modynamics of the return electron transfer. An excellent correlation is observed in the present work presumably because, unlike previous work, the compounds studied are similar in structure and dimensions and do not undergo significant chemical reactions either within or outside the geminate radical pair and because accurate redox parameters were obtained.

Rhodium μ-Amido and μ-Imido A-Frame Complexes: Tautomeric Equilibria with a Deprotonated Bis(diphenylphosphino)methane Ligand[1]

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Molecular A-frame complexes[2] are one of the larger classes of bimetallic late-transition-metal complexes. While a large number of apex ligands have been incorporated, apex oxo, imido, and amido ligands are unknown.[3,4] The majority of A-frame complexes are based on the bis(diphenylphosphino)methane (dppm) ligand and usually contain the metals Pt, Pd, Rh, or Ir.[3,4a] Since we are interested in preparing μ-oxo and μ-imido complexes of these metals as models for late-transition-metal surface oxides, we began working on expanding the A-frame class to include complexes with these apex ligands.[1] During this work we discovered the first examples of A-frame complexes containing a deprotonated dppm (bis(diphenylphosphino)methanide or dppm-H) ligand and at least two examples where the dppm ligand is involved in a unique tautomeric equilibrium. Although dppm-H ligands have been previously observed, the complexes have been monomers,[5] dimers with non-A-frame structures,[6] or clusters.[7] Our results show that the dppm-H ligand can support the A-frame structure. In addition, we have the first examples of A-frame complexes with bridging amido and imido ligands.

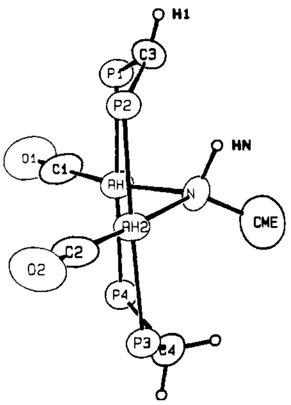

Figure 1. ORTEP view of $Rh_2(\mu\text{-NHMe})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ (**1a**) 50% probability ellipsoids. Phenyl rings are omitted for clarity. Selected distances (Å) and angles (deg): P1–C3, 1.738 (8); P2–C3, 1.736 (8); P3–C4, 1.837 (7); P4–C4, 1.851 (7); C3–H1, 0.80 (9); Rh1–N, 2.107 (6); Rh2–N, 2.091 (5); N–HN, 1.09 (9); HN–C3, 2.23; P1–C3–P2, 119.3 (4); P1–C3–H1, 119 (7); P2–C3–H1, 115 (7); Rh1–N–Rh2, 94.4 (2); Rh–N–CME, 121.0 (5); Rh2–N–CME, 127.5 (5); RH1–N–HN, 116 (4); Rh2–N–HN, 103 (4); CME–N–HN, 96 (4); N–HN–C3, 128 (4).

Treating yellow $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$[8] with 2 equiv of LiNHR in ether gives a single orange product (**1a**) when R = Me (eq 1). Spectroscopic[9] and X-ray[11] data show **1a** to be a μ-methylamido A-frame complex with a dppm-H ligand. A view of the molecular structure is shown in Figure 1.

$$\begin{gathered}
Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2 + 2LiNHR \xrightarrow{-2LiCl} \\
Rh_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H}) + \\
\textbf{1a},\ R = Me \\
\textbf{1b},\ R = Ph \\
\textbf{1c},\ R = p\text{-MePh} \\
Rh_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2 \quad (1) \\
\textbf{2b},\ R = Ph \\
\textbf{2c},\ R = p\text{-MePh}
\end{gathered}$$

When R = Ph or *p*-MePh a mixture of two products (eq 1, **1b** and **2b** for R = Ph, **1c** and **2c** for R = p-MePh) is obtained as shown by IR.[12] Experiments on the slower NMR time scale show that the two products are in rapid equilibrium, a slow exchange

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[1] Part 2 in a series entitled "Late-Transition-Metal μ-Oxo and μ-Imido Complexes". For part 1, see: Sharp, P. R.; Flynn, J. R. *Inorg. Chem.*, in press.

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[9] Data for **1a**. Anal. Calcd (found) for $Rh_2P_4NO_2C_{53}H_{47}$: C, 60.07 (59.60); H, 4.47 (4.50); N, 1.32 (1.08). IR (cm^{-1}) (CH_2Cl_2) 1965 s and 1949 vs (ν_{CO}); (mineral oil) 3137 w (ν_{NH}). ^1H NMR (300 MHz, C_6D_6, 22 °C) δ 6.8–8.2 (m, 40, Ph), 3.58 and 3.24 (m, 2, CH_2), 3.39 (br m, 1, NH), 2.23 (m, 3, NCH_3), 1.61 (br m, 1, CH). Assignments were confirmed by $^{13}C/^1H$ shift correlation experiments. The NCH_3 peak sharpened and increased in intensity when the NH peak was irradiated. ^{13}C NMR (75 MHz, CD_2Cl_2, 10 °C) δ 193.7 (m, CO), 135–127 (Ph), 43.5 (s, NCH_3), 31.4 (t, J_{CP} = 10.1 Hz, PCH_2P), 9.1 (t, J_{CP} = 53.0 Hz, PCHP). Assignments were confirmed by DEPTH[10] experiments. ^{31}P NMR (121 MHz, CH_2Cl_2/C_6D_6, external H_3PO_4 reference, 22 °C), symmetric AA′BB′XX′ pattern centered at 24 ppm spanning 18–30 ppm. Approximately simulated with the following parameters: $J_{AA'} = J_{BB'} = 30$ Hz; $J_{AB} = J_{A'B'} = 300$ Hz; $J_{AB'} = J_{A'B} = 12$ Hz; $J_{AX} = J_{BX} = J_{A'X'} = J_{B'X'} = 80$ Hz; $J_{AX'} = J_{BX'} = J_{A'X} = J_{B'X} = 12$ Hz; $J_{XX'} = 0$ Hz; $\delta(A) = \delta(A') = 20$ ppm; and $\delta(B) = \delta(B') = 28$ ppm.

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[11] Crystals from toluene: $Rh_2P_4O_2NC_{53}H_{47}\cdot C_7H_8$, fw = 1151.82, d_{calcd} = 1.30, triclinic ($P\bar{1}$), a = 10.459 (12) Å, b = 14.348 (3) Å, c = 20.867 (6) Å, α = 104.96 (2)°, β = 101.12 (4)°, γ = 93.47 (6)°, V = 2948.3 Å^3, and Z = 2. Full-matrix least-squares calculations converged to $R(F_o) = 0.050$ and $R_w(F_o) = 0.081$ for 4075 observations above 2σ. Positions for H1 and HN (see Figure 1) were refined. Full structural details will be reported in a forthcoming publication.

[12] **1b**/**2b** (R = Ph). IR (cm^{-1}) (CH_2Cl_2) 1964 w, 1942 br s, 1929 vs (ν_{CO}); ν_{NH} for **1b** was not observed (mineral oil). ^{31}P NMR (121 MHz, CH_2Cl_2/C_6D_6 (2:1), external H_3PO_4 reference, 22 °C) δ 23.2 (d, J_{RhP} = 145 Hz). **1c**/**2c** (R = *p*-MePh). IR (cm^{-1}) (CH_2Cl_2) 1964 m, 1945 vs, 1927 m (ν_{CO}); (mineral oil) 3138 w (ν_{NH}). ^{31}P NMR (121 MHz, CH_2Cl_2/C_6D_6 (2:1), external H_3PO_4 reference, 22 °C) δ 22.6 (br d, J_{RhP} = 138 Hz). At –80 °C this peak was resolved into a doublet at 21.9 ppm (J_{RhP} = 136 Hz) for **2c** and a symmetric AA′BB′XX′ pattern for **1c** centered at 21 ppm and spanning 13–30 ppm (T_c = –68 °C). Approximate ratio of **1c** to **2c** at -80 °C was 2:3. Assuming an equal population at T_c, $\Delta G^{\ddagger} \sim 40$ kJ/mol.

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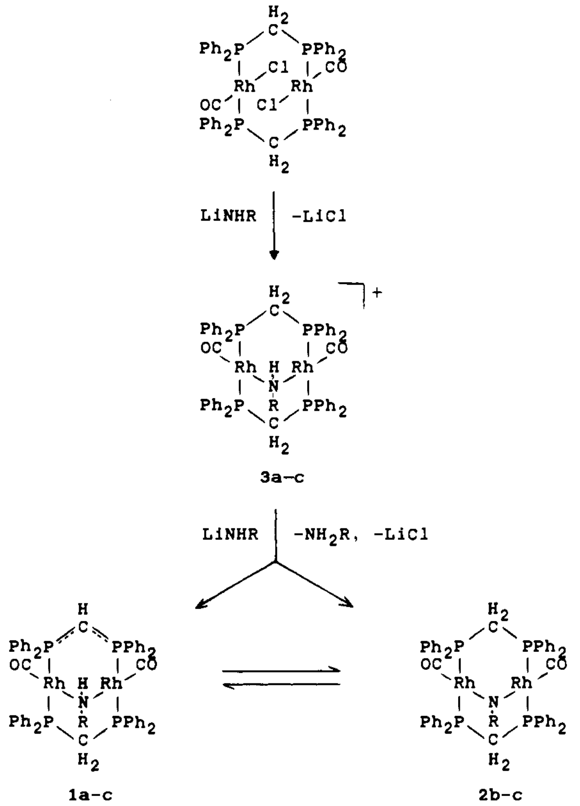
Scheme I



(a, R = Me; b, R = Ph; c, R = p-MePh)

spectrum only being obtained at -80 °C (R = p-MePh, $\Delta G^{\ddagger} \sim$ 40 kJ/mol).[12] A structure similar to **1a** is assigned to **1b**,**c** based on the similarity of the spectroscopic data. The spectroscopic data for **2b**,**c** are very similar to the data for $Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2$[2] and $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2\cdot LiBF_4$.[1] We therefore formulate these products as the imido complexes $Rh_2(\mu\text{-}NR)(CO)_2(\mu\text{-dppm})_2$, **2b** (R = Ph) and **2c** (R = p-MePh). Thus, **1** and **2** are tautomers in a tautomeric equilibrium (Scheme I).[13] Although **1a** is apparently not in equilibrium with its tautomer, at least on the NMR time scale (NMR spectra are invariant from −60 to 100 °C), the structure of **1a** does show how well the hydrogen (HN) is positioned for the shift needed to interconvert the tautomers (Figure 1). Indeed, HN is within hydrogen bonding distance of the methanide carbon, C3.

A likely reaction pathway for the formation of **1** and **2** is shown in Scheme I. Protonation of **1a** or the equilibrium mixtures **1b**/**2b** or **1c**/**2c** gives the proposed intermediate, **3a**, **3b**, or **3c**[14] (eq 2). The protonation is reversed upon addition of LiNHR.

$$\mathbf{1a}\text{ or }\mathbf{1b}/\mathbf{2b}\text{ or }\mathbf{1c}/\mathbf{2c} \underset{\text{LiNHR}}{\overset{H^+}{\rightleftharpoons}} [Rh_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm})_2]^+ \quad (2)$$

$$\mathbf{3a},\ R = Me \qquad \mathbf{3b},\ R = Ph \qquad \mathbf{3c},\ R = p\text{-MePh}$$

In contrast to **3a–c** the isoelectronic complexes $[M_2(\mu\text{-OH})(CO)_2(\mu\text{-dppm})_2]^+$ (M = Rh[15] and Ir[16]) are deprotonated solely at the bridging OH ligand and not at a dppm ligand.[1] While this may be due solely to the difference in acidity of the OH and NHR protons, the incorporation of Li^+ into the OH deprotonation product, $M_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2\cdot LiBF_4$ (most likely by coordination to the μ-oxo ligand), complicates comparisons. The presence of the imido complex when R = Ph (**2b**) or p-MePh (**2c**) but not when R = Me reflects the greater acidity of the amido group in **3b** and **3c** on replacing the methyl group in **3a** with electron-withdrawing phenyl groups. This effect is further illustrated by the ratio of the tautomers (IR, 22 °C) which increases on going from R = Ph (**1b**:**2b** ~ 1:3) to less electron withdrawing R = p-MePh (**1c**:**2c** ~ 1:1).

Preliminary work on the reaction chemistry of **1** and **2** shows facile insertion of CO into the Rh–N bond. Details of this work will be reported in a forthcoming publication.

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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(13) A similar tautomeric equilibrium has been postulated to explain the incorporation of deuterium into the dppm methylene groups of $Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2$.[15]

(14) **3a** (R = Me). Anal. Calcd (found) for $C_{54}H_{48}F_3NO_5P_4Rh_2S\cdot 0.6CH_2Cl_2$ ($CF_3SO_3^-$ salt): C, 52.01 (51.76); H, 3.93 (4.07); N, 1.11 (0.84); P, 9.83 (9.82). IR (cm^{-1}) (CH_2Cl_2) 1993 sh and 1980 vs (ν_{CO}); (mineral oil) 3290 w (ν_{NH}). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.94 (m, 40, phenyl), 5.32 (s, CH_2Cl_2), 4.20 and 3.54 (m, 2 and 2, CH_2), 2.35 (br s, 3, NCH_3), 2.03 (br s, 1, NH). ^{31}P NMR (121 MHz, $CDCl_3/CH_2Cl_2$, external H_3PO_4 reference) δ 21.6 (unsymmetrical doublet with apparent J_{RhP} = 117 Hz). **3b** (R = Ph). IR (cm^{-1}) (CH_2Cl_2) 1995 sh and 1977 vs (ν_{CO}); (mineral oil) 3218 w (ν_{NH}). ^{31}P NMR (121 MHz, C_6D_6/CH_2Cl_2, external H_3PO_4 reference) complex pattern centered at 21 ppm. Data for **3c** (R = p-MePh) are essentially identical.

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In Situ Intercalative Polymerization of Pyrrole in FeOCl: A New Class of Layered, Conducting Polymer-Inorganic Hybrid Materials

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Prepared by the chemical or electrochemical oxidation of pyrrole, polypyrrole ($[(Ppy)^{+y}(X^-)_y]_n$, X = ClO_4^-, BF_4^-, NO_3^-, etc.)[1] is one of the most robust and chemically flexible members of the current generation of electrically conductive polymers.[2] In addition, substantial property modifications can be achieved via "alloying" with other polymers.[1,3] However, despite an extensive

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