

unit by strong  $\sigma$ -donor alkyl ions significantly increases the electron density on rhodium centers and causes a large cathodic shift of redox potentials. ESR results show that the localization of the SOMO of  $[(N_a)_4RhRh(N_p)_4]^+$  complexes on the  $(N_a)_4Rh$  center is due to differences in equatorial bonding environments and twisting of two rhodium planes. Additional polarization of electron density on the two metal centers is related to the  $\sigma$ -donor strength of the axial anion. These complexes can undergo oxidative coordination with  $O_2$  to form  $Rh_2(ap)_4(R)(O_2)$  with a formal  $Rh^{III}_2$  unit. This and previously reported results<sup>16</sup> show dioxygen complexes of the  $Rh_2(ap)_4$  unit with  $Rh^{II}_2$ ,  $Rh^{II}Rh^{III}$ , and  $Rh^{III}_2$  formal oxidation states. The degree of  $O_2$  activation decreases in the order of  $[Rh_2(ap)_4(O_2)]^- > Rh_2(ap)_4(O_2) > [Rh_2(ap)_4(O_2)]^+ > Rh_2(ap)_4(C\equiv CH)(O_2)$  and ranges from the highly reactive superoxide

ion in  $[Rh_2(ap)_4(O_2)]^-$  to the weakly reversibly bound dioxygen in  $Rh_2(ap)_4(C\equiv CH)(O_2)$ .

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**Supplementary Material Available:** Tables S1–S3, listing data collection and processing parameters, anisotropic thermal parameters, and hydrogen atomic coordinates, Figure S4, showing the mass spectra of (a)  $Rh_2(ap)_4(C\equiv CC_6H_5)$  and (b)  $Rh_2(ap)_4(C\equiv CC_5H_{11})$ , Figure S5, containing the molecular packing diagram of  $Rh_2(ap)_4(C\equiv CH)\cdot CH_2Cl_2$ , and Table S6, listing atomic coordinates (7 pages); Table S7, listing observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

## Oxidative-Addition Reactions Involving the Mixed-Valence Complex $[RhRe(CO)_4(Ph_2PCH_2PPh_2)_2]$ . Influence of the Coordinatively Unsaturated Rh(+I) Center on the Saturated Re(-I) Center

David M. Antonelli and Martin Cowie\*

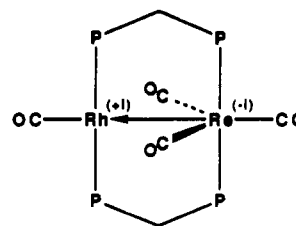
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The mixed-metal complex  $[RhRe(CO)_4(dppm)_2]$  (**1**) ( $dppm = Ph_2PCH_2PPh_2$ ) undergoes facile oxidative-addition reactions with  $H_2$ ,  $Cl_2$ , and  $HCl$  and also reacts with  $HBF_4\cdot Et_2O$  and with the activated alkynes, dimethyl acetylenedicarboxylate (DMA), and hexafluoro-2-butyne (HFB). In the protonation reaction and the alkyne reactions these groups bridge the metals with retention of all carbonyl groups. In the reactions with  $H_2$ ,  $Cl_2$ , and  $HCl$  both atoms of the attacking substrate bridge the metals on opposite sides of the  $RhReP_4$  plane, and loss of one carbonyl group from Re occurs. Loss of one carbonyl from Re can also occur for the alkyne complexes, and this is accompanied by donation of a pair of electrons from Rh. The structure of the protonated complex  $[RhRe(CO)_4(\mu-H)(dppm)_2][BF_4]\cdot H_2O$  (**2**) has been determined crystallographically. This compound crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 17.257(3)$  Å,  $b = 12.235(2)$  Å,  $c = 26.354(3)$  Å,  $\beta = 102.31(1)^\circ$ ,  $V = 5436(3)$  Å<sup>3</sup>, and  $Z = 4$ . On the basis of 5535 unique observations and 388 parameters varied, the structure has refined to  $R = 0.043$  and  $R_w = 0.060$ . Protonation at the Rh–Re bond has resulted in a lengthening of this separation from 2.7919 (6) to 3.0036 (7) Å, and a rearrangement of the carbonyl groups on Re, from a trigonal arrangement in **1** to an arrangement in which they occupy three meridional sites of an octahedron in **2**.

### Introduction

Oxidative-addition reactions are of fundamental importance in organometallic chemistry<sup>1,2</sup> and offer additional challenges in polynuclear complexes owing to the possible involvement of the adjacent metals.<sup>3–6</sup> As part of an investigation into the reactivity of low-valent diphosphine-bridged heterobinuclear complexes,<sup>7–10</sup> we have undertaken a study of the oxidative addition and related reactions involving the mixed-metal species  $[RhRe(CO)_4(dppm)_2]$  (**1**). The structural characterization of this species led to its formulation as a mixed-valence complex in which a donor–acceptor bond links the coordinatively unsaturated Rh(+I) center and the

saturated Re(-I) center.<sup>11</sup> Whether compound **1** is formulated



**1**

as a Rh(I)/Re(-I) species, as suggested, or as a more conventional Rh(0)/Re(0) species, it was felt that the low oxidation states of the metals and the coordinative unsaturation at Rh should make the complex prone to oxidative addition reactions. It was of interest to establish the influence of each metal on the other and, in particular, to establish whether the coordinatively unsaturated Rh(+I) center would increase the reactivity of the otherwise inert  $Re(CO)_3P_2^-$  moiety. The related dirhenium complex  $[Re_2(CO)_6(dppm)_2]$ , in which both metals are coordinatively saturated,

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Table I. Spectral Data<sup>a</sup>

compd	IR, cm <sup>-1</sup>	NMR	
		$\delta(^{31}\text{P}\{^1\text{H}\})^d$	$\delta(^1\text{H})^e$
[RhRe(CO) <sub>4</sub> (μ-H)(dppm) <sub>2</sub> ][BF <sub>4</sub> ] (2)	2046 (m), 2001 (s), 1937 (s), 1908 (s); <sup>b</sup> 2010 (s), 1945 (s), 1930 (s) <sup>c</sup>	24.5 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 112 Hz), 3.4 (m)	4.02 (bs, 4 H), -11.94 (m, 1 H, <sup>1</sup> J <sub>Rh-H</sub> = 22.5 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 7.0 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 12.4 Hz)
[RhRe(CO) <sub>3</sub> (μ-H) <sub>2</sub> (dppm) <sub>2</sub> ] (3)	1925 (s), 1838 (s); <sup>b</sup> 1947 (m), 1916 (s), 1838 (vs) <sup>c</sup>	31.8 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 141 Hz), 18.2 (m)	3.89 (bs, 4 H), -8.21 (m, 2 H, <sup>1</sup> J <sub>Rh-H</sub> = 25.1 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 9.8 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 10.0 Hz)
[RhRe(CO) <sub>3</sub> (μ-Cl) <sub>2</sub> (dppm) <sub>2</sub> ] (4)	1967 (s), 1905 (s), 1820 (s) <sup>b</sup>	23.3 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 120 Hz), 9.8 (m)	4.32 (m, 2 H), 3.83 (m, 2 H), -9.76 (m, 1 H, <sup>1</sup> J <sub>Rh-H</sub> = 24 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 8.1 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 12 Hz)
[RhRe(CO) <sub>3</sub> (μ-H)(μ-Cl)(dppm) <sub>2</sub> ] (5)	1960 (m), 1929 (s), 1853 (s) <sup>c</sup>		
[RhRe(CO) <sub>5</sub> (dppm) <sub>2</sub> ] (6)	2010 (s), 1988 (s), 1964 (s), 1918 (vs), 1892 (vs) <sup>c</sup>	11.4 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 152 Hz), -1.6 (m)	
[RhRe(CO) <sub>4</sub> (μ-DMA)(dppm) <sub>2</sub> ] (7)	2001 (m), 1949 (s), 1860 (s), 1831 (w); <sup>b</sup> 1985 (m), 1947 (s), 1863 (m) <sup>c</sup>	20.7 (dm <sup>1</sup> J <sub>Rh-P</sub> = 155 Hz), 2.0 (m)	4.58 (m, 2 H), 3.19 (s, 3 H), 2.64 (m, 2 H), 1.70 (s, 3 H)
[RhRe(CO) <sub>4</sub> (μ-HFB)(dppm) <sub>2</sub> ] (8)	1987 (m), 1955 (s), 1879 (m); <sup>c</sup> 2005 (m), 1953 (s), 1868 (s), 1839 (w) <sup>b</sup>	15.9 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 144 Hz), 1.2 (m)	4.14 (m, 2 H), 3.18 (m, 2 H)
[RhRe(CO) <sub>3</sub> (μ-DMA)(dppm) <sub>2</sub> ] (9)	2000 (m), 1891 (m), 1811 (s) <sup>c</sup>	17.4 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 124 Hz), 7.8 (m)	3.71 (m, 2 H), 3.50 (m, 2 H), 2.70 (s, 3 H), 2.00 (s, 3 H),
[RhRe(CO) <sub>3</sub> (μ-HFB)(dppm) <sub>2</sub> ] (10)	2009 (m), 1895 (m), 1816 (s) <sup>c</sup>	15.4 (dm, <sup>1</sup> J <sub>Rh-P</sub> = 122 Hz), 5.1 (m)	3.73 (m, 2 H), 3.47 (m, 2 H)

<sup>a</sup> Abbreviations used: IR, w = weak, m = medium, s = strong; NMR, m = multiplet, dm = doublet of multiplets, s = singlet, bs = broad singlet. <sup>13</sup>C{<sup>1</sup>H} NMR spectral data are given in the text. Unless otherwise noted these were obtained at -40 °C in CD<sub>2</sub>Cl<sub>2</sub>, except for compound 7, which was obtained in toluene-*d*<sub>8</sub>. Chemical shifts are referenced to TMS. <sup>b</sup> Nujol mull in KBr plates. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solution in KCl cells. <sup>d</sup> Vs 85% H<sub>3</sub>PO<sub>4</sub>; -40 °C in CD<sub>2</sub>Cl<sub>2</sub> solvent. <sup>e</sup> Vs TMS, -40 °C in CD<sub>2</sub>Cl<sub>2</sub> solvent; resonances for the dppm phenyl hydrogens are not given. <sup>f</sup> J<sub>P(M)-H</sub> is the coupling constant between the phosphorus nuclei bound to M and hydrogen.

had been shown to be rather inert, requiring refluxing at 172 °C for the oxidative-addition reactions of H<sub>2</sub> and phenylacetylene to occur.<sup>12</sup> In this paper we report on results of the binuclear oxidative-addition reactions of compound 1, since such reactions are pivotal to our understanding of the functions of adjacent metals in catalysis by multicenter complexes.

### Experimental Section

**General Procedures.** All solvents were dried and distilled under argon before use. Tetrahydrofuran was dried and deoxygenated with Na/Ph<sub>2</sub>CO, as were Et<sub>2</sub>O and hexane. Dichloromethane was dried over P<sub>2</sub>O<sub>5</sub>. Purified argon was used without further treatment. Carbon monoxide and dihydrogen were used as received. Hexafluoro-2-butene was used as received from SCM Specialty Chemicals, and HCl was used as received from Matheson. Hydrated rhodium(III) chloride was obtained from Johnson Matthey Ltd., and Re<sub>2</sub>(CO)<sub>10</sub> was purchased from Strem and sublimed before use. Dimethyl acetylenedicarboxylate (DMA) was used as received from Aldrich. All other chemicals were also used as received without further purification. Compound 1, [RhRe(CO)<sub>4</sub>(dppm)<sub>2</sub>] (dppm = bis(diphenylphosphino)methane),<sup>11</sup> and iodobenzene dichloride<sup>13</sup> were prepared as previously described.

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 162.0 MHz for <sup>31</sup>P, 400.1 MHz for <sup>1</sup>H, and 100.6 MHz for <sup>13</sup>C. Unless otherwise noted, all <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C except for compound 7, which was run in toluene-*d*<sub>8</sub> at that temperature. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P<sub>2</sub>O<sub>5</sub>, freeze-pump-thaw degassed, and vacuum distilled into the 5-mm NMR tube containing the sample, which was then flame sealed.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrometer, either as solids (Nujol mulls on KBr plates) or solutions (KCl cell windows, 0.5-mm path lengths). Spectral parameters for the compounds prepared are found in Table I. Elemental analyses were performed by the microanalytical service within the department.

**Preparation of Compounds.** (a) [RhRe(CO)<sub>4</sub>(μ-H)(dppm)<sub>2</sub>][BF<sub>4</sub>]-H<sub>2</sub>O (2). The complex [RhRe(CO)<sub>4</sub>(dppm)<sub>2</sub>] (50 mg, 42.8 μmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and HBF<sub>4</sub>·Et<sub>2</sub>O (6.75 μL, 47.1 μmol) was added by syringe. The solution turned a lighter shade of yellow and was stirred for 1/2 h. Removal of the solvent and recrystallization of the light yellow product from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O yielded 52 mg (96%). The 1 equiv of H<sub>2</sub>O apparently originated from wet HBF<sub>4</sub>·Et<sub>2</sub>O. Anal. Calcd for C<sub>34</sub>H<sub>47</sub>BF<sub>4</sub>O<sub>3</sub>P<sub>4</sub>ReRh: C, 50.84; H, 3.71. Found: C, 51.06; H, 3.98.

(b) [RhRe(CO)<sub>3</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>] (3). Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of THF, and the solution was stirred under 1 atm of H<sub>2</sub>. The yellow solution gradually turned dark orange, and after 3 h, a fine yellow precipitate began to settle out. The solution was stirred for an additional 3 h, after which the THF was removed in vacuo. The yellow residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to yield 40 mg (82%) of product (3), which is pale yellow in color. Anal. Calcd for C<sub>53</sub>H<sub>46</sub>O<sub>3</sub>P<sub>4</sub>ReRh: C, 55.65; H, 4.05. Found: C, 55.23; H, 4.39.

(c) [RhRe(CO)<sub>3</sub>(μ-Cl)<sub>2</sub>(dppm)<sub>2</sub>] (4). Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of THF. Iodobenzene dichloride (11.8 mg, 42.8 μmol) in 50 mL of THF was added by cannula. The solution became slightly lighter in color, and after 2 h, a light yellow precipitate began to settle out. After an additional 2 h the product was collected by filtration and washed several times with Et<sub>2</sub>O (5 × 5 mL). Yield: 48 mg (93%). Anal. Calcd for C<sub>53</sub>H<sub>44</sub>Cl<sub>2</sub>O<sub>3</sub>P<sub>4</sub>ReRh: C, 52.49; H, 3.66; Cl, 5.85. Found: C, 52.28; H, 3.94; Cl, 6.22.

(d) [RhRe(CO)<sub>3</sub>(μ-H)(μ-Cl)(dppm)<sub>2</sub>] (5). Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. Anhydrous HCl (0.94 mL, 42.8 μmol) was added by gastight syringe. The yellow solution immediately turned orange and was stirred for an additional 15 min. The solvent was then removed in vacuo, and the resulting orange residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give an orange powder. Yield: 45 mg (92%). Anal. Calcd for C<sub>53</sub>H<sub>45</sub>ClO<sub>3</sub>P<sub>4</sub>ReRh: C, 54.04; H, 3.81; Cl, 3.10. Found: C, 53.79; H, 4.26; Cl, 3.47.

(e) [RhRe(CO)<sub>5</sub>(dppm)<sub>2</sub>] (6). Compound 1 (50 mg, 42.8 μmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and CO gas was vigorously bubbled through the solution for 5 min, causing the solution to turn from yellow to orange. The rate was then slowed to approximately 0.2 mL/s for 20 min. At this point the IR spectrum of the sample, maintained under a CO atmosphere, showed complete conversion to the pentacarbonyl.

(f) [RhRe(CO)<sub>4</sub>(μ-DMA)(dppm)<sub>2</sub>] (7). Compound 1 (50 mg, 42.8 μmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. Dimethylacetylenedicarboxylate (5.2 μL, 42.8 μmol) was then added. A yellow precipitate formed instantly. The flask was then purged with CO to prevent formation of 9 and 15 mL of Et<sub>2</sub>O was then added to ensure complete precipitation of the yellow product. The solid was collected and washed with 3 × 5 mL of Et<sub>2</sub>O. Yield: 46 mg (82%). Anal. Calcd for C<sub>60</sub>H<sub>50</sub>O<sub>8</sub>P<sub>4</sub>ReRh: C, 54.93; H, 3.81. Found: C, 55.20; H, 4.17.

(g) [RhRe(CO)<sub>4</sub>(μ-HFB)(dppm)<sub>2</sub>] (8). Compound 1 (50 mg, 42.8 μmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> to which excess HFB (20 mL) was added. After 5 min of stirring, CO was rapidly passed over the solution and a yellow precipitate began to form. Addition of 10 mL of Et<sub>2</sub>O, while the purge of carbon monoxide was maintained, completed the precipitation. The product was collected by filtration under CO and washed with 3 × 10 mL of Et<sub>2</sub>O to yield 40 mg (70%) of a light yellow powder. Anal. Calcd for C<sub>48</sub>H<sub>44</sub>F<sub>6</sub>O<sub>3</sub>P<sub>4</sub>ReRh: C, 52.30; H, 3.30; F, 8.56. Found: C, 52.49; H, 3.81; F, 8.77.

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**Table II.** Crystallographic Data for  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}$ 

$\text{C}_{54}\text{BFH}_{47}\text{O}_5\text{P}_4\text{ReRh}$	$fw = 1275.8$
$a = 17.257 (3) \text{ \AA}$	space group: $P2_1/n$
$b = 12.235 (2) \text{ \AA}$	$T = 22 \text{ }^\circ\text{C}$
$c = 26.354 (3) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}$
$\beta = 102.31 (1)^\circ$	$\rho = 1.559 \text{ g}\cdot\text{cm}^{-3}$
$\mu = 27.262 \text{ cm}^{-1}$	transm coeff = 0.901–1.113
$V = 5436 (3) \text{ \AA}^3$	$R^a = 0.043$
$Z = 4$	$R_w^a = 0.060$

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

**Table III.** Positional and Thermal Parameters for the Inner-Core Non-Hydrogen Atoms of  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}^a$ 

atom	x	y	z	$B,^b \text{ \AA}^2$
Re	0.19822 (2)	0.16665 (3)	0.01131 (2)	2.254 (7)*
Rh	0.33338 (5)	0.32321 (7)	0.01506 (3)	2.61 (2)*
P(1)	0.1455 (2)	0.2166 (2)	-0.0782 (1)	2.47 (6)*
P(2)	0.2771 (2)	0.3877 (2)	-0.0674 (1)	2.74 (6)*
P(3)	0.2642 (2)	0.1003 (2)	0.0958 (1)	2.60 (6)*
P(4)	0.4041 (2)	0.2519 (2)	0.0931 (1)	2.73 (6)*
O(1)	0.2154 (7)	-0.0732 (7)	-0.0280 (4)	7.5 (3)*
O(2)	0.1778 (4)	0.3988 (6)	0.0556 (3)	3.9 (2)*
O(3)	0.0321 (4)	0.1130 (8)	0.0286 (3)	5.2 (2)*
O(4)	0.4280 (6)	0.5308 (7)	0.0331 (4)	7.2 (3)*
C(1)	0.2106 (7)	0.015 (1)	-0.0146 (4)	4.1 (3)*
C(2)	0.1887 (6)	0.3168 (8)	0.0382 (4)	2.8 (2)*
C(3)	0.0958 (6)	0.1314 (9)	0.0229 (4)	3.1 (2)*
C(4)	0.3922 (7)	0.450 (1)	0.0259 (5)	4.0 (3)*
C(5)	0.2198 (6)	0.2826 (9)	-0.1082 (4)	2.8 (2)*
C(6)	0.3719 (6)	0.1155 (9)	0.1067 (4)	2.9 (2)*
H(1)	0.310 (6)	0.177 (8)	-0.002 (4)	2.0 <sup>c</sup>

<sup>a</sup> Other atom parameters are given in the supplementary material.

<sup>b</sup> Starred  $B$  values are for atoms refined anisotropically.  $B$  values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$ . <sup>c</sup> Thermal parameter for H(1) was not refined.

(h)  $[\text{RhRe}(\text{CO})_3(\mu\text{-DMA})(\text{dppm})_2]$  (9). Compound 1 (50 mg, 42.8  $\mu\text{mol}$ ) was dissolved in 5 mL of THF, and DMA (5.2  $\mu\text{L}$ , 42.8  $\mu\text{mol}$ ) was added by syringe. The yellow solution instantly turned dark maroon and was then refluxed for  $1/2$  h. The solvent was removed in vacuo, and recrystallization from  $\text{CH}_2\text{Cl}_2$ /pentane yielded 46 mg (86%) of a blood red complex (9). Anal. Calcd for  $\text{C}_{59}\text{H}_{50}\text{O}_7\text{P}_4\text{ReRh}$ : C, 55.14; H, 3.89. Found: C, 54.57; H, 4.11.

(i)  $[\text{RhRe}(\text{CO})_3(\mu\text{-HFB})(\text{dppm})_2]$  (10). Compound 1 (50 mg, 42.8  $\mu\text{mol}$ ) was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ . Excess (20 mL) hexafluorobutene was then added by syringe. The light yellow solution quickly turned dark red and was then stirred for an addition  $1/2$  h. The solvent was removed in vacuo and the red residue recrystallized from  $\text{CH}_2\text{Cl}_2$ /Et<sub>2</sub>O. Yield: 46 mg (83%). Anal. Calcd for  $\text{C}_{57}\text{H}_{44}\text{F}_6\text{O}_3\text{P}_4\text{ReRh}$ : C, 52.51; H, 3.37; F, 8.74. Found: C, 52.83; H, 3.66; F, 8.99.

**X-ray Data Collection.** Yellow crystals of  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}$  were obtained by slow diffusion of Et<sub>2</sub>O into a concentrated  $\text{CH}_2\text{Cl}_2$  solution of the complex. Several suitable crystals were mounted and flame-sealed under argon in glass capillaries to minimize decomposition. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of Mo K $\alpha$  radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 well-distributed reflections in the range  $20.0 \leq 2\theta \leq 24.0^\circ$ . A monoclinic cell was established by the usual peak search and reflection indexing programs, and the systematic absences established the space group as  $P2_1/n$  (a nonstandard setting of  $P2_1/c$ ).

Intensity data were collected at 22  $^\circ\text{C}$  by using the  $\theta/2\theta$  scan technique to a maximum of  $2\theta = 50.0^\circ$ . Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals of X-ray exposure. There was no significant systematic decrease in the intensities of these standards so no correction was applied. A total of 9660 unique reflections were measured and processed in the usual way, using a value of 0.04 for  $p$ ;<sup>14</sup> of these, 5535 were observed and used in subsequent calculations. Absorption corrections were applied to the

**Table IV.** Selected Distances ( $\text{\AA}$ ) in  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}^a$ 

Re–Rh	3.0036 (7)	P(2)–C(5)	1.825 (8)
Re–P(1)	2.418 (2)	P(2)–C(31)	1.819 (9)
Re–P(3)	2.415 (2)	P(2)–C(41)	1.823 (9)
Re–C(1)	2.00 (1)	P(3)–C(6)	1.829 (8)
Re–C(2)	1.989 (8)	P(3)–C(51)	1.835 (8)
Re–C(3)	1.907 (9)	P(3)–C(61)	1.831 (8)
Re–H(1)	2.05 (8)	P(4)–C(6)	1.819 (8)
Rh–P(2)	2.323 (2)	P(4)–C(71)	1.803 (9)
Rh–P(4)	2.326 (2)	P(4)–C(81)	1.83 (1)
Rh–C(4)	1.84 (1)	O(1)–C(1)	1.14 (1)
Rh–H(1)	1.86 (8)	O(2)–C(2)	1.134 (9)
P(1)–C(5)	1.832 (8)	O(3)–C(3)	1.163 (9)
P(1)–C(11)	1.828 (8)	O(4)–C(4)	1.16 (1)
P(1)–C(21)	1.844 (8)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. Bond lengths for the  $\text{BF}_4^-$  anion and the phenyl groups are given in the supplementary material.

**Table V.** Angles (deg) in  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}^a$ 

Rh–Re–P(1)	89.95 (5)	Re–P(1)–C(5)	112.3 (3)
Rh–Re–P(3)	88.52 (5)	Re–P(1)–C(11)	114.2 (3)
Rh–Re–C(1)	117.7 (3)	Re–P(1)–C(21)	119.9 (3)
Rh–Re–C(2)	61.5 (2)	C(5)–P(1)–C(11)	103.1 (4)
Rh–Re–C(3)	151.5 (3)	C(5)–P(1)–C(21)	103.3 (4)
Rh–Re–H(1)	38 (2)	C(11)–P(1)–C(21)	102.0 (4)
P(1)–Re–P(3)	171.70 (8)	Rh–P(2)–C(5)	112.2 (3)
P(1)–Re–C(1)	86.9 (3)	Rh–P(2)–C(31)	112.2 (3)
P(1)–Re–C(2)	94.1 (2)	Rh–P(2)–C(41)	118.2 (3)
P(1)–Re–C(3)	92.5 (3)	C(5)–P(2)–C(31)	99.9 (4)
P(1)–Re–H(1)	90 (2)	C(5)–P(2)–C(41)	105.9 (4)
P(3)–Re–C(1)	86.5 (3)	C(31)–P(2)–C(41)	106.8 (4)
P(3)–Re–C(2)	92.3 (2)	Re–P(3)–C(6)	112.1 (3)
P(3)–Re–C(3)	92.7 (3)	Re–P(3)–C(51)	118.5 (3)
P(3)–Re–H(1)	84 (2)	Re–P(3)–C(61)	113.4 (3)
C(1)–Re–C(2)	178.6 (4)	C(6)–P(3)–C(51)	106.1 (4)
C(1)–Re–C(3)	90.8 (4)	C(6)–P(3)–C(61)	102.9 (4)
C(1)–Re–H(1)	81 (2)	C(51)–P(3)–C(61)	102.2 (4)
C(2)–Re–C(3)	90.1 (4)	Rh–P(4)–C(6)	113.2 (3)
C(2)–Re–H(1)	99 (2)	Rh–P(4)–C(71)	115.6 (3)
C(3)–Re–H(1)	170 (2)	Rh–P(4)–C(81)	112.4 (3)
Re–Rh–P(2)	91.09 (6)	C(6)–P(4)–C(71)	103.9 (4)
Re–Rh–P(4)	92.70 (6)	C(6)–P(4)–C(81)	102.4 (4)
Re–Rh–C(4)	160.1 (3)	C(71)–P(4)–C(81)	108.2 (4)
Re–Rh–H(1)	42 (2)	Re–C(1)–O(1)	176.9 (9)
P(2)–Rh–P(4)	172.40 (9)	Re–C(1)–O(2)	173.6 (8)
P(2)–Rh–C(4)	88.0 (3)	Re–C(3)–O(3)	177.4 (8)
P(2)–Rh–H(1)	95 (3)	Rh–C(4)–O(4)	179 (1)
P(4)–Rh–C(4)	90.6 (3)	P(1)–C(5)–P(2)	113.5 (4)
P(4)–Rh–H(1)	84 (3)	P(3)–C(6)–P(4)	113.9 (4)
C(4)–Rh–H(1)	158 (2)	Re–H(1)–Rh	100 (4)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. Angles involving the  $\text{BF}_4^-$  anion and the phenyl rings are given in the supplementary material.

data<sup>15</sup> by using the method of Walker and Stuart.<sup>16</sup> The crystallographic data are summarized in Table II.

**Structure Solution and Refinement.** The structure was solved by conventional Patterson techniques to obtain the Rh and Re positions, while all other atoms were located by the usual sequence of full-matrix least-squares and difference Fourier techniques. All atoms of the complex cation and the anion were located. In addition, two peaks appeared on difference Fourier maps in the vicinity of the  $\text{BF}_4^-$  anion. On the basis of the <sup>1</sup>H NMR spectrum, which showed the presence of water, and the locations of these peaks, which were within hydrogen-bonded distances from the  $\text{BF}_4^-$  anion, these peaks were identified as the oxygen atoms of H<sub>2</sub>O molecules. Refinement of their occupancy factors established that each one was  $1/2$  occupancy. Although the bridging hydride ligand was clearly located, attempts to refine its thermal parameter resulted in a slightly negative value. Since the positional parameters of this atom were well behaved, its thermal parameter was fixed and its position allowed

- (15) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.  
 (16) Stuart, D.; Walker, N. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

to refine. All hydrogen atoms of the dppm ligands were included as fixed contributions in their idealized positions at 0.95 Å from the attached carbon atoms having the appropriate hybridization. The thermal parameters were fixed at 1.2 times the isotropic  $B$  of the attached carbon atom.

Atomic scattering factors<sup>17,18</sup> and anomalous dispersion terms<sup>19</sup> were taken from the usual tabulations.

## Results

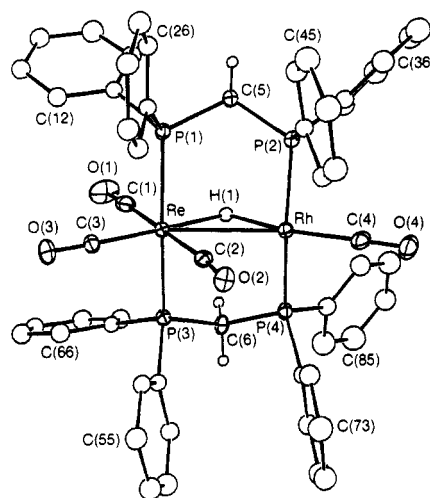
The spectroscopic data for the compounds are tabulated in Table I and are also presented in the Discussion. The structure of  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]\cdot\text{H}_2\text{O}$  was determined and is discussed below. The positional and isotropic thermal parameters for this compound are given in Table III, and bond lengths and angles are given in Tables IV and V, respectively.

## Discussion

Treatment of  $[\text{RhRe}(\text{CO})_4(\text{dppm})_2]$  (**1**) with 1 molar equiv of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  leads to the formation of the protonated species  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]$  (**2**). Protonation is readily monitored by the increase in carbonyl stretching frequencies, from ca. 1800–1959  $\text{cm}^{-1}$  in **1**<sup>11</sup> to ca. 1908–2046  $\text{cm}^{-1}$  in **2** (see Table I), consistent with oxidation of the complex (vide infra) and the resulting positive charge on **2**. The isoelectronic species  $[\text{RhW}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2]$ , has a very similar pattern of stretches (1978 (m), 1942 (s), 1838 (s), 1818 (s)  $\text{cm}^{-1}$ ),<sup>11</sup> which are shifted to lower frequencies in this neutral species. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** has a doublet of multiplets at  $\delta$  24.5 and a multiplet at  $\delta$  3.4, corresponding to the Rh-bound and the Re-bound phosphorus nuclei, respectively, essentially as expected for an  $\text{AA}'\text{BB}'\text{X}$  spin system and similar to the spectra previously observed in related dppm-bridged RhRe complexes.<sup>9,11</sup> In the high-field region of the  $^1\text{H}$  NMR spectrum a multiplet appears at  $\delta$  -11.94. Selective phosphorus decoupling experiments clearly indicate that the hydride ligand bridges both metals, displaying coupling to all four phosphorus nuclei and to Rh (see Table I). Whether the precursor, compound **1**, is considered a Rh(0)/Re(0) species or a mixed-valence Rh(+I)/Re(-I) complex, as we favor, protonation has resulted in a formal oxidation of the complex by two units such that both metals can be considered to be in the +I oxidation state.

Although protonation of a metal-metal-bonded complex to give a hydrido-bridged species is not unusual, the mixed-valence formulation suggested for **1** does raise some questions regarding the structural changes that might occur upon protonation. Compound **1** is isoelectronic with the species  $[\text{MM}'(\text{CO})_3(\text{dppm})_2]$  (M, M' = Rh, Ir),<sup>20–22</sup> which have also been formulated as mixed-valence  $\text{M}(+\text{I})/\text{M}'(-\text{I})$  complexes.<sup>22</sup> Protonation of the homobinuclear Rh<sub>2</sub> and Ir<sub>2</sub> complexes resulted in a transformation from their non-A-frame structures, in which the phosphines on one metal were mutually cis, to an A-frame-related structure in which the phosphines on both metals were mutually trans.<sup>23,24</sup> Surprisingly, protonation of the Rh/Ir analogue<sup>22</sup> gave a different structural type in which all carbonyls remained terminal, although again the phosphines appeared to adopt a trans arrangement. It was therefore of interest to establish whether protonation of **1** would result in a significant structural transformation, which might, in our interpretation, be viewed as occurring through oxidation of the trigonal-bipyramidal Re(-I) center to give Re(+I).

The X-ray structure determination of **2** clearly shows that a significant structural transformation has indeed occurred, as shown for the cation in Figure 1. The diphosphines still adopt a trans

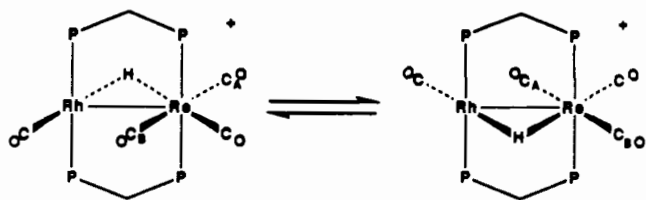


**Figure 1.** Perspective view of the  $[\text{RhRe}(\text{CO})_4(\mu\text{-H})(\text{dppm})_2]^+$  cation, showing the numbering scheme used. Phenyl rings are numbered sequentially around the ring. Thermal ellipsoids are shown at the 20% level except for the methylene hydrogens, which are shown artificially small, and phenyl hydrogens, which are omitted.

arrangement on the metals, having P-M-P angles of ca. 172°. Although the agreement within each set of Re-P and Rh-P distances is excellent, the former are significantly longer (average 2.417 (2) Å vs 2.325 (2) Å) owing to the larger covalent radius of Re. This effect is also displayed in the metal-carbonyl distances, which are again longer for Re. In addition, the two mutually trans carbonyls on Re (C(1)O(1), C(2)O(2)), which are in direct competition for  $\pi$  electron density on Re, have longer Re-C distances (2.00 (1), 1.989 (8) Å) than that involving C(3)O(3) (1.907 (9) Å). The Rh-H(1) and Re-H(1) distances (1.86 (8), 2.05 (8) Å, respectively) are not significantly different, and owing to the uncertainty involved in positioning the hydrogen in the vicinity of the two heavy metals, little can be inferred about the bonding of this hydride except that it is bridging in an approximately symmetric manner. Protonation has resulted in a substantial increase in the Rh-Re bond length, from 2.7919 (6) Å in **1**<sup>11</sup> to 3.0036 (7) Å in **2**, in keeping with the formation of a three-center, two-electron Rh-H-Re bond. In addition to the lengthening of the metal-metal bond, a significant change in the carbonyl positions has occurred upon protonation. The  $\text{Re}(\text{CO})_3$  moiety is no longer approximately trigonal, and this unit has twisted about the P-Re-P axis with H(1) occupying the sixth site of an approximately octahedral geometry, such that all angles about Re (ignoring the Rh-Re interaction) are close to values expected for an octahedron (see Table V). This transformation, from an approximate trigonal-bipyramidal arrangement in **1** to an octahedral environment in **2**, is consistent with an oxidation of Re(-I) to Re(+I). Although carbonyl C(2)O(2) is twisted toward Rh, the Rh-C(2) and Rh-O(2) separations (2.694 (9), 3.229 (6) Å, respectively) are longer than one set of such interactions in **1**<sup>11</sup> and therefore appear not to be unusual. We therefore suggest that there is no significant interaction of Rh with this carbonyl group. This view is supported by the lack of Rh coupling to this carbonyl group in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (vide infra). The geometry at Rh is distorted from square planar such that the fourth coordination site opposite C(4) is actually midway along the Re-H(1) bond. This can be seen from the Re-Rh-C(4) and H(1)Rh-C(4) angles of 160.1 (3) and 158 (2)°, respectively.

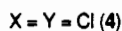
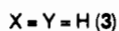
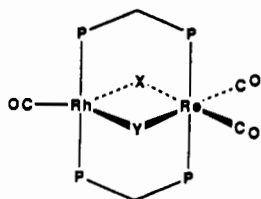
At ambient temperature compound **2** is fluxional, so rather than the four expected carbonyl resonances in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ), only three are observed, at  $\delta$  194.6 (triplet,  $^2J_{\text{P}(\text{Re})-\text{C}} = 13$  Hz), 189.3 (singlet), and 182.8 (doublet of triplets,  $^1J_{\text{Rh}-\text{P}} = 72$  Hz,  $^2J_{\text{P}(\text{Rh})-\text{C}} = 14$  Hz), in a 2:1:1 intensity ratio, respectively. The equivalence of the two mutually trans carbonyls on Re ( $(\text{CO})_A$  and  $(\text{CO})_B$ ) apparently results from their exchange, which is brought about by movement of the hydride ligand between the metals with accompanying twisting of the metal-carbonyl framework shown as follows.

- (17) Cromer, D. J.; Waber, H. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A.  
 (18) Stewart, R. F.; Davidson, E. F.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.  
 (19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.  
 (20) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285.  
 (21) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637.  
 (22) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.  
 (23) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.  
 (24) Sutherland, B. R.; Cowie, M. *Can. J. Chem.* **1986**, *64*, 464.



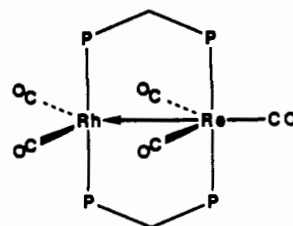
This fluxionality also results in the appearance of only one resonance for the dppm-methylene protons in the  $^1\text{H}$  NMR spectrum owing to the time-average mirror symmetry about the  $\text{RhReP}_4$  core. Similar fluxional processes have previously been noted in related hydrido-bridged systems.<sup>11,22,25</sup> At  $-90^\circ\text{C}$  the two high-field carbonyl resonances have remained essentially unchanged but the low-field signal has split into two broad unresolved signals at  $\delta$  197.1 and 191.6, resulting in four equal-intensity carbonyl resonances, consistent with the observed solid-state structure.

Compound **1** also undergoes facile oxidative addition reactions with  $\text{H}_2$ ,  $\text{Cl}_2$ , and  $\text{HCl}$  to give the structurally analogous species **3**, **4**, and **5**, respectively, as shown. In the reaction with  $\text{H}_2$  the



product,  $[\text{RhRe}(\text{CO})_3(\mu\text{-H})_2(\text{dppm})_2]$  (**3**), has two bridging hydride ligands. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum again displays a pattern typical of an  $\text{AA}'\text{BB}'\text{X}$  spin system, and the IR spectrum displays the expected three carbonyl stretches in solution. In the  $^1\text{H}$  NMR spectrum the resonance for the two chemically equivalent hydride ligands is observed at  $\delta$   $-8.21$  and can be shown, through selective  $^{31}\text{P}$  decoupling experiments, to display coupling to Rh and to the two sets of chemically inequivalent phosphorus nuclei (bound to Rh or Re). Confirmation that **3** is a tricarbonyl species is obtained from the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a 70%  $^{13}\text{CO}$ -enriched sample, which shows one resonance (a doublet of triplets,  $^1J_{\text{Rh-C}} = 69$  Hz,  $^2J_{\text{P(Rh)-C}} = 18$  Hz) at  $\delta$  191.0 for the single carbonyl on Rh and one resonance (a triplet,  $^2J_{\text{P(Re)-C}} = 7$  Hz) at  $\delta$  201.2 for the two carbonyls on Re, having the appropriate integrations. The structure proposed for **3** is a hybrid of the structures proposed for the homobinuclear analogues  $[\text{Re}_2(\text{CO})_4(\mu\text{-H})_2(\text{dppm})_2]$ <sup>12</sup> and  $[\text{Rh}_2(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2]$ .<sup>26</sup> A structure like that of the related dihydride  $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-H})(\text{dppm})_2]$ ,<sup>22</sup> having one hydride bridging both metals and the other terminally bound to the third-row metal, can be ruled out by the spectral data unless the complex is fluxional, for which there is no evidence down to  $-80^\circ\text{C}$ .

The reaction of **1** with  $\text{H}_2$  is reversible, so that under a CO purge compound **1** is regenerated from **3**. If **1** is maintained under an atmosphere of CO, a new species (**6**) having carbonyl stretches in the IR spectrum, at 2010 (s), 1988 (s), 1964 (s), 1918 (vs), and 1892 (vs)  $\text{cm}^{-1}$ , is observed. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** at  $-40^\circ\text{C}$  displays a broad multiplet at  $\delta$   $-1.6$  and a doublet of multiplets ( $^1J_{\text{Rh-P}} = 151$  Hz) at  $\delta$  11.4, and the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a  $^{13}\text{CO}$ -enriched sample shows only one broad peak at  $\delta$  202, even at  $-60^\circ\text{C}$ , suggesting that facile carbonyl exchange over both metal centers is occurring. This facile carbonyl exchange is consistent with the ease with which **1** undergoes  $^{13}\text{CO}$  scrambling when exposed to  $^{13}\text{CO}$ . Although carbonyl exchange in **1** is not observed at ambient temperature, exposure of **1** to  $^{13}\text{CO}$  results in total scrambling, over both metals, suggesting the involvement of the pentacarbonyl species **6**. The structure proposed for this



**6**

species is based on the above spectroscopic data and on the structural determination of the isoelectronic species,  $[\text{IrOs}(\text{CO})_5(\text{dppm})_2][\text{BF}_4]$ ,<sup>27</sup> which displays a trigonal-bipyramidal coordination at Ir and a geometry at Os not unlike that at Re in compound **1**. The fifth carbonyl ligand on **6** is very labile and is lost immediately upon flushing the reaction solution with  $\text{N}_2$  or Ar, yielding **1**, or upon protonation, yielding **2**. As was the case for compound **1**, we again propose a mixed-valence  $\text{Rh}(+1)/\text{Re}(-1)$  formulation in which a  $\text{Re}\rightarrow\text{Rh}$  dative bond connects the metals.

Reaction of compound **1** with  $\text{PhICl}_2$  (a convenient stoichiometric source of  $\text{Cl}_2$ ) results in the formation of the highly insoluble species  $[\text{RhRe}(\text{CO})_3(\mu\text{-Cl})_2(\text{dppm})_2]$  (**4**). Although the poor solubility of **4** precluded an NMR investigation, its formulation (as diagrammed earlier) seems clear, on the basis of its elemental analysis and on a comparison of its IR spectrum with that of **3** (see Table I). This structure is similar to that proposed for the diarsine-bridged dirhenium analogue,  $[\text{Re}_2(\text{CO})_4(\mu\text{-Cl})_2(\text{dpam})_2]$  ( $\text{dpam} = \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ),<sup>28</sup> and as observed for the related  $[\text{Re}_2(\text{CO})_6(\mu\text{-Cl})_2(\text{dpam})_2]$ .<sup>29</sup> Compound **1** also reacts instantly with 1 equiv of dry gaseous  $\text{HCl}$  to give  $[\text{RhRe}(\text{CO})_3(\mu\text{-H})(\mu\text{-Cl})(\text{dppm})_2]$  (**5**), the mixed hydrido-chloro analogue of compounds **3** and **4**. The spectroscopic data are again comparable to those of **3** and **4** (Table I) and also compare well with the related data for the isoelectronic thiolato-bridged species,  $[\text{RhRe}(\text{CO})_3(\mu\text{-H})(\mu\text{-SEt})(\text{dppm})_2]$ ,<sup>9</sup> the structure of which was determined crystallographically. All evidence suggests the structure shown earlier. The hydrido ligand is clearly bridging, as shown by the  $^1\text{H}$  NMR spectra with and without selective  $^{31}\text{P}$  decoupling, which indicate that the high-field hydride resonance at  $\delta$   $-9.8$  is coupled to Rh and to both sets of phosphorus nuclei. Although the chloro ligand cannot unequivocally be identified as bridging, the close similarities between **5** and the ethanethiolato-bridged species strongly supports this formulation. Addition of more than 1 equiv of  $\text{HCl}$  to compound **1** results in formation of the insoluble dichloride species, **4**. Compound **5** is also converted to **4** upon standing in  $\text{CH}_2\text{Cl}_2$ , the half-life being about 85 min at room temperature; however, **5** could be handled briefly in this solvent with no apparent problem.

These facile reactions of  $\text{H}_2$ ,  $\text{Cl}_2$ , and  $\text{HCl}$  with **1**, to yield the respective tricarbonyl species **3**, **4**, and **5**, are surprising in that in all cases loss of one carbonyl group from Re has occurred. On the basis of the inertness of the related saturated species  $[\text{Re}_2(\text{CO})_6(\text{dppm})_2]$  at ambient temperature,<sup>12</sup> it is clear that the coordinatively unsaturated Rh center is pivotal to the reactivity of **1**. Presumably initial reaction is at Rh, with loss of CO being accompanied by movement of the hydrido and chloro groups to the bridging positions, to alleviate the unsaturation at Re brought about by CO loss. For the chloride-containing species, electron-precise compounds result owing to the lone pairs of electrons on Cl, which can be donated to Re. However, for the dihydride species **3**, an electron deficient structure can be invoked involving three-centered  $\text{Re-H-Rh}$  bonds.

Reactions of metal complexes with multiple-bond-containing groups, such as alkynes bearing electronegative substituents, can also be regarded as oxidative additions,<sup>30</sup> and we find that com-

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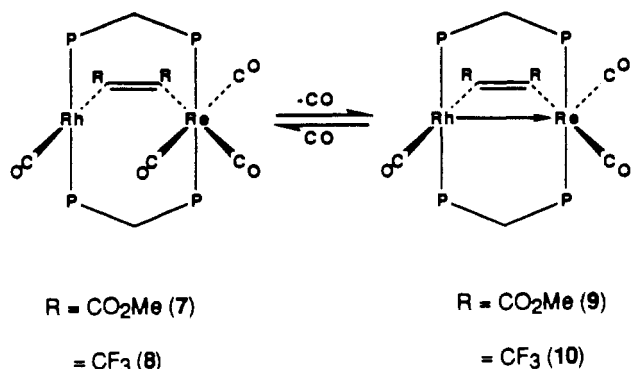
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compound **1** reacts readily with dimethyl acetylenedicarboxylate (DMA) or hexafluoro-2-butyne (HFB) to yield the respective tetracarbonyl, alkyne-bridged products,  $[\text{RhRe}(\text{CO})_4(\mu\text{-RC}\equiv\text{CR})(\text{dppm})_2]$  ( $\text{R} = \text{CO}_2\text{Me}$  (**7**),  $\text{CF}_3$  (**8**)). The IR spectra of these species in the carbonyl region look very reminiscent of that obtained for the sulfido-bridged species,  $[\text{RhRe}(\text{CO})_4(\mu\text{-S})(\text{dppm})_2]$  ( $\nu(\text{CO}) = 1990, 1953, 1868, 1830 \text{ cm}^{-1}$ ),<sup>9</sup> suggesting an analogous formulation for the complexes and a dianionic formulation for the bridging alkyne, which would then bind parallel to the Rh–Re axis as a cis-dimetalated olefin. This would yield a square-planar geometry for the Rh(+I) center and an octahedral geometry for Re(+I). Consistent with this formulation, the <sup>1</sup>H NMR spectrum of **7** shows two resonances for the chemically inequivalent methyl protons, and the <sup>19</sup>F NMR spectrum of **8** displays two quartets (<sup>5</sup>J<sub>FF</sub> = 6 Hz) for the two inequivalent CF<sub>3</sub> groups. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of a <sup>13</sup>CO-enriched sample of compound **7** is also consistent with the structure shown, displaying four carbonyl resonances at  $\delta$  195.8 (doublet of triplets, <sup>1</sup>J<sub>Rh–C</sub> = 59 Hz, <sup>2</sup>J<sub>P(Rh)–C</sub> = 12 Hz), 197.1 (broad multiplet), 197.4 (doublet of doublets, <sup>2</sup>J<sub>C–C</sub> = 21 Hz, <sup>2</sup>J<sub>C–C</sub> = 4 Hz), and 214.5 (doublet of doublets, <sup>1</sup>J<sub>Rh–C</sub> = 10 Hz, <sup>2</sup>J<sub>C–C</sub> = 21 Hz). The high-field signal is clearly established as resulting from the unique Rh-bound carbonyl by its large coupling to this metal. Only this resonance displays resolvable coupling to the phosphorus nuclei. Of the remaining three resonances for the Re-bound carbonyls, the two that are mutually trans are identified by the large carbon–carbon coupling (21 Hz). The higher field signal of these also displays small cis coupling (4 Hz) to the carbonyl that is opposite the alkyne group, whereas the low-field signal displays slight coupling (10 Hz) to Rh. This Rh coupling is much less than that expected for a carbonyl group that is bound to Rh either terminally (typically <sup>1</sup>J<sub>Rh–C</sub>  $\cong$  50–70 Hz) or in a bridging manner (typically ca. 35 Hz)<sup>31</sup> and suggests only a weak interaction with this metal. We suggest that this weak interaction results from the carbonyl being forced close to Rh by rotation of the Re(CO)<sub>3</sub> framework to accommodate the bridging alkyne. Significantly, when the metals are bridged by a small hydrido group in compound **2**, no coupling between Rh and the related Re-bound carbonyl is observed. Compounds **7** and **8** readily lose CO in the absence of a CO atmosphere to yield  $[\text{RhRe}(\text{CO})_3(\mu\text{-RC}\equiv\text{CR})(\text{dppm})_2]$  ( $\text{R} = \text{CO}_2\text{Me}$  (**9**),  $\text{CF}_3$  (**10**)). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **10** shows



three carbonyl resonances of equal intensity at  $\delta$  214, 202, and 194, with only the high-field resonance displaying coupling to Rh (<sup>1</sup>J<sub>Rh–C</sub> = 55 Hz). This clearly indicates that one carbonyl group has been lost from the Re center. In order to maintain an 18-electron configuration at Re, one might anticipate that the bridging alkyne would twist perpendicular to the Rh–Re axis thereby functioning as a neutral 4-electron donor as has previously been observed in related systems.<sup>32,33</sup> However, the <sup>1</sup>H NMR spectrum of **9** and the <sup>19</sup>F NMR spectrum of **10**, which show two

different methyl and trifluoromethyl environments, respectively, and the <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which still show AA'BB'X patterns similar to those of the respective precursors, **7** and **8**, suggest that the alkynes have remained parallel to the Rh–Re axis. Furthermore, this has been confirmed in an analogous RhOs complex, which undergoes CO loss to yield  $[\text{RhOs}(\text{CO})_3(\mu\text{-DMA})(\text{dppm})_2][\text{BF}_4]$ , the structure of which has been determined by X-ray techniques.<sup>34</sup> Previous examples in which an alkyne maintained a cis-dimetalated olefin binding mode upon gain or loss of a ligand have been observed;<sup>31,35–40</sup> however, in these cases the change in metal–metal bond order was accompanied by a change in the number of bridging carbonyl or related groups. In this example the additional pair of electrons donated to Re comes from Rh, in an unusual electron reallocation in which the coordinatively *unsaturated* metal functions as the Lewis base, presumably through donation of the pair of electrons in the Rh d<sub>z<sup>2</sup></sub> orbital, which is directed toward Re. Such a process is not common in such complexes and can be thought of as an inorganic equivalent of the anchimeric or neighboring group effect<sup>41,42</sup> observed in organic chemistry. In this case the neighboring Rh atom donates a pair of electrons to assist in stabilizing a carbonyl group on Re. Addition of CO to **9** and **10** regenerates **7** and **8** respectively. Compound **1** did not react with the nonactivated alkynes, diphenylacetylene and 2-butyne, even in refluxing THF.

Attempts to observe oxidative addition of the C–H bond of phenylacetylene to **1** to give a hydride acetylide species, as was observed at 172 °C for  $[\text{Re}_2(\text{CO})_6(\text{dppm})_2]$ <sup>12</sup> did not meet with success. At ambient temperature reaction with **1** was slow, yielding a complex mix of products after 48 h, including 30% starting material. Refluxing in THF again produced a mixture of species. In both cases hydride resonances were not observed in the <sup>1</sup>H NMR spectra. Furthermore, compound **1** did not react with water or alcohols at temperatures below 110 °C (toluene reflux), in contrast to the above dirhenium species, which at 172 °C yielded the respectively hydrido hydroxide and hydrido alkoxide complexes, via oxidative addition of an oxygen–hydrogen bond.<sup>12</sup> Presumably the low affinity of Rh(I) for hard, oxygen-donor ligands<sup>43</sup> inhibits these reactions.

## Conclusions

The presence of the coordinatively unsaturated Rh(+I) center adjacent to the saturated Re center appears to be instrumental in the chemistry of such species. So, for example,  $[\text{RhRe}(\text{CO})_4(\text{dppm})_2]$  (**1**) undergoes facile reactions at ambient temperature with H<sub>2</sub>, Cl<sub>2</sub>, HCl, and activated alkynes, whereas the analogous complex  $[\text{Re}_2(\text{CO})_6(\text{dppm})_2]$ , which has no site of unsaturation, required vigorous heating at ca. 172 °C before similar reactions were observed.<sup>12</sup> Although the reactions of **1** with alkynes did not result in carbonyl loss at ambient temperature, the products in the other reactions resulted from facile carbonyl loss from Re. Carbonyl loss in these species is facilitated by the bonding involving the bridging hydride and halide species, which can alleviate the coordinative unsaturation at Re (most simply for the halides by dative bond formation utilizing a lone pair of electrons on Cl). However, subsequent CO loss from the alkyne-bridged complexes does occur without a realignment of the bridging alkyne group. It appears that this carbonyl loss is facilitated by the effect of the neighboring Rh, which donates a pair

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of electrons to Re forming a Rh→Re dative bond, regenerating coordinative saturation at Re.

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**Supplementary Material Available:** Tables containing crystal data and details of intensity collection, anisotropic thermal parameters, positional and thermal parameters for the hydrogen atoms, bond lengths and angles within the phenyl groups, and positional and isotropic thermal parameters for all atoms (10 pages); a listing of structure factors (28 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
The University of Iowa, Iowa City, Iowa 52242

## Alkyl Group Effects on CO Insertion into Coordinatively Unsaturated Early-Transition-Metal Alkyls. Preparations and the First Structural Characterizations of Tantalum Enolate-*O* and Tantalum $\eta^2$ -Acyl Complexes

Tara Y. Meyer, Lelia R. Garner, Norman C. Baenziger, and Louis Messerle\*

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Low-pressure carbonylation of the mono(peralkylcyclopentadienyl)tantalum(V) alkyls ( $\eta$ -C<sub>5</sub>Me<sub>4</sub>R)TaR'Cl<sub>3</sub> (R = Me, Et; R' = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Me, CH<sub>2</sub>CMe<sub>3</sub>) yields either the O-bound enolate or the  $\eta^2$ -acyl as shown by IR/NMR spectroscopy and X-ray diffractometry. The *p*-tolyl enolate ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ta(OCH=CHC<sub>6</sub>H<sub>4</sub>-*p*-Me)Cl<sub>3</sub>, derived directly from carbonylation of the tantalum 4-methylbenzyl precursor, is shown to possess a *cis* configuration in solution and in the solid state. Key structural features from a single-crystal X-ray diffraction study of the tetrahydrofuran-ligated enolate complex include a nearly planar enolate with a O(1)–C(1)–C(2)/phenyl least-squares plane dihedral angle of 7 (7)°, a short C(1)–C(2) distance of 1.30 (2) Å, a Ta–O(1) distance of 1.947 (9) Å, and a large Ta–O(1)–C(1) angle of 142.7 (8)°. The mechanism of formation of the enolate from carbonylation of the 4-methylbenzyl complex is discussed. The previously reported acyl ( $\eta$ -C<sub>5</sub>Me<sub>4</sub>R)Ta[C(O)CH<sub>2</sub>CMe<sub>3</sub>]Cl<sub>3</sub> has been reexamined and found to possess a symmetric, strongly distorted  $\eta^2$ -acyl coordination by solution <sup>1</sup>H NMR spectroscopy and solid-state X-ray diffractometry. Key features from the molecular structure determination include a large Ta–C(1)–C(2) angle of 167 (1)°, a C(1)–O bond length of 1.27 (1) Å, a Ta–O bond distance of 2.108 (9) Å, a Ta–C(1) bond distance of 2.07 (1) Å, and a  $\Delta$  [= *d*(Ta–O) – *d*(Ta–C)] value of 0.04 Å, which is the lowest reported for transition-metal  $\eta^2$ -acyls. The molecular structures of ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ta(OCH=CHC<sub>6</sub>H<sub>4</sub>-*p*-Me)Cl<sub>3</sub> and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ta[C(O)CH<sub>2</sub>CMe<sub>3</sub>]Cl<sub>3</sub> are the first structural determinations of a tantalum enolate and of a tantalum  $\eta^2$ -acyl.

### Introduction

The migratory CO insertion reaction is very prominent in organotransition-metal chemistry, homogeneous catalysis, and organometallic applications in organic synthesis for carbon–carbon bond formation.<sup>1</sup> CO insertion into transition-metal alkyls normally generates the  $\eta^1$ - or  $\eta^2$ -acyl derivatives, with the latter<sup>2</sup> most common with the early transition metals, lanthanides, and actinides (though late-transition-metal complexes with  $\eta^2$ -acyls are also known<sup>3</sup>).

In some cases, transition-metal acyls have been converted into metal-bound enolates through thermolysis,<sup>4</sup> catalyzed H migration,<sup>5</sup> or acyl C<sub>α</sub> deprotonation.<sup>6</sup> Such rearrangements may be facile with transition-metal  $\eta^2$ -acyls because of their substantial oxycarbenoid/carbenium<sup>7</sup> character, and examples of intermolecular coupling of postulated  $\eta^2$ -acyls to enediolates<sup>8</sup> and enolates

(via coupling with an acetone ligand<sup>9</sup> or directly from alkyl carbonylation<sup>10</sup>) are known. Main-group and transition-metal enolates are of major importance in organic synthesis for reactions such as aldol condensations and olefin synthesis,<sup>11</sup> and group 4 enolate complexes have been used in aldol chemistry to control stereochemistry.<sup>12</sup> Enolate complexes of the early transition metals have been prepared via direct addition of an enolate anion to a metal halide<sup>13</sup> and reactions<sup>14</sup> of metal alkylidenes with acyl halides. There is one report of direct cyclic enolate ligand synthesis, via carbonylation of a bis(cyclopentadienyl)zirconacyclopentane, which was suggested to proceed through an acyl complex.<sup>15</sup>

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