand previously found in derivative 2. However, in 5 the Ir coordination sphere is completed by a neutral pyrazole (Scheme 4). The derivative is a 1:1 electrolyte in acetonitrile, and the ¹H NMR spectrum shows two different sets of pz rings, thus confirming the presence of a neutral pyrazole bonded to Ir.

Scheme 4

Such evidence further supports our previous hypothesis on the starting Ph_2Bp ligand as the source of Ph in 2 and Hpz in 5 and on the catalytic role of d^8 Rh(III) and Ir(III) centers on the decomposition pattern of the starting Ph_2Bp ligand.

It is worth noting that different decomposition mechanisms of the Ph_2Bp ligand occurred, depending on the coordinated metal: a Ph is in fact captured by Rh during decomposition of $(Ph_2Bpz_2)^-$ with formation of derivative 3, whereas a neutral pzH is bonded to Ir in derivative 5. A reasonable mechanistic hypothesis is proposed in Scheme 5, where the species isolated and characterized are depicted in black and those hypothesized are given in blue.

The presence of traces of moisture in the acetonitrile reaction mixture can afford steps $A \rightarrow B \rightarrow C \rightarrow D$, and the last species has been isolated for M = Ir (derivative 5). A proof of this decomposition path has been the isolation of 5 also from an acetonitrile solution of 4 after standing in the atmosphere for 1 day. The additional step $D \rightarrow E$ seems favored for M = Rh, as confirmed by the isolation of derivative 2. 2 can be recovered also from an acetonitrile solution of 1 after 24 h. Step $D \rightarrow E$ requires attack of a phenyl arising from a side-decomposition reaction of the starting Ph_2Bp ligand through B-C hydrolysis. The final step $E \rightarrow F$ seems reasonable on the basis of the fact that the same cationic species with M = Rh (derivative 3) has been obtained by a metathesis reaction in acetonitrile between 1 and AgClO₄.

The X-ray molecular structures of $1 \cdot H_2O$, 2, 3, and 5 are shown in Figures 1-4, and relevant bond lengths and angles are reported in the captions of Figures 1-4, respectively. In the four structures the coordination geometry around the central metal atom is of the three-legged piano-stool type. The complex 1·H₂O (Figure 1) was found to crystallize with one crystallization water molecule coming from humidity traces present in the dichloromethane/light petroleum mixture. In 1·H₂O only a half-molecule is present in the asymmetric unit because of the presence of a crystallographically imposed mirror plane passing through rhodium, chlorine, and boron atoms and one phenyl group of the diphenylbis(pyrazolyl)borate ligand and bisecting the Cp* ring and the second phenyl ring of the pz₂BPh₂ ligand. The coordination geometry at the rhodium atom is pseudo-octahedral and is similar to that found in the ruthenium complex $[Ru(\eta^6-p-cymene)(\kappa^2-Ph_2Bp)Cl]$,³⁴ from which it differs in the presence of a Cp* ring in place of the η^6 -p-cymene. The Rh-Cl distance of 2.423(2) Å is very



Scheme 5



close to that found in the related complex RhCp*Tp*Cl (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) (2.429(1) Å).⁷ The average Rh–C(Cp*) distance is 2.154 Å, and the Rh– centroid(Cp*) distance is 1.80 Å. The water molecule of crystallization whose hydrogen atoms were not located establishes a weak nonclassical H bond (O1w···HC = 2.61 Å) with one H atom of a phenyl ring.

The molecular structure of complex 2 is shown in Figure 2. The coordination geometry around the Rh atom is pseudooctahedral, with the Rh atom coordinated by an η^5 -Cp* ring, an η^1 phenyl ring, and a chelate B(OH)(pz)Ph₂ ligand. The most interesting feature of 2 resides in the uncommon B(OH)(pz)-Ph₂ ligand that has been found, for example, in a pseudooctahedral W complex¹⁰ where the metal atom is in addition coordinated by two CO ligands and by an η^3 -pyrazolyl-3penten-2-yl ligand showing a further interaction with the metal through a pyrazole nitrogen. The N(1)-Rh-O(1) bite angle, as expected for a five-membered metallacycle, is narrower $(78.1(1)^{\circ})$ than the N(1)-Rh-N(1') bite angle in 1 $(86.1(2)^{\circ})$, in which a six-membered metallacycle adopts a boat conformation, and similar to that observed in 3 (see below) for the analogous O(6)-Rh-N(1) bite angle $(75.8(2)^{\circ})$. The Rh-C(Cp*) average distance is 2.190 Å, and the Rh-centroid distance is 1.83 Å, whereas the Rh-C(4)(phenyl) distance of 2.028(3) Å falls in the range observed for similar σ bonds and is almost identical with that found in 3 of 2.037(4) Å (see below). The Rh-O(1) distance (2.157(2)

Å) is longer than that found in the rhodium boronate complex ${\rm Rh}({\rm PEt}_3)_3[{\rm OB}({\rm OH})(p{-}{\rm tolyl})]$ ³⁵ ${\rm (Rh-O(1) = 2.102(2) Å)}$.

The molecular structure of 3 is shown in Figure 3. The cation differs from 2 mainly in the nature of the $B(OH)_2pz$ ligand, which is κ^2 coordinated to the metal through the N(1) and O(1) atoms. The resulting five-membered metallacycle Rh–N(1)–N(2)–B–O(1) is approximately flat, the boron atom being tricoordinate. The coordination at the Rh atom is completed by a σ -bonded phenyl ring (Rh–C(phenyl) = 2.037(4) Å) and by an η^5 -Cp* ring (average Rh–C(Cp*) distance 2.177 Å, Rh–centroid distance 1.81 Å). The Rh–O(1) distance of 2.096(4) Å is shorter than the analogous bond in 2. One oxygen of the perchlorate anion interacts with the hydrogen of the hydroxy group coordinated to the metal (O(3)…O(1) = 2.963(7) Å, O(3)…H(11)–O(1) = 168(4)°).

The molecular structure of **5** is shown in Figure 4, and relevant bond lengths and angles are reported in the figure caption. In **5** the iridium atom achieves an octahedral geometry, being coordinated by the B(OH)(pz)Ph₂ ligand, an η^5 -Cp* ring, and a terminally bound pyrazole ring. The N(1)–Ir–O(1) bite angle of the five-membered metallacycle (75.4(2)°) is similar to those already reported for complexes **2** and **3**. The Ir–O(1) and Ir–N(1) distances in the chelate ligand are 2.109(4) and 2.076(5) Å, respectively, and the Ir–N(3) bond length, in which the pyrazole ring is involved, is slightly longer (2.107(3) Å) than the other Ir–N bond. The Ir–centroid distance of 1.77 Å is shorter than the analogous distances

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Figure 1. Molecular structure of $1 \cdot H_2O$ with the atom-numbering scheme. Selected bond lengths (Å) and angles (deg) for 1: Rh–Cl, 2.423(2); Rh–N(1), 2.089(4); Rh–C(14), 2.16(1); Rh–C(15), 2.157(6); Rh–C(16), 2.148(5); N(1)–Rh–N(1'), 86.1(2); N(1)–Rh–Cl, 87.1(2) (symmetry code (I): *x*, -y + 0.5, *z*).



Figure 2. Molecular structure of 2 with the atom-numbering scheme. Selected bond lengths (Å) and angles (deg) for 2: Rh–N(1), 2.077(2); Rh–C(4), 2.028(3); Rh–O(1), 2.157(2); N(1)–Rh–O(1), 78.6(1); Rh–C(22), 2.262(3); Rh–C(23), 2.270(3); Rh–C(24), 2.119(3); Rh–C(25), 2.151(3); Rh–C(26), 2.148(3); N(1)–Rh–O(1), 78.6(1); C(4)–Rh–O(1), 86.0(1); N(1)–Rh–C(4), 91.2(1).

observed in the rhodium complexes. There are interactions between the chloride anion the hydrogen of the hydroxy group bound to Ir and the nitrogen-bound H atom of the pyrazole



Figure 3. Molecular structure of 3 with the atom-numbering scheme. Dotted purple lines indicate the O–H···O(perchlorate) interaction. Selected bond lengths (Å) and angles (deg) for 3: Rh–N(1), 2.069(4); Rh–C(14), 2.037(4); Rh–O(1), 2.096(4); Rh–C(4), 2.137(5); Rh–C(5), 2.180(5); Rh–C(6), 2.146(5); Rh–C(7), 2.217(6); Rh–C(8), 2.205(5); N(1)–Rh–O(6), 75.8(2); N(1)–Rh–C(14), 87.7(2); C(14)–Rh–O(6), 87.8(2).

0(6)



Figure 4. Molecular structure of 5 with the atom-numbering scheme. Dotted purple lines indicate the O–H···Cl and N–H···Cl interactions. Selected bond lengths (Å) and angles (deg) for 5: Ir–N(1), 2.076(5); Ir–O(1), 2.109(4); Ir–N(3), 2.107(5); Ir–C(19), 2.155(7); Ir–C(20), 2.149(6); Ir–C(21), 2.133(7); Ir–C(22), 2.144(7); Ir–C(23), 2.169(6); N(1)–Ir–O(1), 75.4(2); N(3)–Ir–O(1), 84.9(2); N(3)–Ir–N(1), 86.5(2).

ring $(Cl\cdots H(10) - O(1) = 168(5)^{\circ}, Cl\cdots O(1) = 2.987(4)$ Å, N(4)-H(4N)...Cl = 170(5)^{\circ}, N(4)...Cl = 3.170(6) Å).

DFT Calculations. We have undertaken DFT calculations to investigate the competitive reaction products 2 and 5 considering both Rh and Ir metal centers. We simulated four different minima: 2-Rh and 5-Ir, shown in Figure 5, and the



Figure 5. Optimized geometry structures of 2-Rh and 5-Ir complexes.

Table 1. Main Atomic Distances in	Å of 2-Rh, 2-Ir, 5-Rh, and 5-Ir Com	plexes Calculated in Vacuo and in Solution ^a
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	Rh				Ir					
	2			5		2		5		
distance	vac	solv	exptl	vac	solv	vac	solv	vac	solv	exptl
M-C1	2.039	2.041	2.028			2.054	2.054			
M-N3				2.121	2.106		2.300	2.098	2.088	2.108
M-N1	2.075	2.079	2.077	2.085	2.072	2.065	2.064	2.076	2.070	2.077
М-Ср	2.318	2.318	2.190	2.262	2.247	2.281	2.301	2.256	2.259	2.150
М-О	2.155	2.178	2.157	2.143	2.162	2.165	2.182	2.148	2.144	2.109
В-О	1.553	1.547		1.571	1.544	1.558	1.553	1.576	1.551	
B-N2	1.592	1.589		1.599	1.592	1.588	1.584	1.596	1.588	
B-C2	1.615	1.619		1.608	1.620	1.613	1.617	1.607	1.620	
B-C3	1.622	1.627		1.614	1.621	1.620	1.626	1.613	1.621	
M-Cp is the	e average dis	tance betweer	n the metal at	om and the f	five carbon at	oms of the pe	entamethylcyc	lopentadienyl	moiety.	

corresponding 2-Ir and 5-Rh species. The main geometrical parameters optimized in vacuo and in solution are reported in Table 1, where they are compared to available X-ray data for 2-Rh. From the calculation of the Gibbs free energy associated with all the species involved in the process from D to E shown in Scheme 5 (except the Cl⁻ ion), we are able to evaluate the different stability of 5 compared to that of 2 for Rh $(\Delta G_{5,2}[Rh])$ and for the corresponding Ir complexes $(\Delta G_{5-2}[Ir])$. $\Delta G_{5-2}[M]$ is calculated by evaluating the Gibbs free energy difference of the reaction from D to E reported in Scheme 5, considering M = Rh for $\Delta G_{5-2}[Rh]$ and M = Ir for $\Delta G_{5,2}$ [Ir], respectively. From the difference of energy differences $\Delta G_{5,2}[Ir] - \Delta G_{5,2}[Rh]$ we can estimate the relative thermodynamic stabilization of species 5-M with respect to species 2-M when moving from M = Rh to M = Ir. Our calculations provide a value of 1.2 kcal/mol for the $\Delta G_{5,2}[Ir]$ – $\Delta G_{5-2}[Rh]$ difference, indicating that species 5 is more stable than species 2 when the metal is iridium in comparison to rhodium, in line with the experimental evidence. This is due to the different solvation energy (ΔG_{solv}) of the species involved in the reaction. In particular, while ΔG_{solv} of **2-Ir** is 0.8 kcal/mol higher than ΔG_{solv} of **2-Rh**, ΔG_{solv} of **5-Ir** is 2.1 kcal/mol lower than ΔG_{solv} of **5-Rh**, confirming a greater stabilization in solution for the **5-Ir** species.

CONCLUSIONS

Novel Rh(III) and Ir(III) pentamethylcyclopentadienyl compounds 1 and 4 ,containing the diphenylbis(pyrazolyl)borate ligand, have been isolated from dichloromethane under anhydrous conditions. In contrast, by using acetonitrile as solvent and non-anhydrous conditions B-N bond hydrolysis occurs in the ligand Ph2Bp and unusual neutral and ionic species are obtained. In detail, rhodium and iridium have been found to be coordinated by the hydroxy(pyrazolylborate) ligand $B(OH)(pz)Ph_2$. The coordination sphere of the Ir derivative is completed by a neutral pyrazole, whereas the rhodium complex contains an η^1 -phenyl. An uncommon $B(OH)_2(pz)$ ligand κ^2 coordinated to rhodium has instead been found in compound 3, the boron atom being only tricoordinate. To give insight into the formation of these unusual species, we have proposed a mechanism for a decomposition pathway of the diphenylbis(pyrazolyl)borate ligand coordinated to the metal, involving substitution of the chloride with water in the metal environment, followed by B-N hydrolysis and pyrazole replacement by a OH to boron. Additionally, for Rh also B–C activation and phenyl elimination occurs, which in contrast is not suitable for the Ir intermediate, due to a thermodynamic stabilization, as confirmed by DFT calculations.

ASSOCIATED CONTENT

S Supporting Information

CIF files and a table giving crystallographic data for 1-3 and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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