Crystal Structures of Dibromotricarbonylbis[bis(diphenylarsino)methane]tungsten(II) and Dibromodicarbonylbis[bis(diphenylarsino)methane]molybdenum(II)

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Summary In dibromotricarbonylbis[bis(diphenylarsino)-methane]tungsten(II) and dibromodicarbonylbis[bis(diphenylarsino)methane]molybdenum(II) the metal atoms are seven-co-ordinate with capped octahedral environments

THE ligand (dam), [dam = bis(diphenylarsino)methane], reacts with the Group VI halogenocarbonyls [$M(CO)_4X_2$], (M = Mo or W; X = Cl or Br)[1-4] to give the complexes $M(CO)_3(dam)_2X_2$ (I) and $M(CO)_2(dam)_2X_2$ (II). These compounds constitute a unique carbon monoxide-carrying system[5] (equation 1). We report the crystal structures of two typical compounds in this system, (I) with M = W, X = Br and (II) with M = Mo, X = Br.

$$\underset{(I)}{M(CO)_3(dam)_2X_2} \rightleftharpoons \underset{(II)}{M(CO)_2(dam)_2X_2} + CO \qquad (1)$$

Crystal data: Compound (I), $C_{53}H_{44}WBr_2As_4O_3$, triclinic, $M = 1372{\cdot}3$, $a = 19{\cdot}734(20)$, $b = 11{\cdot}590(12)$, $c = 12{\cdot}367(19)$ Å, $\alpha = 103{\cdot}14(10)$, $\beta = 92{\cdot}15(6)$, $\gamma = 87{\cdot}93(11)°$, $U = 2750{\cdot}6$ Å^3, $Z = 2$, $D_c = 1{\cdot}656$, $D_m = 1{\cdot}67(2)$, $F(000) = 1324$, space group $P\bar{1}$. Compound (II), $C_{52}H_{44}MoBr_2As_4O_2$, monoclinic $M = 1256{\cdot}4$, $a = 11{\cdot}543(10)$, $b = 22{\cdot}121(17)$, $c = 19{\cdot}464\ (15)$ Å, $\beta = 94{\cdot}31(11)°$, $U = 4955{\cdot}9$ Å^3, $Z = 4$, $D_c = 1{\cdot}683$, $D_m = 1{\cdot}67(2)$, $F(000) = 2544$, space group $P2_1/c$.

Intensities were recorded using Zr-filtered Mo-K_α radiation on a GE XRD 5 manual diffractometer by the stationary-crystal–stationary-counter method. The structures were solved by Patterson and Fourier syntheses and refined by least squares (M, X, As anisotropic: C, O isotropic). For (I), 3387 independent reflections ($2\theta < 50^{\circ}$) significantly above background have been refined to R 0·092. For (II), 2018 such reflections have been refined to R 0·087. The co-ordination spheres of (I) and (II) are very similar; each metal atom is seven-co-ordinate with a distorted capped octahedral environment. In (I), a carbonyl group occupies the capping position. The capped face contains two carbonyl groups and an arsenic atom, while the uncapped face contains two bromine atoms and an arsenic atom; both (dam) ligands are monodentate. The only change in configuration found in (II) is that one of the carbonyls in the capped face is replaced by an arsenic atom; thus one of the two (dam) ligands becomes chelating. This confirms a prediction made from n.m.r. studies.[5] In both (I) and (II), the angles subtended at the metal atom by the unique carbon atom and atoms in the capped face and uncapped face respectively average to 72 and 128°. Some differences in angles arise from the four-membered ring in (II). Thus the As(2)–Mo–As(3) angle is 66·5(15)° in (II), less than the C(2)–W–As(2) angle of 77·8(13)° in (I). The As(2)–C(3)–As(3) angle in (II) is 91·6(21)° compared to a mean value of 116·5° for As–C–As angles in the monodentate ligand.

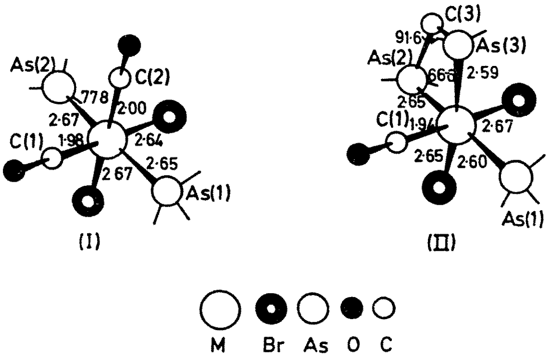

FIGURE. *Projections of the co-ordination spheres of* (I) *and* (II) *viewed down the vector from the* CO *group in the capping position (omitted from the diagram) to the metal atom. Standard deviations are* M–As, Br 0·01, M-C 0·04 Å.

The various ideal seven-co-ordinate configurations are thought to have similar energies[6] and thus it is significant that the replacement of a carbonyl group in (I) by the bulky and less electronegative Ph_2As grouping in (II) has made so little difference to the capped octahedral configuration. The M–Br bond distances in the two structures are comparable and although there is some variation in M–As bond length, neither of the bonds in the chelating ligand in (II) are particularly weak. It is therefore somewhat surprising that, in the formation of (I) from (II), a M–As bond is broken and a carbonyl group added, although carbon monoxide is not a reactive ligand under the conditions used. The bis(diphenylphosphino)methane complexes, analogous to (II),[7] do not take up carbon monoxide. The steric strain in a four-membered ring containing phosphorus would be similar to one containing arsenic and therefore the difference in reactivity is presumably due to the difference in strength in M–P and M–As bonds, phosphorus being a better σ donor and π acceptor than arsenic.

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