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# ASSEMBLAGE OF MULTIMETAL COMPLEXES USING THE DIPHOSPHOXANE (P–O–P) LINKAGE

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## Summary

Heterobimetallic complexes can be prepared using the monodentate diphosphoxane ligand in $Mo(CO)_5PPh_2OPPh_2$. Reactions with $Cr(CO)_5CH_3CN$ and $Fe_2(CO)_9$ yielded the corresponding bimetallic products. The structure of $Mo(CO)_5PPh_2OPPh_2Fe(CO)_4$ was established by a single-crystal X-ray study. Cell data: Space group $P\bar{1}$, monoclinic, $a$ 10.533(2), $b$ 10.993(2), $c$ 16.439(3) Å; $\alpha$ 97.86(2), $\beta$ 92.34(1), $\gamma$ 116.20(1)°; $Z = 2$, $D_c$ 1.561 g cm$^{-3}$. $R_F$ is 0.037 for 3830 observed reflections. The diphosphoxane ligand was found to bridge an octahedral Mo and the axial site of a trigonal bipyramidal Fe. Reaction of two equivalents of $Mo(CO)_5PPh_2OPPh_2$ with $(PhCN)_2PdCl_2$ produced the trimetallic complex *trans*-$PdCl_2[PPh_2OPPh_2Mo(CO)_5]_2$. The trimetallic complexes $P[OPR_2Mo(CO)_5]_3$ were prepared from the reaction of $PCl_3$ with $Na[OPR_2Mo(CO)_5]$ (R = Ph, OEt). Similarly, a bimetallic complex $PhP[OP(OEt)_2Mo(CO)_5]_2$ can be prepared from $PhPCl_2$. These products illustrate the usefulness of the diphosphoxane linkage in the synthesis of multimetal complexes.

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## Introduction

Multimetallic complexes containing similar or distinct metals have received considerable attention due to their potential for cooperative or sequential reactivities [1]. Bridging diphosphine ligands, especially bis(diphenylphosphino)methane and its derivatives, have been used extensively to prepare homo- and hetero-bimetallic complexes [2]. We have been investigating the coordination chemistry of diphos-

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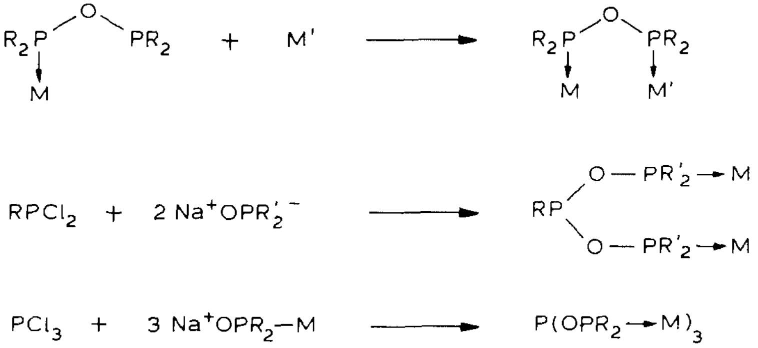
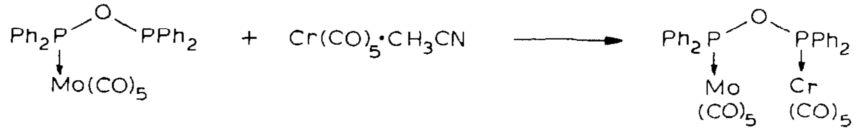
phine monoxide ($OP_2R_4$) and its diphosphoxane tautomer ($R_2POPR_2$) [3–5]. We have found that bi- and tri-metallic complexes linked by P–O–P bonds can now be readily synthesized using the following routes:

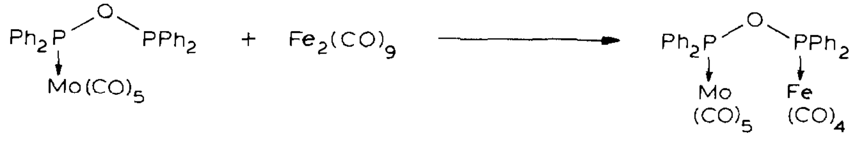


## Results and discussion

The monodentate tetraphenyldiphosphoxane ligand in $Mo(CO)_5PPh_2OPPh_2$ readily displaced labile donors on other metals to give bridged bimetallic products. From $Cr(CO)_5 \cdot CH_3CN$ we isolated a light yellow complex characterized as $Mo(CO)_5$–$Ph_2OPPh_2$–$Cr(CO)_5$ (I). Reaction with $Fe_2(CO)_9$ yielded the yellow complex $Mo(CO)_5$–$PPh_2OPPh_2$–$Fe(CO)_4$ (II) whose structure was confirmed by an X-ray structural study.



(I)



(II)

The molecule II contains a tetraphenyldiphosphoxane bridging a six-coordinate Mo and a five-coordinate Fe (Fig. 1). Angles around the Mo atom are slightly distorted from an octahedral geometry with values from 84.3(2)° for C(2)–Mo–C(3) to 94.6(2)° for C(1)–Mo–C(4). The Fe atom has a slightly distorted trigonal bipyramidal geometry with the phosphorus in the expected axial position.

Comparison of observed bond distances around Mo with other reported $Mo(CO)_5$-phosphine structures suggests the $\mu$-$Ph_2POPPh_2$ ligand to be a better $\pi$-acceptor than $PPh_3$ [6]. Supporting this is the Mo–P(1) bond distance of 2.483(1) Å. In addition, the axial Mo–C(5) of 2.026(5) Å and C(5)–O(5) of 1.135(6) Å are reasonably close to the average values of Mo–$C_{eq}$ of 2.03(1) Å and C–$O_{eq}$ of 1.14(1) Å.

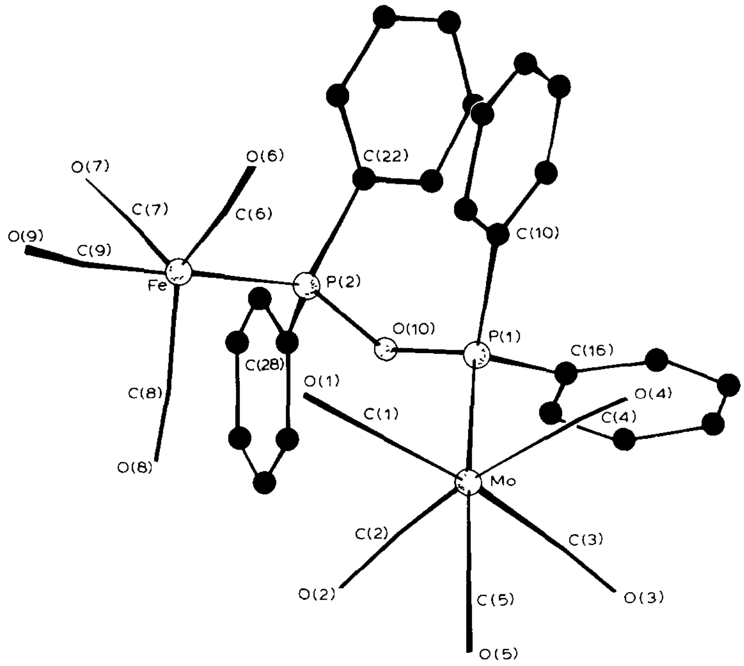


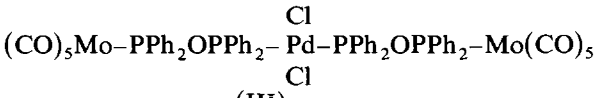
Fig. 1. The molecular structure of $Mo(CO)_5PPh_2OPPh_2Fe(CO)_4$ (II).

Carbonyl bond lengths around Fe show marginal differences. The values of axial Fe–C(9) at 1.798(5) Å and C(9)–O(9) at 1.136(6) Å can be compared to the respective average values of equatorial Fe–C at 1.77(1) Å and C–O at 1.15(1) Å. Analogous data for $Fe(CO)_4PPh_3$ and $Fe(CO)_4PPh_2H$ show essentially similar axial and equatorial carbonyl Fe–C and C–O distances [7]. One further observation is the unusually short Fe–P(2) distance of 2.209(2) Å which is outside the range of 2.224(3)–2.372(2) Å found in typical Fe–phosphine complexes [7,8].

The bridging P–O–P angle at 146.4(2)° can be compared to the value of 142° found in $(C_5H_5)Mn(CO)_2PMe_2OPMe_2Mn(CO)_2(C_5H_5)$ and contrasted with the chelating P–O–P angle of only 103.3(1)° in *cis*-$(CO)_4Mo(PPh_2OPPh_2)$ [9,4]. The two P–O distances are slightly asymmetrical with P(1)–O(10) at 1.641(3) Å and P(2)–O(10) at 1.630(3) Å. Other selected bond distances are listed in Table 1. Important bond angles are presented in Table 2.

Reaction of two equivalents of $Mo(CO)_5PPh_2OPPh_2$ with $(PhCN)_2PdCl_2$ yielded a yellow solid $PdCl_2[PPh_2OPPh_2Mo(CO)_5]_2$ (III). Analysis of its $^{31}P$ NMR spectrum (Table 3) and the observation of a single Pd–Cl stretch in its infrared spectrum at 365 $cm^{-1}$ suggest a *trans*-geometry [10,11].

$(PhCN)_2PdCl_2 + 2\ Mo(CO)_5PPh_2OPPh_2 \rightarrow$



$$(CO)_5Mo\text{–}PPh_2OPPh_2\text{–}\underset{Cl}{\overset{Cl}{Pd}}\text{–}PPh_2OPPh_2\text{–}Mo(CO)_5$$

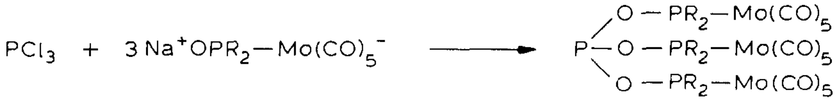
(III)

TABLE 1

SELECTED BOND DISTANCES IN Å (Esd's refer to last digit)

| | | | |
|---|---|---|---|
| Mo–P(1) | 2.483(1) | Fe–P(2) | 2.209(2) |
| Mo–C(1) | 2.047(5) | Fe–C(6) | 1.763(5) |
| Mo–C(2) | 2.002(5) | Fe–C(7) | 1.768(5) |
| Mo–C(3) | 2.007(5) | Fe–C(8) | 1.789(5) |
| Mo–C(4) | 2.055(5) | Fe–C(9) | 1.798(5) |
| Mo–C(5) | 2.026(5) | | |
| P(1)–O(10) | 1.641(3) | P(2)–O(10) | 1.630(3) |
| P(1)–C(10) | 1.826(5) | P(2)–C(22) | 1.825(5) |
| P(1)–C(16) | 1.812(5) | P(2)–C(28) | 1.815(5) |
| C(1)–O(1) | 1.135(6) | C(6)–O(6) | 1.154(6) |
| C(2)–O(2) | 1.148(6) | C(7)–O(7) | 1.155(6) |
| C(3)–O(3) | 1.152(6) | C(8)–O(8) | 1.138(6) |
| C(4)–O(4) | 1.130(6) | C(9)–O(9) | 1 136(6) |
| C(5)–O(5) | 1.135(6) | | |

Sodium salts of the coordinated diphenylphosphinous acid $Mo(CO)_5PPh_2OH$ and diethylphosphite $Mo(CO)_5P(OEt)_2OH$ react readily with $PCl_3$ to give white trimetallic complexes linked by P–O–P bridges (IV, V):



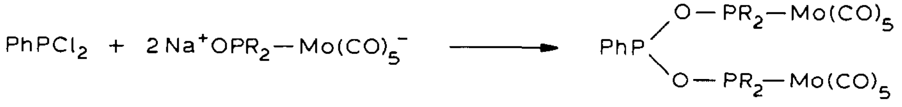
( IV , R = OEt ,
V , R = Ph )

TABLE 2

SELECTED BOND ANGLES IN DEGREES (Esd's refer to last digit)

| | | | |
|---|---|---|---|
| P(1)–Mo–C(1) | 92.6(1) | P(2)–Fe–C(6) | 94.5(2) |
| P(1)–Mo–C(2) | 88.9(1) | P(2)–Fe–C(7) | 87.8(2) |
| P(1)–Mo–C(3) | 89.2(1) | P(2)–Fe–C(8) | 90.6(2) |
| P(1)–Mo–C(4) | 89.8(1) | P(2)–Fe–C(9) | 175.7(2) |
| P(1)–Mo–C(5) | 178.0(1) | | |
| C(1)–Mo–C(2) | 90.6(2) | C(6)–Fe–C(7) | 121.0(2) |
| C(1)–Mo–C(4) | 94.6(2) | C(6)–Fe–C(8) | 118.4(2) |
| C(1)–Mo–C(5) | 89.0(2) | C(6)–Fe–C(9) | 89.4(2) |
| C(2)–Mo–C(3) | 84.3(2) | C(7)–Fe–C(8) | 120.5(2) |
| C(2)–Mo–C(5) | 92.3(2) | C(7)–Fe–C(9) | 88.5(2) |
| C(3)–Mo–C(4) | 90.6(2) | C(8)–Fe–C(9) | 89 3(2) |
| C(3)–Mo–C(5) | 89.4(2) | | |
| C(4)–Mo–C(5) | 88.8(2) | | |
| P(1)–O(10)–P(2) | 146.4(2) | | |
| Mo–P(1)–C(10) | 120.2(1) | Fe–P(2)–O(10) | 117.0(1) |
| Mo–P(1)–O(10) | 112.5(1) | Fe–P(2)–C(22) | 118.3(1) |
| Mo–P(1)–C(16) | 110.7(1) | Fe–P(2)–C(28) | 111.4(1) |
| C(10)–P(1)–C(16) | 103.3(2) | C(22)–P(2)–O(10) | 105 0(2) |
| C(10)–P(1)–O(10) | 106 7(2) | C(22)–P(2)–C(28) | 103.2(2) |
| C(16)–P(1)–O(10) | 101.3(2) | C(28)–P(2)–O(10) | 99.7(2) |

Use of $PhPCl_2$ led to the corresponding bimetallic complexes:



$$PhPCl_2 + 2\,Na^+OPR_2{-}Mo(CO)_5^- \longrightarrow PhP\begin{matrix}\diagup O{-}PR_2{-}Mo(CO)_5\\ \diagdown O{-}PR_2{-}Mo(CO)_5\end{matrix}$$

( VI, R = OEt,
VII, R = Ph )

## The spectral data

Proton-decoupled $^{31}P$ NMR data are presented in Table 3. Assignments for I and II are based on the larger coordination shift of Cr versus Mo and the similar environments of Mo–P in both complexes [12]. Since complex III is very susceptible to hydrolysis the $CDCl_3$ solvent must be vigorously dried before use. The observed AA′XX′ pattern consists of two sets of apparent triplets. Each of the center peaks is further split into a doublet by about 2–3 Hz. The calculated $J$ value of P–Pd–P at 550 Hz is consistent with its suggested *trans* geometry [10]. Both IV and V displayed a low-field doublet (area 3) and a higher-field triplet (area 1). For complex VI, an AXX′ spectrum is observed with the center peak of the triplet actually a close-lying doublet. This is analogous to the pattern reported for $RP[P(O)(OR')_2]_2$ and the tripolyphosphate anion [13]. The possibility of VI having a tautomeric structure $Mo(CO)_5P(OEt)_2OP(O)PhP(OEt)_2Mo(CO)_5$ containing a phosphoryl group with a P–P bond is ruled out by the relatively simple NMR spectrum and the absence of any strong phosphoryl bands in the 1150–1300 $cm^{-1}$ region of the infrared spectrum.

The infrared data in the carbonyl region are presented in Table 4. Mixed metal complexes I and II each show two sharp CO stretches above 2000 $cm^{-1}$ as expected.

TABLE 3

$^{31}P[^1H]$ NMR DATA OF COMPLEXES I TO VII

| Complexes | Solvent | Chem. shifts (ppm) | $^2J(PP)$ (Hz) |
|---|---|---|---|
| $Mo(CO)_5PPh_2OPPh_2Cr(CO)_5$ (I)<br>X A | $CDCl_3$ | 175.1(d), 151.9(d)<br>A X | 64 |
| $Mo(CO)_5PPh_2OPPh_2Fe(CO)_4$ (II)<br>X A | $C_6D_6$ | 176.4(d), 156.8(d)<br>A X | 63 |
| $Mo(CO)_5PPh_2OPPh_2$-<br>A X<br>Cl<br>$Pd{-}PPh_2OPPh_2Mo(CO)_5$ (III)<br>Cl X′ A′ | $CDCl_3$ | 153.9(t) [a], 108.8(t) [a]<br>A X | 550 (XX′)<br>50 (AX) |
| $P[{-}OP(OEt)_2Mo(CO)_5]_3$ (IV)<br>X A | $C_6D_6$ | 146.6(d), 115.0(q)<br>A X | 8 |
| $P[OPPh_2Mo(CO)_5]_3$ (V)<br>X A | $CDCl_3$ | 142.6(d), 138.8(q)<br>A X | 21 |
| $PhP[{-}OP(OEt)_2Mo(CO)_5]_2$ (VI)<br>A X | THF | 153.2(t) [b], 149.3(d) [b]<br>A X | 24 |
| $Na[OP(OEt)_2Mo(CO)_5]$ (VII) | THF | 129.0 | |

[a] Apparent triplets, center peaks further split by 2–3 Hz. [b] Apparent triplet and doublet, center of triplet further split by 5 Hz.

TABLE 4

INFRARED ABSORPTIONS OF THE COMPLEXES IN THE CARBONYL REGION (KBr)

| Complexes | Absorptions ($cm^{-1}$) |
|---|---|
| I | 2067(w), 2056(w), 1997(w), 1948(sh), 1922(s, bd) |
| II | 2066(w), 2051(w), 1988(w), 1975(sh), 1960(sh), 1947(s), 1925(s) |
| III | 2066(w), 1996(w), 1960(sh), 1942(s), 1930(s, bd) |
| IV | 2072(w), 1998(w), 1965(s, bd), 1955(s, bd) |
| V | 2080(w), 1998(sh), 1945(s, bd) |
| VI | 2070(w), 1997(w), 1970(sh), 1940(s, bd) |
| VII | 2061(w), 1989(w), 1945(sh), 1922(s, bd) |

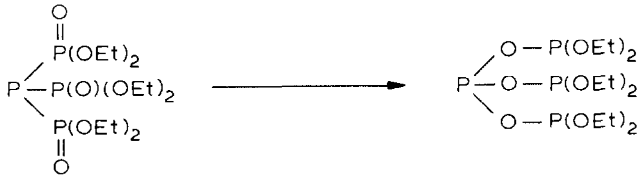
They also exhibit strong P–O–P asymmetrical stretches at 845 and 880 $cm^{-1}$, respectively [14,15]. Complex III has this band at 887 $cm^{-1}$. These values can be compared to that of the starting complex $Mo(CO)_5PPh_2OPPh_2$ at 860 $cm^{-1}$ [4]. This indicates no drastic changes in P–O–P angle upon the ligand's bridging a second metal. Similarly, complex V has a strong and broad band at 830 $cm^{-1}$ which may be assigned to the P–O–$PPh_2$ asymmetrical stretching vibration.

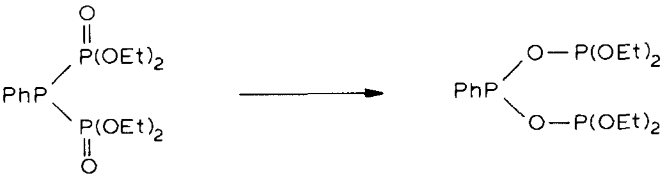
## Conclusion

The ability of the monodentate $PPh_2OPPh_2$ ligand to coordinate a second metal parallels the reported coordination chemistry of the monodentate $Ph_2P(CH_2)_nPPh_2$ ligands [21]:

$$\begin{tikzcd} & \text{M-PXP-M}' \\ \text{M-PXP} \arrow[ur, "\text{M}'\text{L}"] \arrow[dr, "\text{M}'\text{L}_2"'] & \\ & \text{M-PXP-M}'\text{-PXP-M} \end{tikzcd}$$

An additional feature of the P–O–P bridge is the ease of assemblage of complexes like IV, V and VI from monometallic precursors. Compounds IV and VI can be regarded as coordination-stabilized tautomers of the known phosphonyl-phosphines $P[P(O)(OEt)_2]_3$ and $PhP[P(O)(OEt)_2]_2$ respectively:





Potentially diverse combinations of metal centers may be assembled in multimetallic complexes through the linking of coordinated phosphine halides with ligated phosphinous acids to form P–O–P bridges.

## Experimental

All reactions and purifications were performed under dry, deoxygenated nitrogen in Schlenk glassware. Methylene chloride and n-hexane were distilled from $CaH_2$. THF and toluene were distilled from sodium benzophenone ketyl. Dichlorophenylphosphine, $PCl_3$, and diethylphosphite were obtained from Organometallics Inc., E. Hempstead, N.H. and distilled before use. $Fe_2(CO)_9$ and $Mo(CO)_6$ were used as purchased from Alfa. The complexes $Mo(CO)_5PPh_2OPPh_2$, $Cr(CO)_5CH_3CN$, $(PhCN)_2PdCl_2$, and $Mo(CO)_5PPh_2OH$ were prepared as described by literature procedures [4,15,16,17].

Infrared spectra were recorded using a Perkin–Elmer 283 spectrometer. $^{31}P$ NMR spectra were run on a JEOL-FX 90Q FT-NMR spectrometer with D-lock and chemical shifts are reported as referenced to external 85% $H_3PO_4$. All new complexes (I to VII) gave satisfactory C, H, and N analyses which were performed by the UNH Instrumentation Center.

### *Preparation of $Mo(CO)_5PPh_2OPPh_2Cr(CO)_5$ (I)*

An amount of 300 mg (0.48 mmol) of $Mo(CO)_5PPh_2OPPh_2$ and 115 mg (0.48 mmol) of $Cr(CO)_5CH_3CN$ were stirred in 5 ml of $CH_2Cl_2$ for 20 h. To the light yellow solution was added 4 ml of hexane and the solution slowly concentrated to about 2–3 ml. A light yellow powder (250 mg, 60%) was isolated by filtration and drying. Analytical samples can be obtained by recrystallization from $CH_2Cl_2$/hexane.

### *Preparation of $Mo(CO)_5PPh_2OPPh_2Fe(CO)_4$ (II)*

An amount of 250 mg (0.40 mmol) of $Mo(CO)_5PPh_2OPPh_2$ and 250 mg (0.69 mmol) of $Fe_2(CO)_9$ were stirred in 15 ml of THF for 20 h. After filtration through Celite, the filtrate was evaporated to dryness and the residue washed with 5 ml of hexane to give 220 mg, 70% of the crude product as a yellow powder. This was recrystallized from $CH_2Cl_2$/hexane to give X-ray quality crystals.

### *Preparation of trans-$PdCl_2[PPh_2OPPh_2Mo(CO)_5]_2$ (III)*

An amount of 345 mg (0.55 mmol) of $Mo(CO)_5PPh_2OPPh_2$ and 100 mg (0.26 mmol) of $(PhCN)_2PdCl_2$ were stirred in 5 ml of toluene for 1 h. The yellow precipitate was filtered, washed with hexane and dried to give 270 mg, 73% of a light yellow solid.

### *Preparation of $Na[OP(OEt)_2Mo(CO)_5]$ (VII)*

An amount of 10 g (37.9 mmol) of $Mo(CO)_6$ and 10 ml of diethylphosphite were refluxed in 50 ml of toluene for 16 h to give a light yellow solution. This was concentrated to 20 ml and extracted twice with 30 ml of water. A solution of 2 g of NaOH in 20 ml of water was added with stirring. The mixture was filtered through Celite and chilled in an ice-bath to give long white needles of the product. This was filtered, washed with cold-water and dried in high-vacuum overnight to give 4–5 g of the salt VII.

*Preparation of* $P[OP(OEt)_2Mo(CO)_5]_3$ *(IV)*

An amount of 900 mg (2.3 mmol) of VII was dissolved in 10 ml of THF. A 0.56 *M* solution of $PCl_3$ in THF was prepared and 1.37 ml withdrawn and added to the above solution of VII. After 10 min, the turbid solution was evaporated to dryness and the residue extracted with 15 ml of hexane. This was filtered through Celite to give a clear filtrate. Evaporation gave an oil which was shown by its $^{31}P$ spectrum to be essentially pure IV. It was further purified by recrystallization from n-hexane at −60°C to give 300 mg, 35% yield of a white solid.

*Preparation of* $P[OPPh_2Mo(CO)_5]_3$ *(V)*

An amount of 125 mg hexane-washed NaH and 1.3 g (2.4 mmol) of $NEt_3H[OPPh_2Mo(CO)_5]$ [15] were stirred in 10 ml of THF. After 20 min, the pale yellow suspension was filtered through a fine frit and the filtrate evaporated to dryness. The white residue was redissolved in 20 ml THF. An amount of 120 mg (0.87 mmol) of $PCl_3$ was dissolved in 10 ml THF and added dropwise. After filtration through Celite, the solvent was removed to give a pale, gummy oil. $^{31}P$ NMR showed this to be mostly the desired product (V). Purification by recrystallization from $CH_2Cl_2$/hexane gave 254 mg (20%) of the white solid V.

*Preparation of* $PhP[OP(OEt)_2Mo(CO)_5]_2$ *(VI)*

An amount of 650 mg (1.65 mmol) of VII was dissolved in 10 ml THF. To this was added dropwise 1.6 ml of a 0.5 *M* solution of $PhPCl_2$ in THF. After stirring for 0.5 h, the turbid solution was evaporated to dryness and extracted with 15 ml of hexane. Filtration through Celite and evaporation of the filtrate gave a white powdery solid. This was washed with cold hexane and dried in vacuum to yield 330 mg, 80% of the product VI. Analytical samples were recrystallized from cold hexane.

TABLE 5

CELL AND DATA COLLECTION PARAMETERS

| | | | |
|---|---|---|---|
| Formula | $C_{33}O_{10}H_{20}P_2FeMo$ | $Z = 2$ | |
| Space group $P\bar{1}$ | triclinic | | |
| $a$ 10.533(2) Å | | $D_{calc}$ | 1.561 g cm$^{-3}$ |
| $b$ 10.993(2) Å | | $\mu$ | 0.042 mm$^{-1}$ |
| $c$ 16.439(3) Å | | $\lambda$ | 0.70932 Mo-$K_{\alpha_1}$ |
| $\alpha$ 97.86(2)° | | | |
| $\beta$ 92.34(1)° | | | |
| $\gamma$ 116.20(1)° | | | |
| Crystal dimensions | 0.2×0.3×0.2 mm | | |
| Data collected | $0 \leqslant 2\theta \leqslant 50°$ | | |
| Scan $\theta/2\theta$ | | | |
| No. of unique reflections | 5948 | | |
| No. of data in final refinement | 3830 | | |
| $R_F$ | = 0.037 | | |
| $R_{wF}$ | = 0.028 | | |

TABLE 6

ATOMIC PARAMETERS $x$, $y$, $z$ and $B_{eq}$ [a] (esds refer to the last digit)

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Mo | 0.64904(5) | 0.41286(5) | 0.67331(3) | 3.113(23) |
| Fe | 1.22651(8) | 0.79262(7) | 0.69700(4) | 3.06(4) |
| P(1) | 0.76506(13) | 0.65772(13) | 0.74210(8) | 2.61(7) |
| P(2) | 1.09471(13) | 0.82420(13) | 0.79084(8) | 2.56(7) |
| O(1) | 0.8545(4) | 0.4705(4) | 0.53155(25) | 8.3(3) |
| O(2) | 0.8602(4) | 0.3625(4) | 0.7890(3) | 7.2(3) |
| O(3) | 0.4692(4) | 0.3358(4) | 0.82377(23) | 7.3(3) |
| O(4) | 0.4092(4) | 0.4618(4) | 0.5800(3) | 8.1(3) |
| O(5) | 0.4903(4) | 0.1001(3) | 0.58806(23) | 7.2(3) |
| O(6) | 1.0781(4) | 0.8305(5) | 0.55664(24) | 8.3(4) |
| O(7) | 1.4756(4) | 1.0264(4) | 0.79201(23) | 6.41(25) |
| O(8) | 1.1473(5) | 0.5129(4) | 0.7264(3) | 8.5(3) |
| O(9) | 1.4194(4) | 0.7587(4) | 0.58233(23) | 6.6(3) |
| O(10) | 0.9291(3) | 0.7082(3) | 0.78256(18) | 2.99(18) |
| C(1) | 0.7803(6) | 0.4521(5) | 0.5817(3) | 5.0(3) |
| C(2) | 0.7877(6) | 0.3806(5) | 0.7431(3) | 4.7(3) |
| C(3) | 0.5305(5) | 0.3653(5) | 0.7674(3) | 4.4(3) |
| C(4) | 0.4972(6) | 0.4460(5) | 0.6110(3) | 4.7(3) |
| C(5) | 0.5476(6) | 0.2128(5) | 0.6181(3) | 4.6(4) |
| C(6) | 1.1310(6) | 0.8150(6) | 0.6146(3) | 4.8(4) |
| C(7) | 1.3755(5) | 0.9340(5) | 0.7559(3) | 3.8(3) |
| C(8) | 1.1751(6) | 0.6218(5) | 0.7164(3) | 5.0(4) |
| C(9) | 1.3446(5) | 0.7714(5) | 0.6268(3) | 4.2(3) |
| C(10) | 0.7686(4) | 0.7915(4) | 0.6862(3) | 2.7(3) |
| C(11) | 0.7619(5) | 0.9088(5) | 0.7249(3) | 3.7(3) |
| C(12) | 0.7638(6) | 1.0063(5) | 0.6793(3) | 4.9(4) |
| C(13) | 0.7730(6) | 0.9889(6) | 0.5965(4) | 5.8(4) |
| C(14) | 0.7808(6) | 0.8748(6) | 0.5578(3) | 5.6(4) |
| C(15) | 0.7762(5) | 0.7747(5) | 0.6016(3) | 4.0(3) |
| C(16) | 0.6814(5) | 0.6812(4) | 0.8331(3) | 2.8(3) |
| C(17) | 0.7319(5) | 0.6783(5) | 0.9112(3) | 3.4(3) |
| C(18) | 0.6543(5) | 0.6765(5) | 0.9772(3) | 4.1(3) |
| C(19) | 0.5238(6) | 0.6781(5) | 0.9654(3) | 4.7(3) |
| C(20) | 0.4724(5) | 0.6807(6) | 0.8879(3) | 4.9(4) |
| C(21) | 0.5483(5) | 0.6812(5) | 0.8217(3) | 3.9(3) |
| C(22) | 1.0883(5) | 0.9888(4) | 0.8084(3) | 3.1(3) |
| C(23) | 1.0285(5) | 1.0207(5) | 0.8769(3) | 3.8(3) |
| C(24) | 1.0224(5) | 1.1454(5) | 0.8904(3) | 4.8(3) |
| C(25) | 1.0748(6) | 1.2352(5) | 0.8352(4) | 6.0(4) |
| C(26) | 1.1323(6) | 1.2042(5) | 0.7685(4) | 5.8(4) |
| C(27) | 1.1407(5) | 1.0807(5) | 0.7539(3) | 4.2(3) |
| C(28) | 1.1554(5) | 0.8107(5) | 0.8926(3) | 2.7(3) |
| C(29) | 1.2599(5) | 0.9266(5) | 0.9441(3) | 3.3(3) |
| C(30) | 1.3147(5) | 0.9147(5) | 1.0191(3) | 4.0(3) |
| C(31) | 1.2684(5) | 0.7894(5) | 1.0436(3) | 4.1(3) |
| C(32) | 1.1652(5) | 0.6733(5) | 0.9930(3) | 3.7(3) |
| C(33) | 1.1094(5) | 0.6830(5) | 0.9181(3) | 3.1(3) |
| H(11) | 0.755 | 0.925 | 0.792 | 3.2 |
| H(12) | 0.756 | 1.100 | 0.708 | 4.5 |
| H(13) | 0.779 | 1.071 | 0.562 | 5.2 |
| H(14) | 0.787 | 0.866 | 0.492 | 4.9 |
| H(15) | 0.783 | 0.682 | 0.570 | 3.6 |
| H(17) | 0.834 | 0.671 | 0.920 | 2.9 |

TABLE 6 (continued)

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| H(18) | 0.699 | 0.680 | 1 040 | 3.9 |
| H(19) | 0.465 | 0.681 | 1.019 | 4.0 |
| H(20) | 0.368 | 0.680 | 0.881 | 4.8 |
| H(21) | 0.503 | 0.680 | 0.759 | 3.5 |
| H(23) | 0.987 | 0.948 | 0.922 | 3.8 |
| H(24) | 0.978 | 1.176 | 0.948 | 4.2 |
| H(25) | 1.066 | 1.331 | 0.848 | 5.0 |
| H(26) | 1.166 | 1.283 | 0.728 | 5.1 |
| H(27) | 1.194 | 1.060 | 0.701 | 3.9 |
| H(29) | 1.292 | 1.032 | 0.931 | 3 3 |
| H(30) | 1.400 | 1.005 | 1.059 | 3.5 |
| H(31) | 1.312 | 0.786 | 1.102 | 4.3 |
| H(32) | 1.129 | 0.572 | 1.011 | 3.8 |
| H(33) | 1 025 | 0.590 | 0 879 | 3.1 |

[a] $B_{eq}$ is the arithmetic mean of the principal axes of the thermal ellipsoid.

*X-ray structural determination of II*

The diffraction intensities from a 0.2 × 0.3 × 0.2 mm crystal were collected at 23°C using graphite monochromatized Mo-$K_\alpha$ radiation generated at 50 kV and 16 mA. The $\theta/2\theta$ scan technique was used with line profile analysis [19]. A total of 6163 measurements were made up to 50° in $2\theta$ giving 5948 unique reflections of which 3830 were considered observed with net intensities greater than $2.5\sigma$ ($I_{net}$) based on counting statistics. These were corrected for Lorentz and polarization effects [18]. Cell parameters were obtained from a least-squares treatment of the setting angles for 60 reflections with $2\theta \geqslant 40°$. Further details of the cell and data collection are given in Table 5.

The heavy atoms (Mo and Fe) were found from the Patterson map and the remaining atoms with some difficulty from successive Fourier maps. Non-hydrogen atoms were refined by block-diagonal least squares with counting statistics weights. Hydrogen atoms were included at their calculated positions but were not refined. Scattering factors were taken from the "International Tables for X-ray Crystallography" [20]. Final residuals based on observed reflections are $R_F = 0.037$ and $R_{wF} = 0.028$, and for all the reflections 0.083 and 0.029. All calculations were carried out with the NRC PDP-8e system of programs. Anisotropic thermal parameters, hydrogen atomic parameters and structure factor tables are available from the authors. Atomic parameters and $B_{iso}$ are listed in Table 6.

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## References

1 See for example: M.H. Chisholm, Am. Chem. Soc. Symposium Series, 1981, No. 155; M.H. Chisholm, Trans. Met. Chem., 2 (1978) 321; R. Poilblanc, Nouv. J. Chim., 2 (1978) 145; W.D. Jones and R.G. Bergman, J. Am. Chem. Soc., 101 (1979) 5447; N.E. Shore, ibid., 101 (1979) 7410.

2 See for example: P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 956; J.P. Farr, M.M. Olmstead and A.L. Balch, Inorg. Chem., 22 (1983) 1229; A.L. Balch, Adv. Chem. Ser., (1982) 196; C.P. Kubiak and R. Eisenberg, J. Am. Chem. Soc., 102 (1980) 3637.
3 E.H. Wong, R.M. Ravanelle, E.J. Gabe, F.L. Lee and L. Prasad, J. Organomet. Chem., 233 (1982) 321.
4 E.H. Wong, L. Prasad, E.J. Gabe and F.C. Bradley, J. Organomet. Chem., 236 (1982) 321.
5 E.H. Wong, F.C. Bradley and E.J. Grabe, J. Organomet. Chem., 244 (1983) 235.
6 F.A. Cotton, D.J. Darensbourg and W.H. Ilsley, Inorg. Chem., 20 (1981) 578. See Table IX, p. 583.
7 P.E. Riley and R.E. Davis, Inorg. Chem., 19 (1980) 159. See Table V, p. 164.
8 L.R. Massimbeni, Inorg. Nucl. Chem. Lett., 7 (1971) 187.
9 E. Lindner, S. Hoehne and J.-P. Gumz, Z. Naturforsch. B, 35 (1980) 937.
10 P.E. Pregosin and R.W. Kunz, $^{31}$P and $^{13}$C NMR of Transition Metal Phosphine Complexes, Springer-Verlag, Berlin 1979.
11 D.A. Duddell, C.L. Goggin, R.J. Goodfellow, M.G. Norton and J.G. Smith, J. Chem. Soc. A, (1970) 545.
12 S.O. Grim, D.A. Wheatland and W.J. McFarlane, J. Am. Chem. Soc., 89 (1967) 5573.
13 K.M. Abraham and J.-R. Van Wazer, Inorg. Chem., 15 (1976) 2322; T. Glonek, A.J.R. Costello, T.C. Myers and J.-R. Van Wazer, J. Phys. Chem., 79 (1975) 1214.
14 D.E.C. Corbridge, Top. Phos. Chem., 6 (1969) 282.
15 C.S. Kraihanzel and C.M. Bartish, J. Am. Chem. Soc., 94 (1972) 3572.
16 D.P. Tate, Inorg. Chem., 1 (1962) 433.
17 J.R. Doyle, P.C. Slade and H.B. Jonassen, Inorg. Syn., 6 (1960) 218.
18 Y. Le Page, E.J. Gabe and L.D. Calvert, J. Appl. Cryst., 12 (1979) 25.
19 D.F. Grant and E.J. Gabe, J. Appl. Cryst., 11 (1978) 114.
20 International Tables for X-ray Crystallography, 1974, Vol. 4, Table 2.2B, p. 99, Birmingham, Kynoch Press.
21 J.A. Connor, G.K. McEwin and C.J. Rix, J. Chem. Soc. Dalton, (1974) 589.