Inorg. Chem. **1999,** *38,* 2758−2759

Small Molecule-Induced Intramolecular Electron “Pitch and Catch” in a Rhodium^{I} Complex with Substitutionally Inert Redox-Active Ligands

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Received February 17, 1999

A major goal of our group has been to bridge the fields of inorganic coordination chemistry, ligand design, and electrochemistry by developing a class of hybrid multidentate redox-active hemilabile ligands (RHL) that provide electrochemical control over transition metal coordination environments.[1] When such ligands are bound to certain transition metals of interest, ligand-centered redox reactions can effect the opening and closing of coordination sites via a series of applied potentials. In this manuscript we report the synthesis, characterization, and reactivity of a Rh^{I} complex, *cis*-[Rh{Fe(C_5H_5)($C_5H_4SCH_2CH_2PPh_2$)}$_2$]BF_4 (**1a**), containing the novel substitutionally inert bidentate redox-active ligand Fe(C_5H_5)($C_5H_4SCH_2CH_2PPh_2$). As with RHLs, this ligand provides electrochemical control over the coordination environment of the Rh center but via an entirely different mechanism that involves a reversible small molecule-induced intramolecular two-electron transfer reaction. This unusual process provides valuable insight into the way one can design ligands which allow for the controlled uptake and release of small molecules at transition metal centers.

Compound **1a**[2] and model complexes *cis*-[Rh($RSCH_2CH_2PPh_2$)$_2$]BF_4 (**1b**, R = Ph;[3] **1c**, R = *p*-FC_6H_4; **1d**, R = *p*-$NO_2C_6H_4$) were prepared by treating [Rh(COE)$_2$Cl]$_2$[4] (COE = cyclooctene) with $AgBF_4$, followed by the appropriate ligands,[5] Scheme 1. Complexes **1a**−**d** were isolated as yellow air-sensitive solids and characterized by ^{1}H and ^{31}P NMR spectroscopy and FAB-HRMS, which are consistent with the proposed formulations. The ^{31}P{^{1}H} NMR spectra of **1a**−**d** exhibit the expected doublets between δ 63.3 and 66.5 (J_{Rh-P} = 161−163 Hz) indicative of five-membered chelates on Rh^{I},[6] Table 1.

Table 1. ^{31}P NMR and FT-IR Spectroscopic Data for **1**−**3**[a]

	1a	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**	**3a**
δ	63.3	63.4	64.2	66.5	45.0	49.2	49.5	47.2	37.9
J_{Rh-P}	163	162	161	162	111	103	101	111	108
ν_{CO}	−	−	−	−	2014 1966	2017 1972	2017 1972	2018 1980	−

[a] FT-IR spectra were recorded in CH_2Cl_2 at 25 °C, cm^{-1}; ^{31}P{^{1}H} NMR spectra were taken at 25 °C in CD_2Cl_2 for **1**−**2** and in CD_3CN for **3a** at 25 °C; coupling constants are in Hz (external ref 85% H_3PO_4).

To probe the general reactivity of **1a**−**d**, they were treated with small, potentially coordinating molecules such as CO and CH_3CN, Scheme 1. All reacted with the π acid, CO, to yield analogous five-coordinate **2a**−**d**,[7] but none reacted with the σ donor, CH_3CN, even when the complexes were dissolved in neat CD_3CN. For example, when a CH_2Cl_2 solution of **1a** was treated with CO (1 atm), the new complex [Rh{Fe(C_5H_5)($C_5H_4SCH_2CH_2PPh_2$)}$_2$(CO)]BF_4 (**2a**) formed quantitatively as determined by FT-IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy,[8] Table 1. The variable temperature ^{31}P{^{1}H} NMR and the room-temperature FT-IR spectra of **2a** show that it exists in solution as at least two five-coordinate isomers in dynamic equilibrium at room temperature (see Supporting Information for more detailed spectroscopic data). Note that **2b**−**d** exhibit similar spectra under comparable conditions, Table 1. Moreover, the CO ligands in **2a**−**d** can be removed in vacuo in the solid state to quantitatively reform **1a**−**d**.

A single crystal of one of the isomers was grown by layering a CH_2Cl_2 solution of **2b** with pentane under 1 atm of CO. An X-ray diffraction study of this crystal revealed a structure with slightly distorted square pyramidal geometry (inset, Scheme 1). To our knowledge, this is the first example of a crystallographically characterized square pyramidal Rh^{I} complex. The base of the pyramid in this complex is defined by P(1), P(2), S(2), and C(5) (maximum deviation 0.06 Å) with the line defined by Rh(1) and S(1) tilted by 19° from a line perpendicular to the base (see Supporting Information for further structural details).

The cyclic voltammogram of **1a** in CH_2Cl_2/0.1 M *n*-Bu_4NPF_6 exhibits two reversible waves ($E_{1/2}$ = +0.250 V, +0.435 V vs Fc/Fc$^+$), assigned to sequential oxidation of the Fe(C_5H_5)(C_5H_4) moieties and an irreversible wave (E_{pa} = +1.62 V vs Fc/Fc$^+$), assigned to Rh^{I} oxidation.[9] For comparison, the cyclic voltammogram of the model complex **1b** under analogous conditions shows an irreversible wave assigned to Rh^{I} oxidation at a more oxidative potential (E_{pa} = +0.660 V vs Fc/Fc$^+$) than those assigned to the Fe(C_5H_5)(C_5H_4) moieties in **1a**. Oxidation of the Fe(C_5H_5)(C_5H_4) moieties in **1a** also can be effected by the reaction of **1a** with 2 equiv of $AgBF_4$ in CH_2Cl_2. This oxidation affords the paramagnetic complex [Rh^{I}{Fe^{III}(C_5H_5)($C_5H_4SCH_2CH_2PPh_2$)}$_2$]-

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(1) (a) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem.* **1998**, *110*, 936. (b) Allgeier, A. M.; Slone, C. S.; Mirkin, C. A.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 550. (c) Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1624. (d) Allgeier, A. M.; Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Organometallics* **1994**, *13*, 2928. (e) Slone, C. S.; Mirkin, C. A.; Yap, G. P. A.; Guzei, I. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 10743. (f) Sassano, C. A.; Mirkin, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 11379.

(2) For **1a**: ^{1}H NMR (CD_2Cl_2) δ 7.38−7.16 (m, 20H, Ar), 4.51 (t, J_{H-H} = 1.5 Hz, 4H, η^5-C_5H_4), 4.49 (t, J_{H-H} = 1.5 Hz, 4H, η^5-C_5H_4), 4.37 (10H, η^5-C_5H_5), 2.75 (m, 4H, CH_2S), 2.44 (m, 4H, CH_2P). FAB-HRMS, *m*/*z*, M$^+$, calcd 963.027; found 963.019.

(3) Complex **1b** as a BPh_4^- salt was reported: Sanger A. R. *Can. J. Chem.* **1986**, *64*, 1870.

(4) Porri, L.; Lionetti, A.; Allegra, G.; Immirizi, A. *J. Chem. Soc., Chem. Commun.* **1965**, 336.

(5) The ligands $RSCH_2CH_2PPh_2$ were synthesized by the method described by DuBois et al.: DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011 and modification thereof.

(6) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

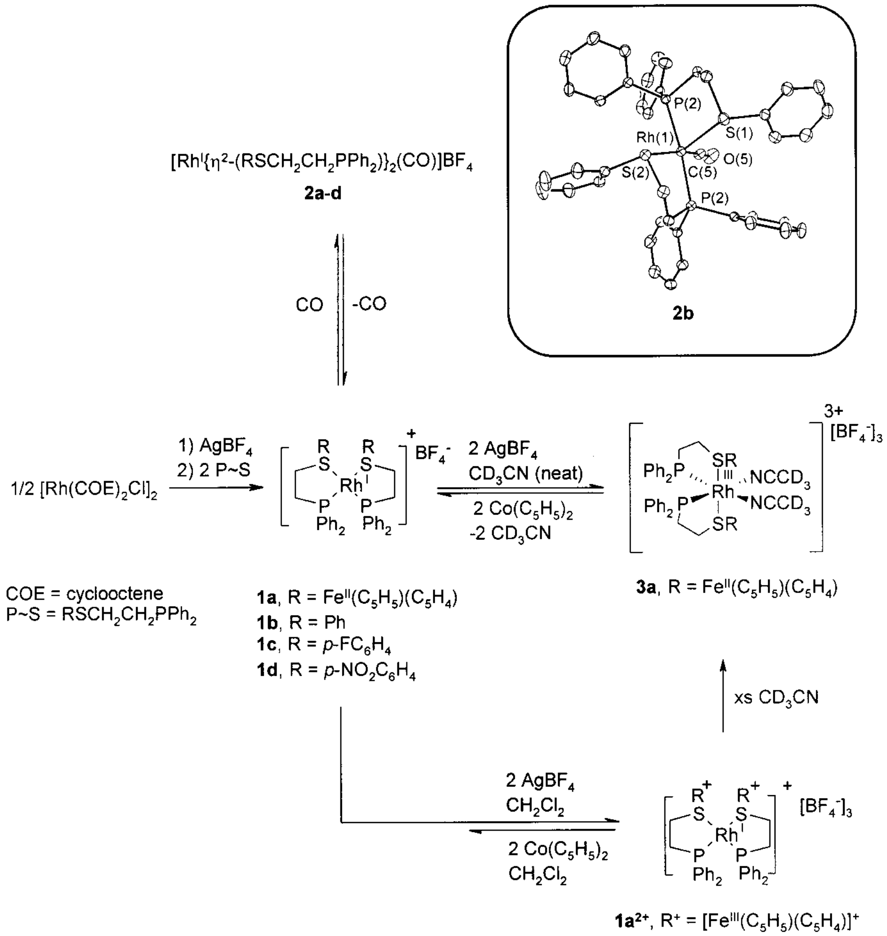
(7) For examples of mono-CO Rh(I) complexes, see: (a) James, B. R.; Mahajan, D. *Can. J. Chem.* **1980**, *58*, 966. (b) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120. (c) Anderson, M. P.; Casalnuovo, A. L.; Johnson, B. J.; Mattson, B. M.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 1649.

(8) For **2a**: ^{1}H NMR (CD_2Cl_2) δ 7.55−7.46 (m, 20H, Ar), 4.19 (t, J_{H-H} = 1.6 Hz, 4H, η^5-C_5H_4), 4.18 (s, 10H, η^5-C_5H_5), 3.88 (t, J_{H-H} = 1.6 Hz, 4H, η^5-C_5H_4) 2.94 (m, 4H, CH_2S), 2.74 (m, 4H, CH_2P).

(9) The assignment of the two reversible waves was confirmed by a rotating disk electrode technique, which was consistent with the total transfer of 2 electrons. The CV of **1a** in CH_3CN shows an irreversible oxidative wave (E_{pa} = +0.185 V).

10.1021/ic990193v CCC: $18.00

Scheme 1



[BF$_4$]$_3$ (**1a**$^{2+}$), Scheme 1, which is stable in solution over several hours but decomposes rapidly in the solid state. Due to its paramagnetism, **1a**$^{2+}$ was only characterized by ES MS and its reactivity, which are consistent with the proposed formulation. Notably, addition of 2 equiv of CoCp$_2$ to **1a**$^{2+}$ cleanly affords **1a**, as evidenced by ^{31}P NMR spectroscopy. Significantly, when CD$_3$CN is added to the CH$_2$Cl$_2$ solution of **1a**$^{2+}$, CD$_3$CN molecules coordinate to the Rh^I center causing intramolecular electron transfer from the Rh^I center to the oxidized Fe(C$_5$H$_5$)(C$_5$H$_4$)$^+$ moieties to afford the six-coordinate Rh^{III} complex *trans,cis,cis*-[Rh^{III}{Fe(C$_5$H$_5$)(C$_5$H$_4$SCH$_2$CH$_2$PPh$_2$)}$_2$(CH$_3$CN)$_2$][BF$_4$]$_3$ (**3a**), Scheme 1.[10] Diamagnetic **3a** was characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental analysis,[11] and by a single-crystal X-ray diffraction study. A single crystal was obtained by slow diffusion of a solution of **3a** in CD$_3$CN into Et$_2$O. The solid-state structure of **3a** reveals an octahedral geometry with *cis*-CD$_3$CN molecules, *cis*-phosphines, and *trans*-thioether groups (see Supporting Information). Significantly, the oxidatively induced transformation is completely reversible; addition of 2 equiv of CoCp$_2$ to a solution of **3a** in CD$_3$CN cleanly regenerates the starting complex **1a**, as evidenced by ^{1}H and ^{31}P NMR spectroscopy.

The reactivity of complex **1a** is fascinating and demonstrates a new way for controlling the uptake and release of small molecules through use of substitutionally inert redox-active ligands. Compound **1a** reacts with the π acid, CO, but is chemically inert with respect to the σ donor ligand, CH$_3$CN. However, ferrocenyl-based oxidation of **1a** changes its Lewis acidity and effects the uptake of CH$_3$CN. As this happens the electron richness of the Rh center is increased, resulting in a redistribution of electrons from the Rh center to the Fe centers within the complex. The net effect is the conversion of a paramagnetic, square planar doubly oxidized Rh^I complex **1a**$^{2+}$ to a diamagnetic, octahedral Rh^{III} complex **3a** with two additional CH$_3$CN ligands. Note that ligands with conventional redox-inactive substituents that vary in their ability to withdraw electron density, like those used in **1b**−**d**, do not effect the uptake of the σ-donating CH$_3$CN ligand. The oxidized ferrocenyl ligands in **1a** provide an electron transfer pathway, which is not available in **1b**−**d**, that facilitates the uptake of two CH$_3$CN ligands and the formation of **3a**.[12]

Acknowledgment. C.A.M. acknowledges NSF (CHE-9625391 and CHE-9357099) and ACS-PRF (No. 30759-AC3) for funding this research. A.L.R. acknowledges NSF (CHE-9628768).

Supporting Information Available: Experimental procedures and spectral data for all new compounds and crystallographic details for **2b** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Electrochemically driven *irreversible* coordination of P(OEt$_3$)$_3$ to a Cr complex, proposed to occur by a similar mechanism, has been reported by Yeung et al.: Yeung, L. K.; Kim, J. E.; Chung, Y. K.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1996**, *15*, 3891.

(11) For **3a**: ^{1}H NMR (CD$_3$CN) δ 8.00−7.00 (m, 20H, Ar), 4.64 (4H, η^5-C$_5$*H*$_4$), 4.60 (4H, η^5-C$_5$*H*$_4$), 4.58 (10H, η^5-C$_5$*H*$_5$), 4.07 (m, 4H, C*H*$_2$), 3.84 (broad, 2H, C*H*$_2$), 3.64 (broad, 2H, C*H*$_2$), 1.78 (6H, C*H*$_3$CN). Anal. Calcd for $C_{52}H_{52}B_3F_{12}Fe_2N_2P_2RhS_2$: C, 47.82; H, 4.02; N, 2.14. Found: C, 47.45; H, 3.95, N, 2.10.

(12) When model complex **1b** was treated with three equivalents of AgBF$_4$ in CH$_3$CN, the six-coordinate Rh^{III} complex [Rh^{III}(PhSCH$_2$CH$_2$PPh$_2$)$_2$(CH$_3$CN)$_2$][BF$_4$]$_3$ (**3b**) formed over the course of 24 h. The difference in rate of oxidation of **1a** (30 s) compared to **1b** under virtually identical conditions clearly establishes the role of the ferrocenylium moieties in **1a** as intramolecular electron-transfer facilitators.