

pyramidal, and the copper ion sits 0.178 Å above the plane formed from O, N2, and N2'. The Cu-N distances are very similar to those observed for Cu<sub>2</sub>(bpeac)<sup>+</sup>,<sup>6</sup> but the shorter Cu-O bond (2.03 Å in **6** vs. 2.08 Å in the binuclear complex) may simply reflect the fact that, for **6**, the charge of the metal ion is balanced by that of the phenolate ion. Note that, for the binuclear analogue, there are *two* positively charged metal ions per phenolate group; therefore, the electrostatic attraction should be weaker, making the Cu-O bonds longer. Other distances and angles within the complex are unexceptional.<sup>9</sup>

Despite being coordinatively saturated, the tripod complexes with N<sub>3</sub>O donor sets react with CO in solution at room temperature, apparently by dissociation of the amino nitrogen atom.<sup>10</sup> These carbonyl adducts have not been isolated; however, the solution infrared spectrum shows a strong band between 2070 and 2100 cm<sup>-1</sup>, indicative of the terminal carbonyl group (Table I).<sup>11</sup> Only the complex with a thioether ligand fails to react with CO at room temperature. It apparently binds carbon monoxide at low temperature since the emission spectrum changes when CO is added.

At 77 K, all of the complexes (with and without CO) show a low-energy emission between 390 and 550 nm when excited with light having a wavelength between 280 and 310 nm (Table I).<sup>12</sup> We associate this emission with a Cu → pyrazole charge-transfer state on the basis of our results from investigating several different Cu(I) complexes including those having *no* aromatic residues other than pyrazole or imidazole and spanning the range of coordination numbers 2-4.<sup>13</sup> To our knowledge, this is the *first* demonstration of luminescence from synthetic copper carbonyl complexes, and we suggest that this property might eventually provide a convenient probe for comparing synthetic analogues with copper proteins once the luminescence properties of copper complexes with other donor sets (particularly those containing imidazole) have been established. The carbonyl derivative of hemocyanin, for instance, shows

an emission at 550 nm.<sup>14</sup> Further work on the spectroscopic behavior and reactivity of these complexes is currently in progress.

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**Registry No.** **1**, 100113-67-5; **2**, 100113-68-6; **3**, 100113-69-7; **4**, 100113-70-0; **5**, 100113-71-1; **6**, 100113-73-3; Cu(bpeat)(BF<sub>4</sub>), 100113-75-5; Cu(bpeaa)(BF<sub>4</sub>), 100113-77-7; Cu(bpeata)(BF<sub>4</sub>), 100113-79-9; Co(bpeap)(BF<sub>4</sub>), 100113-81-3; Mn(bpeap)(ClO<sub>4</sub>), 100113-83-5; HOC<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>, 95-55-6; CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>, 90-04-0; HSC<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>, 137-07-5; CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>, 2987-53-3; CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-*o*-NH<sub>2</sub>, 95-53-4; HOC<sub>6</sub>H<sub>4</sub>-*o*-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, 19966-11-1; CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-*o*-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, 28005-76-7; HSC<sub>6</sub>H<sub>4</sub>-*o*-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, 100113-72-2; CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>-*o*-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, 100055-33-2; CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-*o*-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, 28005-74-5; NaC<sub>3</sub>H<sub>3</sub>N<sub>2</sub>, 40958-82-5; ethylene oxide, 75-21-8.

**Supplementary Material Available:** Tables S1-S4, including final positional and thermal parameters, bond distances and angles, and values of *F*<sub>o</sub> and *F*<sub>c</sub> for **6** (10 pages). Ordering information is given on any current masthead page.

(14) Finazzi-Agro, A.; Zolla, L.; Flamigni, L.; Kuiper, H. A.; Brunori, M. *Biochemistry* **1982**, *21*, 415-418.

(15) Fellow of the Alfred P. Sloan Foundation, 1985-1987.

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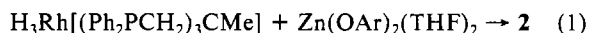
Received October 1, 1985

## Relationship of Adduct Formation to Bimolecular Reductive Elimination from Rhodium Polyhydrides

Sir:

Nucleophilic attack by a transition-metal hydride on a coordinatively unsaturated complex is implicated in certain bimolecular reductive eliminations,<sup>1,2</sup> in inner-sphere electron transfer<sup>3</sup> and in the "condensation route" to produce hydride dimers and clusters.<sup>4</sup> We report here several results that support the idea that  $\mu$ -hydrides provide a pathway for bimolecular reductive elimination to yield heterobimetallic species.

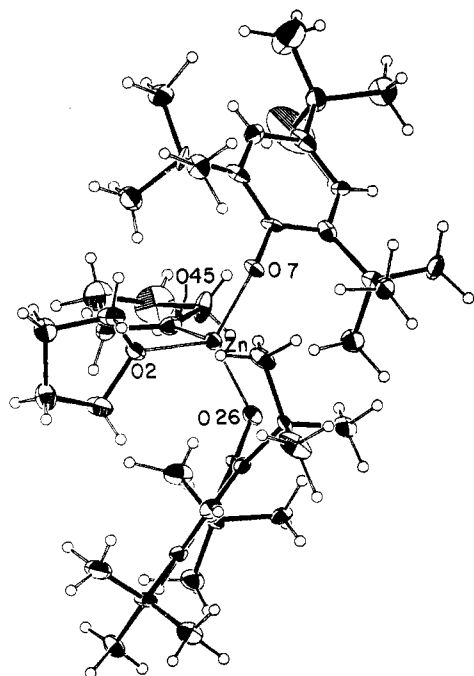
Zinc was attractive to us as a participant in bimolecular reductive elimination since this metal is a component of the catalyst that transforms CO/H<sub>2</sub> mixtures to methanol.<sup>5</sup> The need for a *soluble* zinc bis(alkoxide) was satisfied by the synthesis<sup>6</sup> of Zn(OAr)<sub>2</sub>(THF)<sub>2</sub> (Figure 1), Ar = 2,4,6-tri-*tert*-butylphenyl. The reaction of equimolar H<sub>3</sub>Rh[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>3</sub>CMe]<sup>7</sup> (**1**) with Zn(OAr)<sub>2</sub>(THF)<sub>2</sub> proceeds in benzene at 25 °C with the formation of bimetallic compound **2** (eq 1).



The <sup>1</sup>H and selectively hydride-coupled <sup>31</sup>P NMR spectra of **2** both show AA'A''MXX'X'' patterns<sup>8</sup> analogous to that of **1**,

- (1) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.
- (2) Sartain, W. J.; Selegue, J. P. *Organometallics* **1984**, *3*, 1922.
- (3) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759.
- (4) Venanzi, L. M. *Coord. Chem. Rev.* **1983**, *43*, 251.
- (5) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.
- (6) From Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and HOAr in THF. Crystallographic data: space group P2<sub>1</sub>/c with (-161 °C) *a* = 17.604 (9) Å, *b* = 15.607 (8) Å, *c* = 17.679 (8) Å,  $\beta$  = 114.19 (2)°, and *Z* = 4. *R*(*F*) = 0.062 and *R*<sub>w</sub>(*F*) = 0.061 for 2961 reflections with *F* > 2.33σ(*F*). Positional and thermal parameters are available as supplementary material.
- (7) Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89.
- (8) <sup>1</sup>H NMR (360 MHz, 22 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.52 s (*m*-H, 4 H), 7.03 m (PPh, 12 H), 6.85 m (PPh, 18 H), 2.00 s (*t*-Bu, 36 H), 1.91 d (*J*(PH) = 6.5 Hz, PCH<sub>2</sub>, 6 H), 1.46 s (*t*-Bu, 18 H), 1.1 m (CCH<sub>3</sub>, 3 H), -8.7 m (RhH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (40.5 MHz, 30 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  18.7 d (*J*(RhP) = 93 Hz); unchanged at -80 °C in toluene. IR (Nujol): 1920 (m), 1810 (m) cm<sup>-1</sup>,  $\nu$ (RhH<sub>3</sub>Zn).

- (7) (a) Shaw, J., unpublished results. Anal. Calcd for Co(bpeap)BF<sub>4</sub>·H<sub>2</sub>O: C, 41.76; H, 4.35; N, 15.23. Found: C, 42.16; H, 4.29; N, 15.18. (b) Schwartz, B. J., unpublished results. Anal. Calcd for Mn(bpeap)ClO<sub>4</sub>· $\frac{1}{2}$ THF: C, 44.41; H, 4.56; N, 14.39. Found: C, 44.47; H, 4.70; N, 13.91.
- (8) The crystal structure of **6** was determined by the same procedure and with the same system as described previously (cf. ref 11). Crystal data for **6**: orthorhombic; *a* = 14.613 (5) Å, *b* = 13.023 (5) Å, *c* = 8.297 (4) Å; *Z* = 4; space group *Pnma*; Mo K $\alpha$  radiation; 908 independent nonzero [*I* > 3 $\sigma$ (*I*)] reflections, with 2 $\theta$  between 2 and 55°; *R* = 3.8%; *R*<sub>w</sub> = 3.4%. The copper atom position was located by the Patterson function, and all non-hydrogen atoms were located on difference Fourier maps.
- (9) At first glance, it might appear that the Cu-O-CB1 angle is unusually small; however, that angle is dictated by the five-membered chelate formed by the *o*-aminophenol unit and is in the same range as the corresponding angles observed for both the Cu(I) and the Cu(II) derivatives of bpeac. Cu<sub>2</sub>(bpeac)<sup>+</sup>:<sup>2</sup> Cu1-O-CB1 = 111.6 (8)°; Cu2-O-CB1 = 113.9 (8)°. Cu<sub>2</sub>(bpeac)(OAc)<sup>2+</sup>:<sup>3</sup> Cu1-O1-CB1 = 113.9 (12)°; Cu2-O1-CB1 = 112.6 (12)°. Cu<sub>2</sub>(bpeac)(N<sub>3</sub>)<sup>2+</sup>:<sup>4</sup> Cu1-O1-CB1 = 110.6 (5)°; Cu2-O1-CB1 = 110.8 (5)°.
- (10) We base this conclusion on the results of variable-temperature NMR studies. For both of the copper complexes with N<sub>3</sub>O donor sets, we observe only a single set of sharp resonances for the pyrazole protons that show no line broadening between 20 and -60 °C. If one of the pyrazolyl ligands dissociates upon CO binding, we would expect to see two sets of signals for the inequivalent pyrazolyl groups or some type of temperature-dependent coalescence or line broadening of the signals caused by a ligand-exchange process. This behavior is different from that observed by Karlin for a related binuclear complex in which the ligand contains two pyridylethyl side arms bound to each copper(I) ion. A crystal structure of an adduct with triphenylphosphine shows one of the pyridyl groups has dissociated upon phosphine binding: Karlin, K. D.; Gultneh, Y.; Cruse, R. W.; Hayes, J. C.; Zubieta, J. *Rev. Port. Quim.* **1985**, *27*, 20-21. The difference between the two systems probably results from the fact that in the complexes reported here, the amino group is attached directly to an aromatic ring and is therefore much less basic than the benzylic amino donors in Karlin's ligand.
- (11) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013-6018 and references therein.
- (12) Corrected emission spectra were recorded on an SLM Smart 8000 spectrofluorimeter at 77 K. A frozen glass of each complex in methanol/ethanol was used for these studies. For the carbonyl adducts, the solution was first saturated with CO and then frozen in liquid nitrogen.
- (13) Sorrell, T. N.; Borovik, A. S., manuscript in preparation.



**Figure 1.** ORTEP drawing of  $\text{Zn}(\text{O}-2,4,6-t\text{-Bu}_3\text{H}_2\text{C}_6)_2(\text{THF})_2$ . Selected structural parameters:  $\text{Zn}-\text{O}7 = 1.886$  (6) Å,  $\text{Zn}-\text{O}26 = 1.885$  (7) Å,  $\text{Zn}-\text{O}2 = 2.069$  (7) Å;  $\text{Zn}-\text{O}45 = 2.086$  (6) (angles)  $\text{O}2-\text{Zn}-\text{O}45 = 95.22$  (27)°,  $\text{O}7-\text{Zn}-\text{O}26 = 121.77$  (28)°.

indicating a stereochemically rigid facial octahedral geometry at rhodium. The  $^{31}\text{P}$  NMR spectrum of **2** shows  $J(\text{RhP}) = 93$  Hz, essentially unchanged from the corresponding value (90 Hz) in **1**; no change in rhodium oxidation state is thus indicated. These data, together with the  $^1\text{H}$  NMR integrations, suggest simple adduct formation.

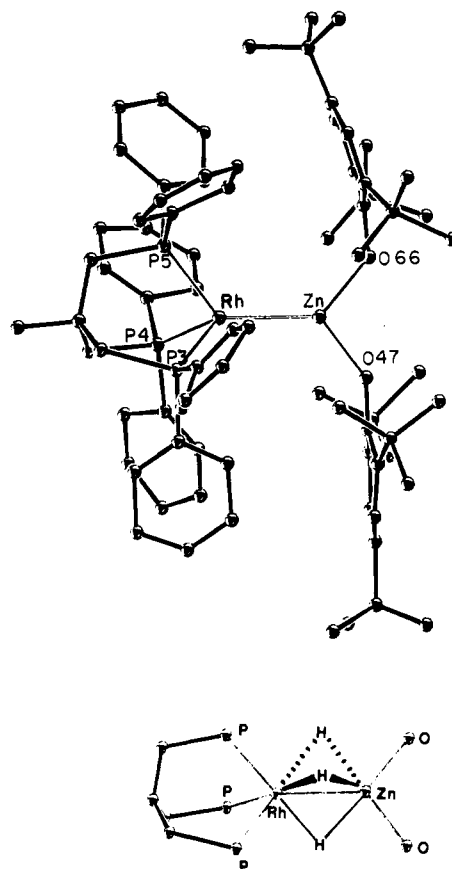
The detailed structure of adduct **2** was established by X-ray diffraction.<sup>9</sup> This reveals (Figure 2) Rh, Zn, and the two oxygens to be coplanar. The AA'A'MXX'X" spin system, the placement of zinc on the idealized  $C_3$  axis of the  $\text{RhP}_3$  unit (all angles  $\text{ZnRhP}$  equal at  $121\text{--}129^\circ$ ),<sup>10</sup> and the three equivalent Rh-P bond lengths taken together permit the conclusion that all three hydride ligands bridge rhodium and zinc, for a  $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{Rh}(\mu\text{-H})_3\text{Zn}(\text{OAr})_2$  formulation. The Rh-Zn separation, 2.533 (7) Å, is identical with the sum of single-bond covalent radii,<sup>11</sup> and is considerably shorter than the Mo-Zn separation (2.793 Å) in  $\text{Cp}_2\text{MoH}_2\text{ZnBr}_2(\text{DMF})$ .<sup>12</sup> Adduct formation causes a major reduction in the  $\text{OZnO}$  angle from what it was in  $\text{Zn}(\text{OAr})_2(\text{THF})_2$ ;  $121.8$  (3)° decreases to  $103.8$  (14)°.

A reductive elimination follows adduct formation when a zinc compound of the stronger base  $\text{N}(\text{SiMe}_3)_2^-$  is used (eq 2). The

$$[\text{MeC}(\text{CH}_2\text{PR}_2)_3]\text{RhH}_3 + \text{Zn}[\text{N}(\text{SiMe}_3)_2] \rightarrow$$

$$[\text{MeC}(\text{CH}_2\text{PR}_2)_3]\text{RhH}_2\text{ZnN}(\text{SiMe}_3)_2 + \text{HN}(\text{SiMe}_3)_2 \quad (2)$$


- (9) Crystallographic data on crystals grown by layering pentane on toluene: space group  $Pbca$  with ( $-161^\circ\text{C}$ )  $a = 26.896$  (24) Å,  $b = 19.35$  (18) Å,  $c = 31.322$  (33) Å, and  $Z = 8$ .  $R(F) = 0.143$  and  $R_w(F) = 0.141$  for 2993 reflections with  $F > 2.33\sigma(F)$  based on a refinement model with independent non-hydrogen atoms, anisotropic only for Zn, Rh, and P (362 parameters). The crystal employed (the best available) suffered an unusually large number (2802) of data with a net intensity of zero. This was subsequently traced to probable loss of lattice solvent, prior to data collection, leaving a detectable "hole" in the unit cell. Check reflections varied randomly within  $\pm 3\%$  during data collection.
- (10) This contrasts to the situation in  $\text{Cu}[(\mu\text{-H})_2\text{IrHP}_3]_2^+$ , where one hydride per iridium remains terminal and the  $\text{CuIrP}$  angles are unequal: Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 6874.
- (11) Rh radius from  $\text{RhMeI}_2(\text{PPh}_3)_2$ : Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Organometallics* **1984**, *3*, 855. Zinc radius from  $(\text{MeZnOme})_4$ : Shearer, H. H. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2046.
- (12) Crotty, D. E.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 2346.



**Figure 2.** ORTEP drawings of  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{Rh}(\mu\text{-H})_3\text{Zn}(\text{OAr})_2$ . Selected structural parameters:  $\text{Rh}-\text{P}3 = 2.317$  (12) Å,  $\text{Rh}-\text{P}4 = 2.329$  (14) Å,  $\text{Rh}-\text{P}5 = 2.333$  (12) Å,  $\text{Zn}-\text{O}47 = 1.93$  (3) Å,  $\text{Zn}-\text{O}66 = 1.96$  (3) Å; (angles)  $\text{Zn}-\text{Rh}-\text{P}3 = 120.5$  (2)°,  $\text{Zn}-\text{Rh}-\text{P}4 = 129.1$  (4)°,  $\text{Zn}-\text{Rh}-\text{P}5 = 126.4$  (4)°,  $\text{Rh}-\text{Zn}-\text{O}47 = 125.6$  (10)°,  $\text{Rh}-\text{Zn}-\text{O}66 = 130.6$  (10)°. Proposed hydride positions (trans to phosphorus) are shown in the lower figure.

reaction, which occurs on time of mixing at  $25^\circ\text{C}$  in benzene, yields products ( $\text{R} = \text{Me}$  and  $\text{Ph}$ ) which are fluxional at  $22^\circ\text{C}$  by both  $^1\text{H}$  and  $^{31}\text{P}$  NMR but may be resolved into two  $^{31}\text{P}$  chemical shifts at  $-80^\circ\text{C}$  and 142 MHz.<sup>13</sup> The reduction in **3** of metal-hydride stretching frequency by  $80\text{ cm}^{-1}$  from the corresponding value ( $1900\text{ cm}^{-1}$ ) in **1** suggests bridging hydrides, an idea consistent with the reduced activation energy for fluxionality in  $[\text{MeC}(\text{CH}_2\text{PR}_2)_3]\text{RhH}_2\text{ZnN}(\text{SiMe}_3)_2$  compared to that in **1**. A definitive structural characterization, as well as reactivity studies, of **3** will be the subject of a future publication.

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**Supplementary Material Available:** Listings of atomic positional and thermal parameters and fully numbered ORTEP diagrams for  $\text{Zn}(\text{OAr})_2(\text{THF})_2$  and  $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{RhH}_2\text{Zn}(\text{OAr})_2$  (5 pages). Ordering information is given on any current masthead page.

- (13) For  $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{RhH}_2\text{ZnN}(\text{SiMe}_3)_2$ :  $^1\text{H}$  NMR (360 MHz,  $22^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.55 m (PPh, 12H), 6.81 m (PPh, 18H), 2.10 br m ( $\text{PCH}_2$ ), 1.2 br m ( $\text{CCH}_3$ ), 0.57 s ( $\text{SiMe}_3$ , 18H), -8.7 qd ( $J(\text{PH}) = 36$  Hz,  $J(\text{RhH}) = 17$  Hz, RhH, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (40.5 MHz,  $30^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  27.6 d ( $J(\text{RhP}) = 111$  Hz); at  $-80^\circ\text{C}$  in toluene broad resonances (intensity 2:1) appear at 34 and 18 ppm.  $^{31}\text{P}$  NMR, selectively hydride-coupled: d of t ( $J(\text{RhP}) = 111$ ,  $J(\text{PH}) = 36$ ) at  $30^\circ\text{C}$ . IR (Nujol):  $1820\text{ cm}^{-1}$  (br),  $\nu(\text{RhH}_2\text{Zn})$ .

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