# REDOX REACTION ON TREATING fac- OR mer-[Mo(CO)<sub>3</sub>(dppm-PP')(dppm-P)] (dppm = $Ph_2PCH_2PPh_2$ ) WITH Hg(SCN)<sub>2</sub> AND CRYSTAL STRUCTURE OF THE SEVEN-COORDINATE PRODUCT [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-PP')(dppm-P)]

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## (Received 3 July 1986)

Abstract— $[Mo(CO)_2(NCS)_2(dppm-PP')(dppm-P)]$  (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) is formed in a rapid and clean redox reaction when *fac*- or *mer*- $[Mo(CO)_3(dppm-PP')(dppm-P)]$  is treated with Hg(SCN)<sub>2</sub>: dppm-chelate ring-opening with formation of a heterobimetallic species is not observed. The X-ray crystal structure of the product shows the molecule to contain seven-coordinate Mo(II) with "*cis*" CO groups, both monodentate and chelating dppm ligands, and with N-bonded NCS groups. The coordination geometry is intermediate between a capped trigonal prism and a capped octahedron. Crystals of  $[Mo(CO)_2$ (NCS)<sub>2</sub>(dppm-PP')(dppm-P)] are orthorhombic, space group Pna2<sub>1</sub>, with a = 21.583(7) Å, b = 12.775(4) Å, c = 18.484(5) Å, and Z = 4; the final R factor was 0.046 for 3181 observed reflections.

We have described the reactions of Group VI metal carbonyl bis(diphenylphosphino)methane (dppm) derivatives of types fac-[M<sup>1</sup>(CO)<sub>3</sub>(dppm-PP')(dppm-P)] (M<sup>1</sup> = Mo or W) or mer- $[M^{1}(CO)_{3}(dppm-PP')(dppm-P)]$  (M<sup>1</sup> = Cr, Mo or W) with labile Rh(I) or Ir(I) carbonyls to give high yields of heterobimetallic complexes containing the trans, trans- $[M^{1}(\mu-dppm)_{2}M^{2}](M^{2} = Rh \text{ or } Ir)$  skeleton.<sup>1</sup> Similar dppm-chelate ring-opening reactions are induced by the treatment of  $[M^{1}(CO)_{3}(dppm-$ PP')(dppm-P)] with copper(I) chloride or iodide, or with (Ph<sub>3</sub>P)AgCN, resulting in stable heterobimetallics of type  $[M^{1}(CO)_{3}(\mu-dppm)_{2}M^{2}X]$ (M<sup>1</sup> = Cr, Mo or W; M<sup>2</sup> = Cu, X = Cl or I; $M^2 = Ag$ , X = CN), and preliminary results show that treatment with (Ph<sub>3</sub>P)AuCl gives similar heterobimetallic complexes containing a  $[M^{1}(\mu$  $dppm)_2Au$ ] (M<sup>1</sup> = Mo or W) frame.<sup>2</sup> Mixed Group VI metal-platinum complexes of type  $[M^{1}(CO)_{3}(\mu$  $dppm)_2PtH(X)$ ] (M<sup>1</sup> = Cr, Mo or W; X = Cl or Br) have also been prepared by treating mer-[ $M^{1}(CO)_{3}(dppm-PP')(dppm-P)$ ] with trans-[ $PtH(X)(PPh_{3})_{2}$ ].<sup>3</sup>

## **RESULTS AND DISCUSSION**

We report here on a different and contrasting behaviour when mercury(II) salts are used: these generally oxidize [Mo(CO)<sub>3</sub>(dppm-PP')(dppm-P)] to a mononuclear Mo(II) complex rather than induce ring-opening and formation of a heterobimetallic species. Thus treatment of fac- or mer- $[Mo(CO)_3(dppm-PP')(dppm-P)]$  with HgCl<sub>2</sub> in dichloromethane at 20°C gives [Mo(CO)<sub>2</sub>(dppm- $PP'_{2}$ Cl]Cl in good (> 60%) yield, together with metallic mercury. We have also prepared this complex by treating  $cis{Mo(CO)_2(dppm-PP')_2}$  with chlorine; the corresponding bromo and iodo complexes  $[Mo(CO)_2(dppm-PP')_2X]X$  (X = Br or I) have been prepared previously by treating cis- $[Mo(CO)_2(dppm-PP')_2]$  with X<sub>2</sub>.<sup>4</sup>

Similarly, treatment of either fac- or mer-[Mo(CO)<sub>3</sub>(dppm-PP')(dppm-P)] with Hg(SCN)<sub>2</sub> in dichloromethane gives mercury metal and golden yellow crystals of the seven-coordinate Mo(II) complex [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-PP')(dppm-P)] in a

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very rapid and clean reaction. This complex has previously been prepared by treating  $[MoCl_2(CO)_4]$ with ammonium thiocyanate followed by dppm, and our IR data (Nujol mull: v<sub>CN</sub> 2095 and 2070 cm<sup>-1</sup>,  $v_{CO}$  1960 and 1890 cm<sup>-1</sup>) are very similar to those reported before.<sup>5</sup> The  ${}^{31}P-{}^{1}H$  NMR spectrum of [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-PP')(dppm-P)] in CD<sub>2</sub>Cl<sub>2</sub> (not previously recorded) showed : a doublet at  $\delta$  -25.3 ppm, assigned to the non-coordinating phosphorus atom; a multiplet at 34.6 ppm due to the coordinated phosphorus atom of the monodentate dppm ligand; and a broad hump at 5.3 ppm, assigned to the chelating dppm phosphorus atoms. At  $-50^{\circ}$ C this broad resonance was resolved into two 1:1:1:1 quartets at -17.2 and 28.2 ppm, the temperature dependence of the spectrum presumably a result of ligand scrambling about the seven-coordinate molybdenum(II) centre.

It seems likely that the Mo(II) complexes described above are formed via Mo-Hg bonded intermediates. Treatment of  $[M(CO)_4(bipy)]$ (M = Mo or W, bipy = 2,2'-bipyridine) with HgX<sub>2</sub> (X = Cl, Br, I or SCN) has been shown to give complexes of type  $[M(CO)_3(bipy)(HgX)X]$ .<sup>6,7</sup> These M-Hg species were found to be unstable in polar solvents, decomposing to give metallic mercury.<sup>7</sup> Thus we tentatively propose that *fac*- or *mer*- $[Mo(CO)_3(dppm-PP')(dppm-P)]$  initially reacts with HgX<sub>2</sub> to give  $[Mo(CO)_2(dppm-PP')(dppm-P)(HgX)X]$ , which subsequently decomposes to give the observed product and mercury metal.

Single crystals of  $[Mo(CO)_2(NCS)_2(dppm-PP')(dppm-P)]$  suitable for an X-ray diffraction study were obtained as golden yellow prisms from acetone-methanol. The structure (Fig. 1) confirms



Fig. 1. Molecular structure of  $[Mo(CO)_2(NCS)_2(dppm-PP')(dppm-P)]$ , showing the principal atomic numbering.

the seven-coordination around Mo(II) with "cis" CO groups, both bi- and monodentate dppm ligands, and with N-bonded NCS ligands; all these features were predicted from the IR and <sup>1</sup>H NMR data.<sup>5</sup> The choice of an idealized coordination geometry in a seven-coordinate complex is often not simple and has been the subject of several recent articles.<sup>8-11</sup> One simple procedure is to compare the interbond angles at the metal centre (Table 1) with the values computed for various idealized polyhedra.<sup>8,10-12</sup> This procedure reveals the coordination geometry about the Mo(II) centre to be intermediate between a capped trigonal prism [with N(1) in the unique capping position, P(1), N(2), P(3) and C(4) in the capped quadrilateral face, and P(2) and C(3) in the unique edge] and a capped octahedron [with C(3)in the capping position, P(2), P(3) and C(4) in the capped face, and P(1), N(1) and N(2) in the uncapped face]. This geometry is similar to several other M(II) complexes (M = Cr, Mo or W) containing CO and PR<sub>3</sub> ligands,<sup>8</sup> e.g. [MoCl<sub>2</sub>(CO)<sub>2</sub> (PMe<sub>2</sub>Ph)<sub>3</sub>],<sup>13</sup> and in particular the interbond angles at Mo in the present structure are very

Table 1. Bond lengths (Å) and angles (°) for [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-*PP'*)(dppm-*P*)], with estimated standard deviations in parentheses

(a) Coordination sphere	
MoN(1)	2.159(7)
MoN(2)	2.195(8)
Mo-C(3)	1.96(1)
Mo-C(4)	1.98(1)
<b>Mo</b> — <b>P</b> (1)	2.597(3)
Mo—P(2)	2.514(2)
Mo-P(3)	2.554(2)
N(2)MoC(4)	169.2(3)
P(1)—Mo—P(3)	160.0(1)
N(1)MoP(2)	148.5(2)
N(1)MoC(3)	140.4(4)
P(1)—Mo—C(3)	126.3(3)
P(2)—Mo—P(3)	126.2(1)
N(2) - Mo - C(3)	115.7(3)
P(2)—Mo—C(4)	107.8(3)
P(3)—Mo—C(4)	99.9(3)
P(1)—Mo—C(4)	90.9(3)
P(1) - Mo - N(1)	86.7(2)
N(1) - Mo - N(2)	85.1(3)
P(1)—Mo—N(2)	84.9(2)
N(1)	84.8(3)
N(2)	81.5(2)
N(2)P(2)	79.4(2)
N(1)—Mo—P(3)	77.6(2)
C(3)MoC(4)	74.8(4)
P(3)—Mo—C(3)	73.2(3)
P(2)—Mo—C(3)	71.0(3)
P(1)P(2)	64.8(1)
	(continued)

(b) Ligand geometry (selected parameters)	
N(1)—C(1)	1.15(1)
N(2)—C(2)	1.15(1)
C(1)— $S(1)$	1.65(1)
C(2)—S(2)	1.63(1)
C(3)O(3)	1.16(1)
C(4)—O(4)	1.15(1)
P(1)—C(5)	1.86(1)
P(2)C(5)	1.82(1)
P(3)C(6)	1.84(1)
P(4)C(6)	1.90(1)
<b>P(1)</b> — <b>C</b> (11)	1.834(5)
P(1)—C(21)	1.818(5)
P(2)C(31)	1.841(5)
P(2)—C(41)	1.812(5)
P(3)—C(51)	1.840(5)
P(3)C(61)	1.833(5)
P(4)—C(71)	1.868(5)
P(4)C(81)	1.850(6)
Mo-N(1)-C(1)	175.8(7)
Mo - N(2) - C(2)	159.7(7)
N(1)-C(1)-S(1)	178.7(8)
N(2)-C(2)-S(2)	177.4(8)
MoC(3)O(3)	176.8(9)
Mo-C(4)-O(4)	178.4(8)
Mo - P(1) - C(5)	92.5(3)
Mo - P(2) - C(5)	96.3(3)
P(1) - C(5) - P(2)	96.0(4)
Mo-P(3)-C(6)	112.3(3)
P(3) - C(6) - P(4)	113.8(5)

Table 1 (continued)

close to those reported for the complex  $[MoCl_2(CO)_2(dppm-PP')(dppm-P)]$ ,<sup>14</sup> in which the introduction of a chelate ring accentuates the distortion more towards the capped trigonal prismatic than the capped octahedral geometry.

The Mo-N bond lengths (see Table 1) differ by ca 0.04 Å with the shorter bond [Mo-N(1)] being in the unique capping position of the capped trigonal prismatic structure, and similar differences are found in the corresponding Mo-Cl bond lengths of the two dichloro complexes mentioned above,<sup>13,14</sup> the shorter bond again being in this site. The Mo-P bond lengths (see Table 1) are all different, in the sequence Mo-P(1) >Mo-P(3) > Mo-P(2), and the same pattern is found in several related complexes, e.g.  $[MoCl_2(CO)_2(dppm-PP')(dppm-P)]$ .<sup>14</sup> Competition for the metal  $d\pi$  electrons presumably lengthens the Mo—P(1) and Mo–P(3) bonds, which are mutually trans, whereas the Mo-P(2) bond is the shortest since it is nearly trans to an NCS group which does not compete as strongly for metal  $d\pi$ electrons. The Mo-P(1) bond may be the longest of the Mo-P bonds because it is additionally somewhat *trans* to the carbonyl group C(3)—O(3) (see Table 1 for angles). The chelate ring angle P(1)—C(5)—P(2) of 96.0(4)° is significantly larger in the present complex than in [MoCl<sub>2</sub>(CO)<sub>2</sub>(dppm-PP')(dppm-P)], where it is 90(1)°, <sup>14</sup> though the present value is in the middle of the range reported in a compilation of data for structures containing chelating dppm.<sup>15</sup> As in the homologous dichloro complex,<sup>14</sup> the four-membered chelate ring is puckered with the methylene C(5) displaced towards N(2) and away from the two carbonyl groups, allowing the bulky phenyl rings to avoid unfavourable intramolecular contacts. This puckering can be considered to be quite strong as measured by the relatively small P(1)-Mo-P(2) bite angle of  $64.8(1)^{\circ}$  and relatively large distance of the methvlene C(5) atom from the P(1)-Mo-P(2) plane (0.67 Å) (see Ref. 15 for an analysis of chelating dppm stereochemistry).

It is noticeable that one of the isothiocyanate groups is bonded to the metal centre in a markedly non-linear fashion [Mo—N(2)—C(2) = 159.7(7)°], but the angle falls well within the range defined by other structural determinations of complexes containing N-bonded thiocyanate ligands.<sup>16-18</sup> The smaller Mo—N(2)—C(2) angle [159.7(7)° compared to Mo—N(1)—C(1) of 175.8(7)°] within the present structure is probably the result of having a CO ligand virtually *trans* [N(2)—Mo—C(4) = 169.2(3)°] to the isothiocyanate group, the resultant decrease in electron density available for bonding being reflected in predominance of

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the resonance form S=C=N rather than  $\bar{S}$ -C=N -M, though the correlation of N-C and C-S distances with the M-N-C angles in this structure is not as distinct as in others.<sup>17,18</sup> Steric or packing effects within the crystal have also been invoked to explain bent M-N-CS angles,<sup>18</sup> but there are no intermolecular contacts significantly less than the sum of van der Waals' radii in the present structure, and the low crystal density ( $D_c = 1.35 \text{ g cm}^{-3}$ ) is indicative of the somewhat loose packing of the molecules within the crystal.

#### **EXPERIMENTAL**

Reactions were carried out in an atmosphere of dry dinitrogen in deaerated, dried solvents. IR spectra were recorded on a Perkin–Elmer 457 grating spectrometer and <sup>31</sup>P–{<sup>1</sup>H} NMR spectra were recorded on a JEOL FX100 instrument operating at 40.25 MHz and with positive chemical shifts to high frequency relative to 85% H<sub>3</sub>PO<sub>4</sub>.

## *Preparation of* [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-*PP'*) (dppm-*P*)]

A stirred solution of fac-[Mo(CO)<sub>3</sub>(dppm-PP')(dppm-P)] (0.200 g, 0.21 mmol) in dichloromethane (8 cm<sup>3</sup>) was treated with  $Hg(SCN)_2$ (0.067 g, 0.21 mmol). The solution turned red almost immediately and carbon monoxide was evolved. After 30 min of stirring a small volume of methanol ( $ca 3 \text{ cm}^3$ ) was added to aid deposition of metallic mercury. The reaction mixture was filtered and methanol added to precipitate out golden yellow crystals of [Mo(CO)<sub>2</sub>(NCS)<sub>2</sub>(dppm-PP')(dppm-P)]. Yield 0.096 g (44%). Analysis found (required): C, 62.4 (62.6); H, 4.2 (4.3); N, 2.6 (2.7)%. A similar yield was obtained when mer- $[Mo(CO)_3(dppm-PP')(dppm-P)]$  was used as the starting material.

## Crystal data

 $C_{54}H_{44}MoN_2O_2P_4S_2$ , M = 1036.91, orthorhombic, a = 21.583(7) Å, b = 12.775(4) Å, c = 18.484(5) Å, U = 5096(2) Å<sup>3</sup>, space group  $Pna2_1$  (No. 33), Z = 4,  $D_c = 1.35$  g cm<sup>-3</sup>, F(000) = 2128, graphite-monochromated Mo- $K_{\alpha}$ radiation,  $\lambda = 0.71069$  Å,  $\mu$ (Mo- $K_{\alpha}$ ) = 4.93 cm<sup>-1</sup>. Golden yellow prisms from acetone-methanol. Crystal dimensions (distance to faces from centre): 0.155 (100,  $\overline{1}00$ ), 0.148 (011,  $0\overline{11}$ ), 0.165 ( $0\overline{11}$ ,  $01\overline{1}$ ) mm.

## Structure determination

Cell dimensions and their standard deviations were obtained by least-squares refinement of diffractometer setting angles for 15 automaticallycentred reflections having  $34^{\circ} < 2\theta < 39^{\circ}$ . Intensities of 3405 independent reflections (*h*, *k*, *l*;  $4^{\circ} < 2\theta < 45^{\circ}$ ) were measured on a Syntex *P*2<sub>1</sub> diffractometer in the  $\omega$ -2 $\theta$  scan mode using scan speeds, according to a prescan intensity, between 2 and 29° min<sup>-1</sup>, and with the scans running from 1° below  $K_{\alpha 1}$  to 1° above  $K_{\alpha 2}$ . The structure analysis used the 3181 reflections with  $I > 2\sigma(I)$  after correction for Lorentz and polarization factors; absorption effects were corrected numerically (maximum and minimum transmission factors for full data set = 0.89 and 0.83).<sup>19</sup>

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for all atoms except H and the phenyl ring C atoms, using the SHELX program system.<sup>19</sup> The phenyl rings were refined as rigid groups with idealized  $D_{6h}$ geometry, the C atoms having individual isotropic thermal parameters and C---C distances of 1.395 Å. All H atoms, many of which were found in difference maps, were included in the calculation at idealized positions with C-H fixed at 1.08 Å; their isotropic temperature factors were treated as two single parameters (for aromatic or methylene H). The refinement for 251 parameters converged to R = 0.046 and  $R_w = \Sigma w^{1/2} \Delta / \Sigma w^{1/2} |F_o| = 0.048$ , employing the weighting scheme  $w = 1/(\sigma^2 F_a +$  $0.0004F_o^2$ ) to give a flat analysis of variance with increasing  $\sin \theta$  and  $(F_o/F_{max})^{1/2}$ . Refinement of the alternative enantiomorphic specification gave larger R-factors (though not significantly so) and the original structure was retained.\* A final difference map was featureless. Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in Ref. 20.

Acknowledgements-We thank the SERC for support and the University of Leeds for a Fellowship (to A.T.H.).

#### REFERENCES

- A. Blagg, G. R. Cooper, P. G. Pringle, R. Robson and B. L. Shaw, J. Chem. Soc., Chem. Commun. 1984, 933.
- A. Blagg, A. T. Hutton, B. L. Shaw and M. Thornton-Pett, *Inorg. Chim. Acta* 1985, 100, L33.
- 3. A. Blagg and B. L. Shaw, unpublished work.
- A. M. Bond, R. Colton and J. J. Jackowski, *Inorg. Chem.* 1975, 14, 2526.
- R. Colton and G. R. Scollary, Aust. J. Chem. 1968, 21, 1435.
- K. Edgar, B. F. G. Johnson, J. Lewis and S. B. Wild, J. Chem. Soc. A 1968, 2851; P. D. Brotherton, J. M. Epstein, A. H. White and S. B. Wild, Aust. J. Chem. 1974, 27, 2667.
- M. P. Pardo and M. Cano, J. Organomet. Chem. 1984, 260, 81.
- 8. M. G. B. Drew, Prog. Inorg. Chem. 1977, 23, 67.
- S. J. Lippard, Prog. Inorg. Chem. 1976, 21, 91; E. L. Muetterties and L. J. Guggenberger, J. Am. Chem. Soc. 1974, 96, 1748; 1977, 99, 3893; J. K. Kouba and S. S. Wreford, Inorg. Chem. 1976, 15, 1463; 1978, 17, 1696; E. B. Dreyer, C. T. Lam'and S. J. Lippard, Inorg. Chem. 1979, 18, 1904; P. Brant, F. A.

<sup>\*</sup> Atomic coordinates, thermal parameters, full bond length and angle data, and structure factor values have been deposited as supplementary material with the Editor from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

Cotton, J. C. Sekutowski, T. E. Wood and R. A. Walton, J. Am. Chem. Soc. 1979, 101, 6588.

- D. J. Szalda, J. C. Dewan and S. J. Lippard, *Inorg. Chem.* 1981, 20, 3851.
- 11. C. M. Giandomenico, J. C. Dewan and S. J. Lippard, J. Am. Chem. Soc. 1981, 103, 1407.
- R. Hoffmann, B. F. Beier, E. L. Muetterties and A. R. Rossi, *Inorg. Chem.* 1977, 16, 511.
- A. Mawby and G. E. Pringle, J. Inorg. Nucl. Chem. 1972, 34, 517.
- 14. M. G. B. Drew, A. P. Wolters and I. B. Tomkins, J. Chem. Soc., Dalton Trans. 1977, 974.

- P. W. R. Corfield, J. C. Dewan and S. J. Lippard, *Inorg. Chem.* 1983, 22, 3424.
- A. Ferrari, A. Braibanti, G. Bigliardi and A. M. Lanfredi, Acta Cryst. 1965, 18, 367.
- 17. A. C. Hazell, J. Chem. Soc. 1963, 5745.
- 18. J. R. Knox and K. Eriks, Inorg. Chem. 1968, 7, 84.
- 19. G. M. Sheldrick, SHELX-76 Program System. University of Cambridge (1976).
- J. A. Ibers and W. C. Hamilton (Eds), *International Tables for X-Ray Crystallography*, Vol. 4. Kynoch Press, Birmingham (1974).