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Rational Design of a Novel Mononuclear Rhodium(II) Complex

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Summary: Reaction of rhodium(I) with a multidentate hemilabile bisphosphine ligand yields a two-legged piano-stool complex whose steric and electronic factors stabilize rhodium(II) upon chemical oxidation. The inherent stabilizing properties of the ligand system allow for the first structural isolation of a novel mononuclear organometallic rhodium(II) complex in a two-legged piano-stool geometry.

Compared to Rh(I) and Rh(III) compounds, there are a small number of mononuclear Rh(II) complexes, and of these complexes only a few contain Rh−C bonds.[1,2] Although monometallic Rh(II) compounds often are observed as transient species in solution, some have been isolated as stable solids and, in a few cases, have been characterized by X-ray crystallography. The monomers that have been characterized by single-crystal X-ray diffraction analyses fall into four categories with respect to coordination geometry: square-planar, octahedral, trigonal bipyramidal, and sandwich complexes.[1a,3] The typical ligand environment for these complexes consists of sterically demanding phosphine, polypyridyl, and aryl moieties, which are believed to inhibit dimerization. Herein, we report the systematic design, synthesis, characterization, and isolation of the first example of a mononuclear organometallic Rh(II) complex in an η^6-arene two-legged piano-stool geometry.

Several years ago, our group identified rhodium(I) bisphosphine η^6-arene complexes that exhibited reversible Rh(I/II) redox couples (Figure 1A). It was observed that slight adjustments to the ligand affected the kinetic and thermodynamic stability of the Rh(II) oxidation state. As a result, a series of bisphosphine complexes were synthesized to test the ligand features that increase the stability of Rh(II) in these types of complexes (**1**−**4**; Figure 1A). When the electronic and steric properties of the arene and the connectivity of the phosphine moieties were systematically varied, the kinetic and thermodynamic stability factors were determined. The

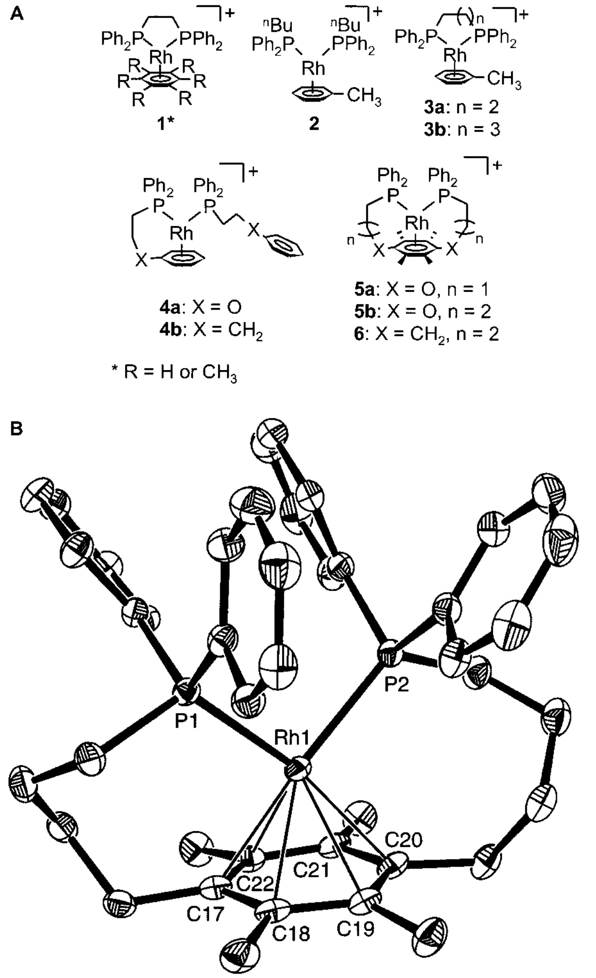

Figure 1. (A) Rhodium(I) two-legged piano-stool complexes **1**−**6**. (B) ORTEP diagram of the Rh(II) complex **6**$^+$. Thermal ellipsoids are shown at 30% probability, and counterions, hydrogen atoms, and lattice solvent are omitted for clarity.

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first set of complexes examined the electron density and steric bulk associated with the pendant arene (**1**; Figure 1A). This study concluded that the addition of methyl substituents on the arene ring kinetically and thermodynamically stabilizes the Rh(II) state due to the increased steric bulk and electron richness of the arene; indeed, a 16 mV/CH_3 decrease in $E_{1/2}$ value upon addition of methyl groups in **1** was observed for the six complexes studied.

The next group of complexes (**2**−**4**, Figure 1A) focused on the importance of phosphine connectivity in the stabilization of Rh(II) in the two-legged piano-stool geometry. The complexes studied all possess tolyl-like aromatic groups differing only in their phosphine connectivity: phosphine chelation, chelate arm length, and tethering of the phosphine group to the arene ring. Complex **2**, with nonchelated phosphines, shows the highest degree of thermodynamic stability, as evidenced by its $E_{1/2}$ value of 505 mV (130 mV lower than for the tolyl version of **1**). The increase in thermodynamic stability is attributed to the complex's ability to accommodate structural changes, namely the widening of the P−Rh−P angle and the lengthening of the Rh−P bond distances, upon oxidation.[4,5] Although thermodynamic stability is gained in **2**, no kinetic stability is obtained, due to the lack of steric bulk about the Rh center. However, kinetic stability is gained by tethering the phosphine group to the arene through an alkyl chain as in **4**. Although several factors that contribute to stabilizing Rh(II) in this coordination geometry were identified through these studies, an isolable form of a mononuclear Rh(II) complex was never achieved.

Taken together, these data suggest that the ideal coordination environment for mononuclear Rh(II) with a two-legged piano-stool geometry would consist of a symmetrical arene ligand with two tethered phosphine moieties, where the arene is sterically protected with electron-donating alkyl moieties and the tethers are long enough to accompany structural changes upon complex oxidation. Herein, we report a study involving three complexes (**5a**, **b** and **6**) that allow us to evaluate this hypothesis. Compound **5a** has been previously reported, and **5b** and **6** were prepared from 1,4-bis(3-(diphenylphosphino)propoxy)-2,3,5,6-tetramethylbenzene and 1,4-bis(4-(diphenylphosphino)butyl)-2,3,5,6-tetramethylbenzene via extensions of literature procedures for forming mononuclear Rh(I) two-legged piano-stool complexes (see the Supporting Information).[6,7,8]

Complexes **5a** ($E_{1/2} = 560$ mV) and **5b** ($E_{1/2} = 530$ mV) exhibit single, one-electron oxidation waves that were completely reversible at all scan rates studied (1 mV/s to 1 V/s). The decrease in $E_{1/2}$ in going from **5a** to **5b** shows that the lengthening of the chelating arms by one methylene unit results in increased thermodynamic stability, presumably due to the increased ability of compound **5b** to accommodate changes in Rh−P bond length and P−Rh−P bond angle upon electrochemical oxidation to the Rh(II) complex.

Unlike the Rh(II) complexes studied prior to this work,[4] which were observed as transient species in solution, **5b** was chemically oxidized to its Rh(II) form, **5b**$^+$, with $AgBF_4$ ($E_{1/2} = 650$ mV/s vs Fc/Fc$^+$ in CH_2Cl_2) and isolated as a red-brown solid in 94% yield. Compound **5b**$^+$ has been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and EPR spectroscopy. Consistent with the formation of a paramagnetic Rh(II) compound, ^1H and $^{31}P\{^1H\}$ NMR spectra of **5b**$^+$ are broad and almost featureless. In addition, the paramagnetic d^7 Rh(II) metal center of **5b**$^+$ was characterized by EPR spectroscopy in 19:1 CD_2Cl_2/$CDCl_3$ as a glass at 77 K ($g_1 = 2.390$, $g_2 = 2.038$, $g_3 = 1.997$) and as a fluid solution at room temp ($g_{av} = 2.11$).

Although complex **5b**$^+$ has increased kinetic and thermodynamic stability, we were unable to characterize it by a single-crystal X-ray diffraction analysis; during crystal growth, disproportionation occurred, resulting in the formation of **5b** and unidentified products. Previous studies showed that replacing the ether groups in **4a** with methylene units, **4b**, resulted in a significant increase in thermodynamic stability of the resulting Rh(II) complex, as evidenced by the decrease in $E_{1/2}$ (**4a**, 573 mV; **4b**, 515 mV).[4] With this in mind, complex **6** was designed, where the electron-withdrawing O atoms in the chelating ligand were replaced with methylene units. Complex **6** has been characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and cyclic voltammetry, in the gas phase by mass spectrometry, and in the solid state by single-

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(6) Synthesis of 1,4-bis[4-(diphenylphosphino)butyl]-2,3,5,6-tetramethylbenzene: A flask equipped with a condenser was charged with diiododurene (1.0 g, 2.6 mmol) and $Pd(PPh_3)_4$ (0.45 g, 15 mol %). An excess of a 0.5 M THF solution of 4-chlorobutyl zinc bromide (∼20 mL) was added to the reaction mixture, and the mixture was refluxed at 80 °C for 12 h under a nitrogen bubbler. The product was isolated after the mixture was charged with NH_4Cl(aq) (20 mL), extracted with Et_2O, followed by column chromatography. The chloro precursor (100 mg, 0.318 mmol) was then reacted with a THF solution of $KPPh_2$ (0.5 M, 1.3 mL, 0.653 mmol) for 2 h. Pure ligand was obtained following extraction, filtration through Celite, and recrystallization from ethanol. ^1H NMR (CD_2Cl_2): δ 1.65 (m, PCH_2CH_2 and $PCH_2CH_2CH_2$, 8H), 2.17 (m, PCH_2, 4H), 2.25 (s, $C_6(CH_3)_4$, 12H), 2.69 (m, $CH_2C_6(CH_3)_4$, 4H), 7.39−7.49 (m, $P(C_6H_5)_2$, 20H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 16.6 (s, $C_6(CH_3)_4$), 26.6 (d, $J_{C-P} = 12.5$ Hz, PCH_2CH_2), 27.9 (d, $J_{C-P} = 9.1$ Hz, $PCH_2CH_2CH_2$), 30.6 (s, $CH_2(C_6(CH_3)_4)$, 31.4 (d, $J_{C-P} = 10.2$ Hz, PCH_2), 128.5 (s, $P(C_p(CH_3)_4)$, 128.6 (d, $J_{C-P} = 3.66$ Hz, $P(C_{6m}(CH_3)_4)$, 132.1 (s, $C_{6o}(CH_3)_4)$, 132.7 (d, $J_{C-P} = 14.58$, $P(C_{6o}(CH_3)_4)$, 136.7 (s, $C_{6i}(CH_3)_4)$, 138.9 (d, $J_{C-P} = 10.2$, $P(C_{6i}(CH_3)_4)$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −15.3 (s). HRMS (EI): *m*/*z* calcd 614.323 12, found 614.323 04. Anal. Calcd for $C_{42}H_{48}P_2$: C, 82.05; H, 7.87; P, 10.08. Found: C, 79.49; H, 7.84; P, 10.06. For **5b**, a solution of 1,4-bis(3-(diphenylphosphino)propoxy)-2,3,5,6-tetramethylbenzene (68.6 mg, 0.111 mmol) in 125 mL of THF was added dropwise at −78 °C to a THF solution of $[Rh(THF)_2(COE)_2]B(C_6F_5)_4$ (see the Supporting Information) over 2 h. The solution was warmed to room temperature over 1 h followed by reflux for 3 days. Upon removal of solvent, layering a CH_2Cl_2 solution of **5b** with Et_2O afforded pure **5b** (57%, 0.088 g). Recrystallization from CH_2Cl_2/C_6H_6 yielded thin red blades of **5b** that were characterized by X-ray crystallography. ^1H NMR (CD_2Cl_2): δ 1.38−1.50 (bm, 4H, $CH_2CH_2CH_2$), 2.35−2.42 (bm, 4H, CH_2P), 2.55 (s, 12H, CH_3), 4.00 (t, 4H, CH_2O, $J_{H-H} = 5.7$ Hz), 7.05−7.20 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.1 (d, $J_{Rh-P} = 204$ Hz). MS (FAB$^+$): *m*/*z* [M]$^+$ calcd 721.1872, found 721.1879. Complex **6** was synthesized in a fashion similar to that for **5b** using $[Rh(THF)_2(COE)_2]PF_6$. Upon addition, the reaction was stirred for 4 h at 50 °C to yield an orange solid. Pure **6** was achieved by precipitation from CH_2Cl_2 with pentane. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of pentane into a saturated CH_2Cl_2 solution of **6** at room temperature. ^1H NMR (CD_2Cl_2): δ 1.665 (bm, $CH_2CH_2(C_6(CH_3)_4)$, 4H), 2.112 (bm, $P(C_6H_5)_2CH_2CH_2CH_2$, 8H), 2.202 (s, $C_6(CH_3)_4$, 12H), 2.700 (bm, $CH_2C_6(CH_3)_4$, 4H), 7.090−7.215 (m, $P(C_6H_5)_2$, 20H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28 (d, $J_{Rh-P} = 204$ Hz). ESMS: *m*/*z* [M]$^+$ calcd 717.22, found 717.2. Anal. Calcd for $C_{42}H_{48}F_6P_3Rh$: C, 58.48; H, 5.61. Found: C, 58.30; H, 5.74.

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crystal X-ray crystallography, and all data are fully consistent with its structural formulation (see Supporting Information).

Complex **6** exhibits a completely reversible wave at all measured scan rates (1 mV/s to 1V/s) with an $E_{1/2}$ value (410 mV vs Fc/Fc$^+$) substantially lower than **5b** and any of the 12 previously studied analogous complexes (505−635 mV). This is a reflection of the increased electron richness of the arene and the structural flexibility of the ligand, which allows the complex to adopt ideal bond lengths and angles upon oxidation. The bulk oxidation of **6** was carried out in a fashion similar to that for **5b**, using $AgPF_6$ as the chemical oxidant. Stirring complex **6** with 1 equiv of $AgPF_6$ in CH_2Cl_2 for 30 min followed by filtration to remove the Ag^0 precipitate resulted in the quantitative formation of **6**$^+$. Complex **6**$^+$ was characterized by ^{1}H and ^{31}P{^{1}H} NMR and EPR spectroscopy. Like **5b**$^+$, **6**$^+$ exhibited broad structureless features in the ^{1}H and ^{31}P{^{1}H} NMR spectra due to its paramagnetic nature. EPR spectroscopy of **6**$^+$ in a CH_2Cl_2 glass was taken at 77 K with $g_1 = 2.353$ and $g_{2,3} = 2.025$ and as a fluid solution with $g_{av} = 2.133$. Surprisingly, no rhodium hyperfine coupling was observed in either **5b**$^+$ or **6**$^+$. A detailed analysis of the differences in EPR and electronic structure will be discussed in a later publication.

Significantly, complex **6**$^+$ also has been characterized by a single-crystal X-ray diffraction analysis (Figure 1B).[10] Selected bond distances and angles are presented in Table 1. Comparing selected bond lengths and angles for **6** and **6**$^+$ allows one to identify some of the structural differences between the two oxidation states. The arene ring in **6** deviates from planarity by adopting a boat confirmation where the C atoms attached to the tethered chelate arms (C17 and C20) are pointed toward the rhodium(I) center. The average Rh−P distance, 2.250 Å, is consistent with **5a**, **b** and the three previously reported Rh(I) complexes in a two-legged piano-stool geometry (Rh−P = 2.217−2.264 Å).[4,9] Upon oxidation to form Rh(II), the arene ring flips so that the carbon atoms (C19 and C22) are pointed away from the rhodium(II) center. In addition to the change in orientation of the arene ring, there is significant shortening of three Rh−C bond distances. This is a reflection of the increased Lewis acidity of the Rh upon oxidation and the ability of the arene ligand to π-donate to the oxidized metal center. The average Rh−P distances lengthened from 2.250 Å to 2.342 Å, indicating a decrease in π back-bonding upon going from Rh(I) to Rh(II). The P−Rh−P angle does not change significantly between the two oxidation states, but it is markedly different from the analogous tetramethyl version of **1** with chelated phosphine groups (83.76°). The lack of change in this angle is attributed to the ligand adopting an optimized geometry in the reduced form of the complex.

Table 1. Selected Distances (Å) and Angles (deg) for Compounds 6 and 6$^+$

6		**6$^+$**	
Rh−P(1)	2.2514(9)	Rh−P(1)	2.3381(7)
Rh−P(2)	2.2501(10)	Rh−P(2)	2.3463(8)
Rh−C(1)	2.314(4)	Rh−C(17)	2.316(2)
Rh−C(5)	2.344(4)	Rh−C(18)	2.319(2)
Rh−C(6)	2.413(4)	Rh−C(19)	2.343(3)
Rh−C(4)	2.314(4)	Rh−C(20)	2.306(3)
Rh−C(2)	2.330(4)	Rh−C(21)	2.315(3)
Rh−C(3)	2.379(4)	Rh−C(22)	2.355(3)
Rh−arene	1.87	Rh−arene	1.84
P(1)−Rh−P(2)	94.89(4)	P(1)−Rh−P(2)	95.41(2)

In summary, this study addresses the factors that stabilize mononuclear Rh(II) in a new coordination environment, and it has allowed us to design and synthesize a series of ligands that indefinitely stabilize this unusual Rh oxidation state. Moreover, it has allowed us to characterize the structural parameters of one of these Rh(II) complexes for the first time, opening the opportunity to systematically study and identify the physical and chemical properties of this novel class of complexes.

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Supporting Information Available: Text giving experimental syntheses of new compounds, figures giving isotropic and anisotropic EPR spectra of **5b**$^+$ and **6**$^+$, and tables giving X-ray crystallographic data; the X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for $C_{44}H_{52}Cl_4F_{12}P_4Rh$ (**6**$^+$): monoclinic, $P2_1/n$, $a = 11.9371(18)$ Å, $b = 32.401(5)$ Å, $c = 12.782(2)$ Å, $\beta = 102.890(3)$°, $V = 4819.2(13)$ Å^3, $Z = 4$, $Z' = 1$, $T = 173(2)$ K, $D_{calcd} = 1.623$ g cm^{-3}, brown plate, Mo Kα = 0.710 71 Å, GOF = 1.103, full-matrix least squares on F^2, $R(F) = 4.45\%$ for 11 247 observed independent reflections ($4 \leq 2\theta \leq 56°$). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-173487 (**5b**), CCDC-175054 (**6**), and CCDC-173489 (**6**$^+$). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).