

**The X-Ray Structures of the Redox-Related Pair  $[\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2]$  and  $[\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2][\text{PF}_6]$ ,  $\text{CH}_2\text{Cl}_2$  (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ): An Experimental Test of the M.O. Bonding Scheme for the  $\mu$ -Alkyne Complexes  $[\text{M}_2(\text{CO})_6(\mu\text{-RC}_2\text{R})]$**

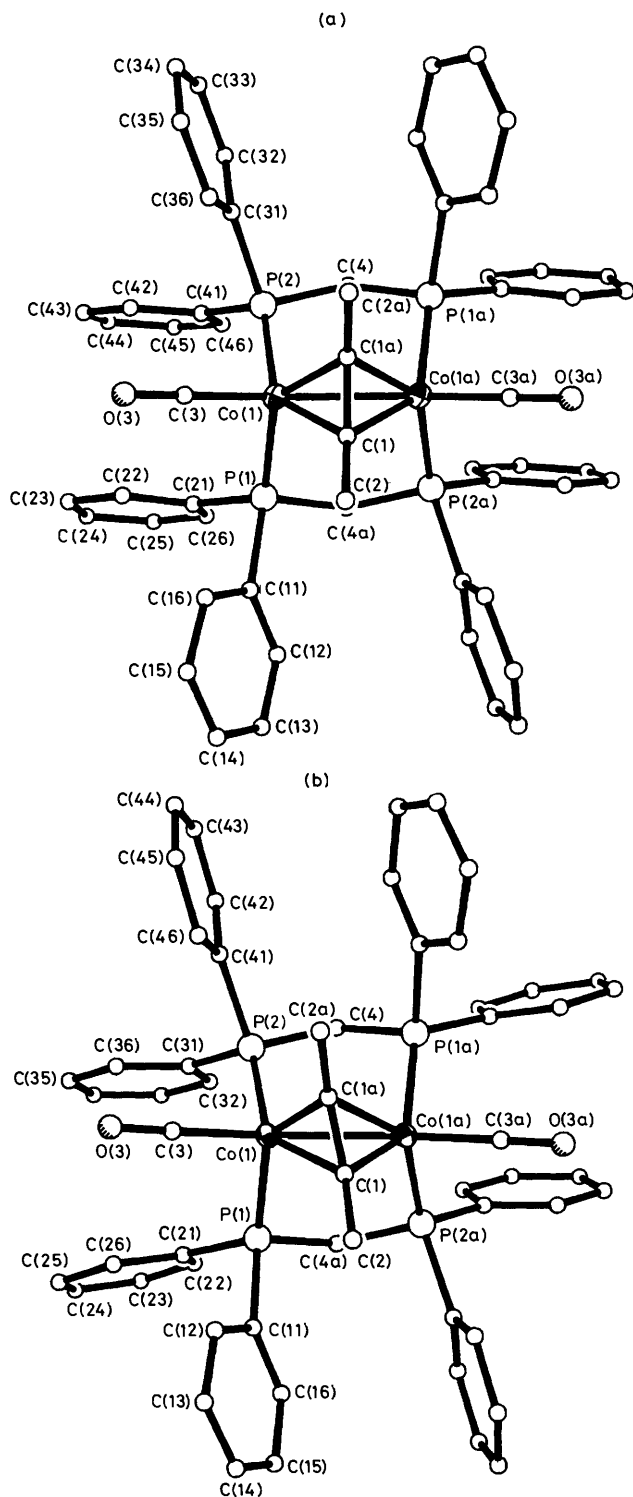
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X-ray structural studies on  $[\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2]^z$  ( $z = 0$  and  $+1$ ) show that one-electron oxidation results in an  $11^\circ$  rotation of the  $\mu$ -alkyne relative to the shortened (by *ca.* 0.1 Å) cobalt–cobalt bond, in accord with predictions based on molecular orbital theory.

The compounds  $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R})]$  are archetypal binuclear acetylene complexes in which the alkyne is essentially orthogonal to the Co–Co bond.<sup>1,2</sup> The electronic and molecular structures of these species have been much studied<sup>3,4</sup> in order to understand the important factors in metal–alkyne bonding. In a general study of the co-ordination of  $\pi$ -hydrocarbon ligands at  $\text{M}_2(\text{CO})_6$  centres, by extended Hückel molecular orbital (e.h.m.o.) methods, Thorn and Hoffmann examined<sup>3</sup> the 32 and 34 valence electron  $\mu$ -alkyne

complexes  $[\text{M}_2(\text{CO})_6(\mu\text{-RC}_2\text{R})]$  ( $\text{M} = \text{Fe}$  and  $\text{Co}$  respectively). Until now their predictions as to the effect of changed electron configuration on the alkyne–metal bonding have remained untested by experiment. We now show, *via* a comparison of the X-ray structures of the redox-related pair  $[\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2]^z$  ( $z = 0$  and  $+1$ , dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), having 34 and 33 valence electrons respectively, that the alkyne rotation predicted by M.O. theory is indeed observed.



**Figure 1.** (a) The molecular structure of (1) viewed along the molecular  $C_2$  symmetry axis. Important molecular dimensions include: bond lengths (Å) Co(1)–Co(1a) 2.513(1), Co(1)–C(1) 1.950(4), Co(1)–C(1a) 1.960(4), Co(1)–P(1) 2.209(1), Co(1)–P(2) 2.197(1), Co(1)–C(3) 1.750(4), C(1)–C(1a) 1.334(8); bond angles ( $^\circ$ ) Co(1a)–Co(1)–C(3) 150.6(1), C(1a)–C(1)–C(2) 132.9(2).

(b) The molecular structure of (1<sup>+</sup>) viewed along the molecular  $C_2$  symmetry axis. Important molecular dimensions include: bond lengths (Å) Co(1)–Co(1a) 2.418(1), Co(1)–C(1) 2.103(3), Co(1)–C(1a) 1.941(4), Co(1)–P(1) 2.243(1), Co(1)–P(2) 2.219(1), Co(1)–C(3) 1.780(4), C(1)–C(1a) 1.309(8); bond angles ( $^\circ$ ) Co(1a)–Co(1)–C(3) 155.1(1), C(1a)–C(1)–C(2) 134.4(2).

**Table 1.** I.r. and e.s.r. spectroscopic, and electrochemical, data for  $[\text{Co}_2(\text{CO})_2(\mu\text{-RC}_2\text{R})(\mu\text{-dppm})_2]^z$  in  $\text{CH}_2\text{Cl}_2$ .

$z$	R	% Yield	$\bar{\nu}(\text{CO})(\text{cm}^{-1})$	$E^\circ/V^a$	$g_{\text{ave}}$
0	Ph	42	1923	0.09	—
+1	Ph	74	1977	0.09	2.110
0	Me	56	1896	–0.09	—
+1	Me	79	1965	–0.09	2.107
0	$\text{CO}_2\text{Me}$	63	1942, 1685 <sup>b</sup>	0.38	—
+1	$\text{CO}_2\text{Me}$	73	2000 1714 <sup>b</sup>	0.38	2.107

<sup>a</sup>  $E^\circ$  at platinum for the reversible couple  $[\text{Co}_2(\text{CO})_2(\mu\text{-RC}_2\text{R})(\mu\text{-dppm})_2]^{0/+1}$ , relative to the saturated calomel electrode. Under the conditions used,  $E^\circ$  for the one electron oxidation of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  is 0.47 V. <sup>b</sup> Ketonic carbonyl.

The red-brown dicarbonyls  $[\text{Co}_2(\text{CO})_2(\mu\text{-RC}_2\text{R})(\mu\text{-dppm})_2]$  (1; R = Me, Ph, or  $\text{CO}_2\text{Me}$ ),<sup>†</sup> prepared from  $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R})]$  and dppm (1:2 ratio) in toluene under reflux, undergo reversible one-electron oxidation at a platinum bead electrode in  $\text{CH}_2\text{Cl}_2$  (Table 1). Chemical oxidation of (1) with the mild oxidant  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  yields (1<sup>+</sup>) as air-stable, brown  $[\text{PF}_6]^-$  salts characterised by i.r. carbonyl bands shifted to higher energy (by ca. 50–70  $\text{cm}^{-1}$ ), broad singlet e.s.r. signals at ca.  $g = 2.1$ , and reversible one-electron reduction waves in the cyclic voltammogram at potentials identical to those for the oxidation of (1).

The X-ray crystal structures<sup>‡</sup> of (1, R = Me) and (1<sup>+</sup>, R = Me) are shown in Figure 1. The effects of oxidation on bond lengths within the  $\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2$  framework are concentrated on the  $\text{Co}_2(\mu\text{-C}_2)$  core. Thus, the metal-metal distance [Co–Co; 2.513(1) Å in (1), 2.418(1) Å in (1<sup>+</sup>)] is markedly shortened and the OC–Co–Co spine is noticeably straightened [C–Co–Co, 150.6(1) $^\circ$  in (1) and 155.1(1) $^\circ$  in (1<sup>+</sup>)]. Most notable, however, is the increased asymmetry in the Co–μ–C distances [Co–C; 1.950(4) and 1.960(3) Å in (1), 1.941(4) and 2.103(3) Å in (1<sup>+</sup>)] which is a consequence of the rotation of the alkyne (by ca. 11 $^\circ$ ) about the molecular  $C_2$  axis of (1) and (1<sup>+</sup>) [C–C and Co–Co vectors are at angles of 90.7 and 102.0 $^\circ$  in (1) and (1<sup>+</sup>) respectively]. In addition to the alkyne being rotated in (1<sup>+</sup>) it is also internally twisted with the  $\text{H}_3\text{C–C–C–CH}_3$  torsion angle rising from 2.2(9) $^\circ$  in (1) to 9.7(9) $^\circ$  in (1<sup>+</sup>), presumably reflecting partial rehybridisation of the μ–C atoms.

<sup>†</sup> All new complexes have satisfactory elemental analyses.

<sup>‡</sup> Crystal data for (1):  $\text{C}_{56}\text{H}_{50}\text{Co}_2\text{O}_2\text{P}_4$ ,  $M = 996.7$ , monoclinic, space group  $C2/c$  (No. 15),  $a = 23.476(4)$ ,  $b = 9.673(2)$ ,  $c = 24.231(4)$  Å,  $\beta = 116.98(2)^\circ$ ,  $U = 4904(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.35$  g  $\text{cm}^{-3}$ ,  $F(000) = 2064$  electrons,  $\mu(\text{Mo–K}\alpha) = 8.4$   $\text{cm}^{-1}$ ,  $T = 295$  K.

Crystal data for (1<sup>+</sup>)· $\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$ :  $\text{C}_{57}\text{H}_{52}\text{Cl}_2\text{Co}_2\text{F}_6\text{O}_2\text{P}_5$ ,  $M = 1226.7$ , monoclinic,  $C2/c$  (No. 15),  $a = 20.343(3)$ ,  $b = 13.835(2)$ ,  $c = 20.589(3)$  Å,  $\beta = 104.98(1)^\circ$ ,  $U = 5597.7(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.46$  g  $\text{cm}^{-3}$ ,  $F(000) = 2508$  electrons,  $\mu(\text{Mo–K}\alpha) = 8.9$   $\text{cm}^{-1}$ ,  $T = 295$  K. Intensity data were collected on a Nicolet P3m diffractometer for a unique quadrant of reciprocal space in the range  $4 < 2\theta < 50^\circ$ , using graphite monochromated Mo– $K\alpha$  X-radiation. Structure solution and refinement (conventional heavy atom methods) gave  $R$  indices 0.052 and 0.050 for (1) and (1<sup>+</sup>)· $\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$  respectively for the 3280 and 3933 unique, observed [ $I > 1.5\sigma(I)$ ], absorption corrected data. In each case the  $[\text{Co}_2(\text{CO})_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2]$  unit shows crystallographically imposed  $C_2$  symmetry as does the  $\text{PF}_6^-$  anion in (1<sup>+</sup>)· $\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$ . The dichloromethane solvate in (1<sup>+</sup>)· $\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$  is disordered about a two-fold axis. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The structural data allow an experimental test of Thorn and Hoffmann's e.h.m.o. calculations on  $[M_2(CO)_6(\mu-RC_2R)]$  ( $M = Fe$  or  $Co$ ) which suggested that depopulation of the  $(a_2)$  h.o.m.o. of **(1)** (assuming  $C_{2v}$  molecular symmetry) would lead to a second-order Jahn-Teller distortion of  $A_2$  symmetry, by alkyne rotation of the type seen in **(1<sup>+</sup>)**. This  $(a_2)$  h.o.m.o. is metal-metal antibonding ( $\pi^*$ ) in character, and removal of one or two electrons from it would therefore be expected to strengthen and shorten the metal-metal bond, again as observed in **(1<sup>+</sup>)**. As discussed by Thorn and Hoffmann, the alkyne rotation distortion is obviated in the 32 electron species  $[Fe_2(CO)_6(\mu-Bu^tC_2Bu^t)]$  (the observed<sup>3</sup> rotation is  $4-5^\circ$ ) by the twisting of one  $Fe(CO)_3$  group relative to the other, giving a staggered  $Fe_2(CO)_6$  conformation (OC-Fe-Fe-CO torsion angles *ca.*  $\pm 45^\circ$ ). In **(1)** and **(1<sup>+</sup>)** such twisting is not possible since the  $\mu$ -dppm ligands enforce a near-eclipsed ('sawhorse') geometry around the  $Co_2$  unit [P-Co-Co-P torsion angles are  $5.5$  and  $9.2^\circ$  for **(1)** and **(1<sup>+</sup>)** respectively, *cf.*  $0.0^\circ$  for the perfectly eclipsed case]. The good quantitative agreement between the amount of alkyne rotation predicted ( $20-30^\circ$  for a two-electron change<sup>3,4</sup>) and observed ( $11^\circ$  for a one-electron change) is particularly noteworthy.

Other aspects of the deformation of **(1)** on oxidation, such as internal twisting of the alkyne and straightening of the

OC-Co-Co-CO spine, were not anticipated by the theoretical studies. Nevertheless, the structural studies on **(1)** and **(1<sup>+</sup>)** taken with e.s.r. spectroscopic studies<sup>5</sup> on the 35 valence electron anion  $[Co_2(CO)_6(\mu-RC_2R)]^-$  provide a detailed picture of the bonding in  $[M_2(CO)_6(\mu-RC_2R)]$ , and in particular of the effects of electron removal from the h.o.m.o., and electron addition to the l.u.m.o., of the dicobalt complexes ( $M = Co$ ).

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