# Triphosphorus Macrocycle Complexes of Divalent Group 6 Transition Metals; Crystal Structure of Bromotricarbonyl-[1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane]-molybdenum(II) Tetraphenylborate†

**Simon J. Coles, Peter G. Edwards,* James S. Fleming and Michael B. Hursthouse**
*Department of Chemistry, University of Wales Cardiff, P.O. Box 912, Cardiff CF1 3TB, UK*

New triphosphamacrocycle complexes of molybdenum(II) and tungsten(II) have been prepared by oxidative addition of halogens to molybdenum and tungsten tricarbonyl complexes of 1,5,9-triphosphacyclododecane and tertiary phosphine analogues. The behaviour of these macrocycle complexes is similar to that of previously reported examples with monodentate tertiary phosphines and the metal(0) precursors give rise initially to seven-co-ordinate salts containing a $[M(CO)_3X(L)]^+$ cation (L = tridentate triphosphamacrocycle) with a halide anion which may be exchanged for other counter ions. The seven-co-ordinate complexes are all fluxional in solution and give rise to temperature-variant NMR spectra. At the low-temperature limit an $AB_2$ pattern was observed in the $^{31}P$ NMR spectra of all the new complexes. The salts all convert slowly into the neutral seven-co-ordinate dicarbonyldihalogeno complexes $[M(CO)_2X_2(L)]$ in solution. These are the first examples of metal complexes of the 1,5,9-triphosphacyclododecane family other than the metal(0) tricarbonyl template complexes upon which the macrocyclic ligands were originally made.

We have recently reported the first tritertiary 1,5,9-triphosphacyclododecane complexes of $Mo^0$ and $W^0$ derived from the trisecondary triphosphacyclododecane molybdenum(0) and tungsten(0) precursors, the latter also being previously unreported.[1] Complexes of phosphorus macrocycles are rare and studies of their chemical properties are of interest; there have been no such studies of complexes of the 1,5,9-triphosphacyclododecane family. In this paper we describe reactions of the molybdenum(0) and tungsten(0) complexes with $Cl_2$, $Br_2$ and $I_2$.

Also, since all previous attempts to liberate the free macrocycle from its molybdenum(0) or tungsten(0) template have failed, we are particularly interested in oxidations of the zerovalent complexes as the triphosphine macrocycles should be relatively more substitution labile in the presence of higher metal oxidation states. The oxidative addition of halogens to carbonyl complexes of $Mo^0$ and $W^0$ has been extensively studied. For example, addition of halogen ($X_2$) to $M(CO)_4L_2$ yields the seven-co-ordinate metal(II) complexes $[M(CO)_3X_2L_2]$ (M = Mo or W; $L_2 = Ph_2PCH_2PPh_2$, $2PEt_3$ or $2PMe_2Ph$) with the loss of 1 equivalent of CO.[2,3] Similar $[Mo(CO)_3X_2L_2]$ complexes have also been prepared by the action of tertiary phosphine on the halogenocarbonyl complexes $[M(CO)_4X_2]$ (M = Mo or W; X = Cl, Br or I; $L_2 = 2PMe_3$ or $Ph_2PCH_2PPh_2$).[4–6] The oxidative addition of halogens to complexes of the type *fac*-$[Mo(CO)_3L_3]$ is of particular interest as these complexes are directly analogous to the 1,5,9-triphosphacyclododecane complexes we have previously prepared. It has been shown that a tricarbonyl cation is initially formed followed by the loss of CO and generation of the neutral seven-co-ordinate species.[7–10] The initial cation can also be isolated as a salt with non-co-ordinating anions such as $BPh_4^-$ where further loss of CO is inhibited.[7,9] In all cases, the complexes formed are seven-co-ordinate, expected ideal geometries for which are pentagonal bipyramidal, capped octahedral and capped trigonal prismatic. Distortions from idealised geometries are common, for example in $[MoBr_2(CO)_2(dppm)(dppm\text{-}P)]$ [dppm = 1,2-bis(diphenylphosphino)methane] the solid-state geometry lies between capped trigonal prismatic and capped octahedral.[10] Conversion barriers between geometries are likely to be small leading to fluxional behaviour in solution which has been demonstrated by a number of $^{31}P$ NMR studies;[11–14] for complexes of the type $[MX(CO)_3L_3]^+$, low-temperature spectra are typically consistent with an $A_2B$ spin system which coalesces upon warming such that a singlet due to rapidly equilibrating tertiary phosphines is observed at elevated temperatures.

## Results and Discussion

The new compounds discussed below are represented in Scheme 1. Selected spectroscopic data are in Table 1 and analytical data in Table 2.

*Molybdenum Compounds.*—Addition of 1 mole equivalent of halogen ($Cl_2$, $Br_2$, $I_2$) to colourless $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ in halogenocarbons results in orange solutions from which yellow ($Cl_2$, $Br_2$) or red-orange ($I_2$) microcrystalline materials may be isolated. Their microanalyses were consistent with the empirical compositions $[Mo(CO)_3X_2\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ (X = Br **1**, I **4** or Cl **9**). A similar reaction occurs between $[Mo(CO)_3\{cyclo\text{-}(Me_3SiCH_2PC_3H_6)_3\}]$ and bromine and between $[Mo(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ and bromine giving yellow (**7**) and red (**11**) compounds respectively which are empirically analogous to **1**. The four complexes **1**, **4**, **7** and **9** behave as 1:1 electrolytes in nitromethane but are essentially non-conductors in dichloromethane, presumably due to close ion-pair formation in the less-polar solvent. Complexes **1**, **4**, **7**, **9** and **11** are then more appropriately assigned the general formula [Mo(CO)$_3$X{(RP-

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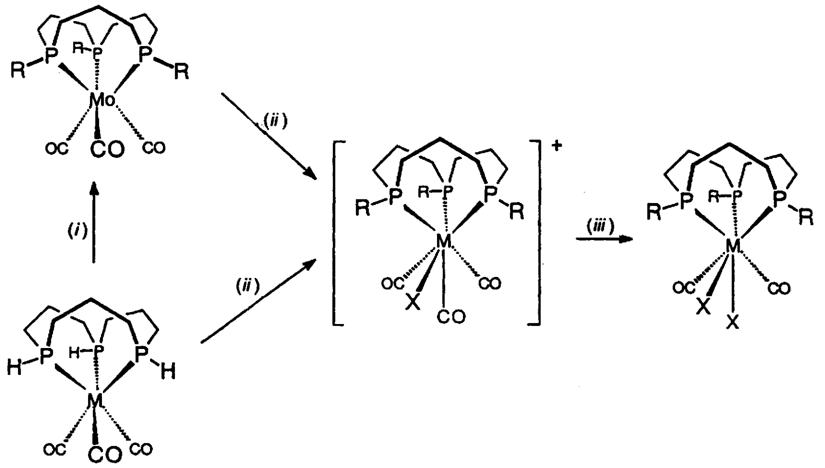
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



**Scheme 1** (*i*) 3LiBu$^n$, 3RX (tetrahydrofuran, thf); (*ii*) $X_2$ ($CH_2Cl_2$); (*iii*) $CH_2Cl_2$, 2–3 d. R = Alkyl, X = halide, M = Mo or W

**Table 1** Selected spectroscopic data for molybdenum(II) and tungsten(II) complexes

| | | IR | $^{31}P$-$\{^1H\}$ NMR[c] | | | | |
|---|---|---|---|---|---|---|---|
| Complex[a] | Colour | $\tilde{\nu}_{CO}$[b]/cm$^{-1}$ | $\delta(P_A)$ | $\delta(P_B)$ | $J_{PP}$/Hz | $T_c$/K | $\Delta G^‡$/ kJ mol$^{-1}$ |
| **1** [MoBr(CO)$_3$L$^1$]Br | Yellow | 2021, 1960, 1925 | 8.3 | −17.6 | 26 | 315 | 57.3 ± 1 |
| **2** [MoBr(CO)$_3$L$^1$]BPh$_4$ | Yellow | 2027, 1965, 1926 | 7.3 | −16.8 | 21 | 325 | 59.3 ± 1 |
| **3** [MoBr$_2$(CO)$_2$L$^1$] | Yellow | 1918, 1816 | | 9.7 | | | — |
| **4** [MoI(CO)$_3$L$^1$]I | Yellow | 2015, 1953, 1925 | 4.5 | −23.8 | 27 | 295 | 53.3 ± 1 |
| **5** [MoI(CO)$_3$L$^1$]BPh$_4$ | Orange | 2016, 1956, 1927 | 1.2 | −24.3 | 26 | 300 | 54.5 ± 1 |
| **6** [MoI$_2$(CO)$_2$L$^1$] | Orange | 1914, 1818 | | 12.4 | | | — |
| **7** [MoBr(CO)$_3$L$^2$]Br | Yellow | 2022, 1960, 1921 | 8.0 | −13.2 | 23 | 325 | 59.7 ± 1 |
| **8** [MoBr$_2$(CO)$_2$L$^2$] | Red | 1921, 1823 | | 2.0 | | | |
| **9** [MoCl(CO)$_3$L$^1$]Cl | Yellow | 2025, 1965, 1922 | 19.3 | −5.9 | 28 | 325 | 55.0 ± 1 |
| **10** [MoCl$_2$(CO)$_2$L$^1$] | Yellow | 1921, 1823 | | 11.4 | | | — |
| **11** [MoBr(CO)$_3$L$^3$]Br | Red | 2051, 1991, 1938 | —[d] | — | — | — | — |
| **12** [MoBr$_2$(CO)$_2$L$^3$] | Off-white | 1933, 1862 | | −31.8 | | | — |
| **13** [MoI(CO)$_3$L$^3$]I | Yellow | 2044, 1995, 1946 | —[d] | — | — | — | — |
| **14** [MoI$_2$(CO)$_2$L$^3$] | Yellow | 1927, 1868 | | −31.1 | | | — |
| **15** [WBr(CO)$_3$L$^3$]Br | Red | 2045, 1984, 1939 | −38.3 | −60.1 | 27 | 335 | 57.7 ± 1 |
| **16** [WBr$_2$(CO)$_2$L$^3$] | Yellow | 1920, 1824 | | −58.8 | | | — |
| **17** [WI(CO)$_3$L$^3$]I | Yellow | 2032, 1965, 1930 | −46.8 | −66.3 | 27 | 325 | 56.2 ± 1 |
| **18** [WI$_2$(CO)$_2$L$^3$] | Yellow | 1921, 1826 | | −61.7 | | | — |

[a] L$^1$ = *cyclo*-(Pr$^i$PC$_3$H$_6$)$_3$, L$^2$ = *cyclo*-(Me$_3$SiCH$_2$PC$_3$H$_6$)$_3$, L$^3$ = *cyclo*-(HPC$_3$H$_6$)$_3$. [b] Spectra run as Nujol mulls. [c] In CDCl$_3$ solution. [d] Dihalogeno complex formed in solution.

$C_3H_6)_3\}]X$ (R = H, Pr$^i$ or Me$_3$SiCH$_2$). Analogous complexes of the type [Mo(CO)$_3$X(L)]X (L = tridentate phosphine[8] or tridentate amine[9]) have been observed readily to undergo anion-exchange reactions and to lose CO by substitution with unco-ordinated halide to give complexes of the type [Mo(CO)$_2$X$_2$(L)].[8,15] Both of these reactions are observed for the macrocycle complexes. Thus **1** and **4** react with NaBPh$_4$ in EtOH–CH$_2$Cl$_2$ to give the corresponding tetraphenylborates **2** and **5** which are 1 : 1 electrolytes in dichloromethane and have the general formula [Mo(CO)$_3$X{(RPC$_3$H$_6$)$_3$}]BPh$_4$. The tricarbonylmolybdenum(II) cationic complexes are further characterised by IR spectroscopy, they all give rise to three bands assignable to ν(CO), due to reduced symmetry in the seven-co-ordinate complexes, and in contrast to the facial molybdenum(0) tricarbonyl precursors which only show two. The wavenumbers of these absorptions are also higher (by around 100 cm$^{-1}$) than those of the precursors which is consistent with the greater positive charge on Mo in the cations.

The halogenohalide complexes **1**, **4**, **7**, **9** and **11** may all be converted into the dihalogenodicarbonyls **3**, **6**, **8**, **10** and **12** respectively and of general formula [Mo(CO)$_2$X$_2$-{(RPC$_3$H$_6$)$_3$}], although some of these reactions are considerably slower than other reported reactions of this type,[4,7,12,14] taking up to several days at room temperature. These complexes were characterised by analysis, spectroscopy, and mass spectrometry (electron impact, EI) for **10** for which a weak molecular ion is observed (*m*/*z* 571 for $^{35}$Cl, 1%) as are peaks due to loss of Pr$^i$ (*m*/*z* 529, 5%) and to sequential loss of carbonyl groups (*m*/*z* 543, 2; 516, 3%). Of interest are the IR data which show two ν(CO) absorptions for each of the complexes at consistently lower frequency than for the cations and at a similar position to those for the neutral molybdenum(0) precursor complexes, and these data correspond closely with previously reported examples.[3,4,7,12,14]

All the complexes are diamagnetic and give rise to NMR spectra. In all cases, singlets are observed in the $^{31}P$-$\{^1H\}$ NMR spectra at ambient temperature or above. Equivalence of the phosphorus atoms is presumably due to a dynamic intramolecular site-exchange process resulting in equilibration of the magnetically inequivalent sites (as would be expected) in the seven-co-ordinate complexes. This was confirmed by variable-temperature studies for selected complexes.

For the iodo salt **5** at the low-temperature limit, a doublet

**Table 2** Analytical and conductivity data for molydenum(II) and tungsten(II) complexes

| Complex | Analysis (%)[a] |  | $\Lambda_m{}^{-1}$/mol cm$^2$ $\Omega^{-1}$ |  |
|---|---|---|---|---|
|  | C | H | $CH_2Cl_2$ | $MeNO_2$ |
| **1** | 35.80 (36.65) | 4.90 (5.55) | 1.2 | 87 |
| **2** | 57.20 (58.25) | 6.66 (6.35) | 91 | — |
| **3** | 35.30 (36.45) | 6.00 (5.95) | — | — |
| **4** | 31.15 (32.15) | 5.65 (4.90) | 2.1 | 83 |
| **5** | 55.25 (55.45) | 6.15 (6.05) | 94 | — |
| **6** | 30.15 (31.85) | 5.15 (5.00) | — | — |
| **7** | 36.50 (35.20) | 7.10 (6.25) | 1.0 | 88 |
| **8** | 32.90 (34.95) | 7.15 (6.45) | — | — |
| **9** | 41.35 (42.80) | 7.60 (6.60) | — | 82 |
| **10** | 41.20 (42.05) | 7.55 (6.85) | — | — |
| **11** | *b* | — | *c* | — |
| **12** | 24.60 (24.80) | 4.05 (3.95) | — | — |
| **13** | *b* | — | *c* | — |
| **14** | 19.90 (21.00) | 3.75 (3.45) | — | — |
| **15** | *b* | — | — | 72[d] |
| **16** | 20.30 (21.22) | 4.00 (3.40) | — | — |
| **17** | *b* | — | — | 74[d] |
| **18** | 17.45 (18.45) | 2.35 (2.95) | — | — |

[a] Calculated values in parentheses. [b] Reliable analytical data were not obtained since this compound was always contaminated with the dihalogenodicarbonyl into which it readily converts. [c] Forms dihalogeno complex in solution. [d] $10^{-6}$ mol dm$^{-3}$ solution.

**Table 3** Selected bond lengths (Å) and angles (°) for [MoBr(CO)$_3${*cyclo*-(Pr$^i$PC$_3$H$_6$)$_3$}]BPh$_4$ **2**

|  |  |  |  |
|---|---|---|---|
| Mo–C(1) | 2.002(8) | P(2)–C(6) | 1.848(9) |
| Mo–C(2) | 2.003(8) | P(2)–C(7) | 1.843(8) |
| Mo–C(3) | 1.984(8) | P(2)–C(16) | 1.857(8) |
| Mo–P(1) | 2.608(2) | P(3)–C(9) | 1.835(9) |
| Mo–P(2) | 2.599(3) | P(3)–C(10) | 1.818(7) |
| Mo–P(3) | 2.552(3) | P(3)–C(19) | 1.854(8) |
| Mo–Br | 2.702(2) | C(1)–O(1) | 1.128(7) |
| P(1)–C(4) | 1.834(8) | C(2)–O(2) | 1.133(8) |
| P(1)–C(12) | 1.839(8) | C(3)–O(3) | 1.156(8) |
| P(1)–C(13) | 1.843(8) |  |  |
| C(3)–Mo–C(1) | 74.9(3) | C(2)–Mo–P(1) | 160.8(2) |
| C(3)–Mo–C(2) | 73.6(3) | P(3)–Mo–P(1) | 88.98(8) |
| C(1)–Mo–C(2) | 106.8(3) | P(2)–Mo–P(1) | 90.09(8) |
| C(2)–Mo–P(3) | 178.4(2) | C(3)–Mo–Br | 69.6(2) |
| C(1)–Mo–P(3) | 76.8(2) | C(1)–Mo–Br | 112.1(2) |
| C(2)–Mo–P(3) | 74.7(2) | C(2)–Mo–Br | 115.3(2) |
| C(3)–Mo–P(2) | 121.8(2) | P(3)–Mo–Br | 161.96(5) |
| C(1)–Mo–P(2) | 163.3(2) | P(2)–Mo–Br | 76.54(7) |
| C(2)–Mo–P(2) | 80.5(2) | P(1)–Mo–Br | 78.04(7) |
| P(3)–Mo–P(2) | 91.18(9) | O(1)–C(1)–Mo | 176.5(6) |
| C(3)–Mo–P(1) | 125.3(2) | O(2)–C(2)–Mo | 178.7(6) |
| C(1)–Mo–P(1) | 78.3(2) | O(3)–C(3)–Mo | 178.8(6) |

and a triplet (conforming to an AB$_2$ spin system) are observed in a ratio of 2:1 respectively. The difference in chemical shift ($\delta_A - \delta_B$) is similar to previously reported values for the complexes [M(CO)$_2$X$_2$(PMe$_3$)$_3$] (M = Mo or W; X = Cl, Br or I) as is the P–P coupling constant [$^2J$(P$_a$–P$_b$) = 26 Hz]. At higher temperatures the pattern collapses, coalescence is observed at 300 K and a singlet is resolved above this temperature (δ −16.1). The value of $\Delta G^‡$ (54 ± 1 kJ mol$^{-1}$) for the process can be estimated from line-shape analysis[16] and falls within the range (52–57 kJ mol$^{-1}$) estimated for the complexes [MI$_2$(CO)$_3$L$_2$] (M = Mo, L = PMe$_2$Ph; M = W, L = PMe$_2$Ph, PMePh$_2$ or PPh$_3$) and is similar to that observed for the chlorochloride analogue **9** ($\Delta G^‡$ 55 ± 1 kJ mol$^{-1}$). The variable-temperature $^{31}$P-{$^1$H} NMR behaviour of the bromo complexes **2** and **7** is similar to that of **5** where AB$_2$ patterns are observed at low temperature although values of $\Delta G^‡$ for the dynamic site-exchange process are somewhat higher (59 ± 1 and 59.7 ± 1 kJ mol$^{-1}$ respectively). The neutral dihalogeno complexes do not give rise to temperature-variant NMR behaviour. Thus for dibromo complexes **3** and **8**, the diiodo complex **6**, and the dichloro complex **10**, singlets are observed even at low temperature in the $^{31}$P-{$^1$H} NMR spectra and chemical shift values are similar to those of the parent molybdenum(0) tricarbonyl complex (δ 10.1). Similar observations were not made for the corresponding secondary phosphine macrocycle complex (**11**) since poor solubility precluded reliable measurements.

The rates of conversion of the halogeno/halide complexes of the tritertiary phosphines into form their dihalogeno counterparts (*i.e.* **1** to **3**, **4** to **6**, *etc.*) appear to be slow and vary little with change of halide. By contrast, the conversions for the secondary phosphine complexes (*i.e.* **11** to **12** and **13** to **14**) are rapid even at low (−78 °C) temperature. Indeed, isolation of the pure complexes [Mo(CO)$_3$X{*cyclo*-(HPC$_3$H$_6$)$_3$}]$^+$X$^-$ (X = Br **11** or I **13**) has not been possible; they have only been identified by IR spectra which shows bands attributable to ν(P–H) and are otherwise similar to those of the other cationic complexes described herein.

Proton NMR spectra for the halogenohalide complexes show only broad resonances in similar positions to those observed for the parent molybdenum(0) tricarbonyl complexes[1] [*e.g.* for **4**, δ 1.86 (CH$_2$), 1.64 (CH$_2$C*H*$_2$), 1.46 (CH) and 1.22 (CH$_3$)]. Spectra of the dihalogeno complexes show complex multiplets in similar positions to those observed for the parent complexes[1] [*e.g.* for **6**, δ 1.85 (CH$_2$), 1.62 (CH$_2$C*H*$_2$), 1.49 (CH) and 1.18 (CH$_3$)]. The spectral resolution is sufficient only for the coupling constants for the CH$_3$ protons to be ascertained (*e.g.* for **6**, $^3J_{PH}$ and $^2J_{HH}$ = 7 and 14 Hz respectively).

*Tungsten Complexes.*—Reactions of halogens with [W(CO)$_3${*cyclo*-(HPC$_3$H$_6$)$_3$}] are similar to those described above for the molybdenum trisecondary macrocycle complex. Thus, in dichloromethane, [W(CO)$_3${*cyclo*-(HPC$_3$H$_6$)$_3$}] reacts with Br$_2$ and I$_2$ to give the halogenohalides, [WBr(CO)$_3${*cyclo*-(HPC$_3$H$_6$)$_3$}]Br **15** and [WI(CO)$_3${*cyclo*-(HPC$_3$H$_6$)$_3$}]I **17** as red and yellow microcrystalline powders respectively. Both compounds were characterised by analytical, spectroscopic and conductivity data. They are conductors in nitromethane, the conductivity being consistent with 1:1 electrolytes. In the IR spectra three ν(CO) bands are observed indicating that both complexes are seven-co-ordinate tricarbonyls. Again the wavenumbers of these IR absorptions are higher than those of the neutral macrocycle tricarbonyl precursor (1910, 1825 cm$^{-1}$), consistent with the complexes being cationic. Both **15** and **17** give rise to singlets in the $^{31}$P NMR spectra at elevated temperature; poor solubilities precluded reliable low-temperature measurements. The value of $\Delta G^‡$ for the fluxional process was estimated to be 58 ± 1 kJ mol$^{-1}$ for the bromobromide complex (**15**) and 56 ± 1 kJ mol$^{-1}$ for the iodoiodide (**17**). Both values are slightly higher than for the molybdenum tertiary phosphine analogues and, as with the molybdenum analogues, the value for the bromobromide is higher than that for the iodoiodide.

The halogenohalides **15** and **17** are both converted slowly into the corresponding dihalogenodicarbonyls which analyse as [WBr$_2$(CO)$_2${*cyclo*-(HPC$_3$H$_6$)$_3$}] **16** and [WI$_2$(CO)$_2${*cyclo*-(HPC$_3$H$_6$)$_3$}] **17** respectively which can be isolated as yellow powders. The conversion is slow and takes several days at room temperature. The products are non-conductors in solution and each gives two ν(CO) bands in the IR spectrum at frequencies very close to those observed for [W(CO)$_3${*cyclo*-(HPC$_3$H$_6$)$_3$}]. Again, singlets are observed in the $^{31}$P NMR spectra at elevated temperature (at δ −58.8 and −61.7 respectively).

*Structure of* [MoBr(CO)$_3${*cyclo*-(Pr$^i$PC$_3$H$_6$)$_3$}]BPh$_4$ **2**.—A view of the structure of the cation of compound **2** is shown in Fig. 1. Selected bond lengths and angles are in Table 3 and

**Table 4** Atomic coordinates ( × $10^4$) for complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 2 855(1) | 7 067(1) | 3 738(1) |
| Br | 515(1) | 7 235(1) | 4 496(1) |
| P(1) | 2 172(2) | 5 753(2) | 2 983(1) |
| P(2) | 1 561(2) | 8 842(2) | 2 877(1) |
| P(3) | 4 737(1) | 6 987(1) | 2 620(1) |
| B | 3 541(6) | 8 361(6) | 8 539(4) |
| O(1) | 4 686(4) | 4 704(4) | 4 228(3) |
| O(2) | 4 034(4) | 8 902(4) | 4 018(3) |
| O(3) | 2 749(4) | 6 856(5) | 5 672(3) |
| C(1) | 4 007(6) | 5 554(6) | 4 072(4) |
| C(2) | 3 601(6) | 8 237(6) | 3 926(4) |
| C(3) | 2 774(6) | 6 943(6) | 4 960(5) |
| C(4) | 1 075(7) | 6 423(8) | 2 247(5) |
| C(5) | 842(10) | 7 552(8) | 1 913(7) |
| C(6) | 473(7) | 8 559(8) | 2 310(5) |
| C(7) | 2 467(8) | 9 632(7) | 2 090(5) |
| C(8) | 3 726(9) | 9 161(8) | 1 825(7) |
| C(9) | 4 467(7) | 8 111(6) | 1 737(5) |
| C(10) | 5 277(7) | 5 718(6) | 2 133(5) |
| C(11) | 4 379(7) | 5 336(6) | 1 805(5) |
| C(12) | 3 438(6) | 4 820(6) | 2 374(5) |
| C(13) | 1 397(6) | 4 754(6) | 3 673(5) |
| C(14) | 2 051(8) | 4 116(7) | 4 422(6) |
| C(15) | 1 113(8) | 3 923(7) | 3 223(5) |
| C(16) | 505(7) | 9 954(6) | 3 482(6) |
| C(17) | 168(8) | 11 018(7) | 2 946(6) |
| C(18) | 1 162(8) | 10 288(7) | 4 069(6) |
| C(19) | 6 143(6) | 7 157(7) | 2 912(5) |
| C(20) | 6 536(7) | 6 446(7) | 3 702(5) |
| C(21) | 7 238(6) | 7 016(7) | 2 200(5) |
| C(22) | 4 934(5) | 7 648(5) | 8 803(4) |
| C(23) | 6 011(5) | 7 915(5) | 8 394(4) |
| C(24) | 7 167(5) | 7 361(5) | 8 643(4) |
| C(25) | 7 304(5) | 6 483(5) | 9 296(4) |
| C(26) | 6 247(5) | 6 196(5) | 9 713(4) |
| C(27) | 5 097(5) | 6 751(5) | 9 482(4) |
| C(28) | 2 922(5) | 9 385(5) | 9 127(3) |
| C(29) | 3 609(5) | 9 913(5) | 9 445(4) |
| C(30) | 3 080(5) | 10 863(5) | 9 852(4) |
| C(31) | 1 812(5) | 11 317(5) | 9 956(4) |
| C(32) | 1 103(5) | 10 808(5) | 9 669(4) |
| C(33) | 1 642(5) | 9 872(5) | 9 260(4) |
| C(34) | 2 646(5) | 7 497(5) | 8 708(4) |
| C(35) | 2 063(5) | 7 177(5) | 9 503(4) |
| C(36) | 1 320(5) | 6 460(5) | 9 666(5) |
| C(37) | 1 115(5) | 6 005(6) | 9 026(5) |
| C(38) | 1 656(6) | 6 296(6) | 8 237(5) |
| C(39) | 2 412(5) | 7 016(5) | 8 085(4) |
| C(40) | 3 649(5) | 8 921(5) | 7 576(4) |
| C(41) | 2 954(5) | 10 019(5) | 7 289(4) |
| C(42) | 2 956(6) | 10 457(6) | 6 450(4) |
| C(43) | 3 651(6) | 9 855(6) | 5 848(4) |
| C(44) | 4 387(6) | 8 773(6) | 6 099(4) |
| C(45) | 4 373(6) | 8 346(6) | 6 921(4) |

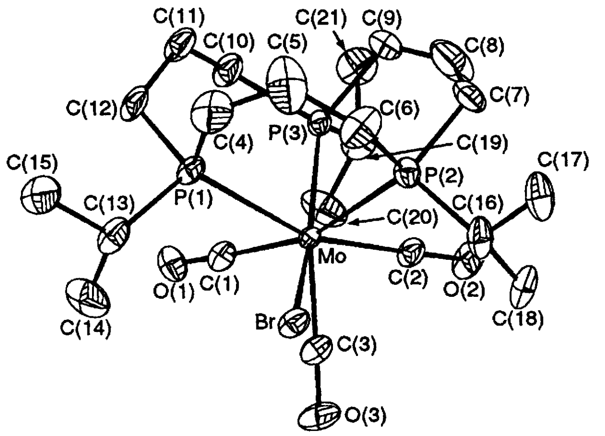


**Fig. 1** Crystal structure and atom numbering scheme of the cation of $[MoBr(CO)_3\{$*cyclo*-$(Pr^iPC_3H_6)_3\}]^+$ **2**. The anion $(BPh_4^-)$ has been omitted for clarity

fractional coordinates in Table 4. The co-ordination geometry around molybdenum appears as a well defined capped octahedron. The octahedron is best defined by the three phosphorus atoms, two of the carbonyls [C(1) and C(2)] and the bromine atom, the cap being the other carbonyl carbon on the triangular face defined by C(1), C(2) and Br. This description provides the best view where the two opposite, staggered, triangular faces are almost co-parallel; if the bromine atom is chosen as the cap, the corresponding faces defined by the three carbonyls and the three phosphorus atoms deviate considerably from coplanarity. It is somewhat surprising that the capping group is a carbonyl ligand and not the Br atom which has the longer metal contact distance [1.984(8) *vs.* 2.702(2) Å respectively]. The average Mo–P and Mo–C distances [2.586(6) and 1.996(8) Å respectively] are similar, within experimental error, to those in the molybdenum(0) percursor [2.5269(8) and 1.981(2) Å respectively]. The very slight lengthening of the Mo–P bonds upon oxidation is presumably due to the increase in co-ordination number. The most closely similar complexes to compare to **2** which have been structurally characterised all contain chelating dppm ligands [dppm = 1,2-bis(diphenylphosphino)methane]. These are the neutral molybdenum(II) complexes, $[MoI_2(CO)_3(dppm)]$, $[MoBr_2(CO)_3(dppm)]$,[17] $[MoBr_2(CO)_2(dppm)(dppm$-*P*$)]$,[10] and $[MoCl_2(CO)_2(dppm)(dppm$-*P*$)]$.[18] For the first pair the structures are reported to be distorted pentagonal bipyramids with the chelating diphosphines in the equatorial plane. In both of these structures the average Mo–P distances [2.4587(15) and 2.453(11) Å respectively] are similar but shorter than that in **2** [2.586(6) Å]. This difference is presumably due to the difference in co-ordination geometry since in the second pair the structures are described as distorted between capped octahedral and capped trigonal prismatic and the Mo–P bond lengths [2.554(2) and 2.541(7) Å respectively] are only slightly shorter than that observed in **2**. The average Mo–Br distances in these examples [2.617(6) and 2.668(1) Å respectively] are also slightly shorter than that in **2**. The slight differences in bond lengths between these seven-co-ordinate complexes are probably due to differences in the steric properties of the ligands. Comparison of the average Mo–C bond length in **2** [1.996(8) Å] with that in $[MoBr_2(CO)_2(dppm)(dppm$-*P*$)]$ [1.953(4) Å], might indicate a decrease in the degree of M–CO π-bonding in the cation compared to that in the neutral dibromotriphosphine complex, as is indicated in the IR spectrum of **2**.

## Experimental

*Procedures.*—All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by refluxing over standard drying agents. The compounds $[Mo(CO)_3\{$*cyclo*-$(HPC_3H_6)_3\}]$,[19] $[W(CO)_3\{$*cyclo*-$(HPC_3H_6)_3\}]$,[1] $[Mo(CO)_3\{$*cyclo*-$(Pr^iPC_3H_6)_3\}]$[1] and $[Mo(CO)_3\{$*cyclo*-$(Me_3SiCH_2PC_3H_6)_3\}]$[1] were prepared as previously reported. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. The $^{31}P$ NMR

**Table 5** Synthetic details for the preparation of complexes **4** and **6–18**

| Product complex | Precursor complex (amount/g, mmol) | Reaction solvent ($V$/cm$^3$) | Reagent[a] (amount/g, mmol) | Reaction | | Recrystallisation | Yield (g, %) | Solubility[b] | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $t$/h | $T$/°C | | | $CH_2Cl_2$ | $C_6H_5Me$ |
| **4** | $[Mo(CO)_3\{(Pr^iPC_3H_6)_3\}]$ (0.53, 1.0) | $CH_2Cl_2$ (60) | $I_2$ (0.25, 1.0) | 0.5 | −78 | $CH_2Cl_2$–$Et_2O$ | 0.56, 72 | s | ss |
| **6** | $[Mo(CO)_3I\{(Pr^iPC_3H_6)_3\}]I$ (0.56, 0.72) | $CH_2Cl_2$ (200) | — | 168 | 25 | $CH_2Cl_2$–$Et_2O$ | 0.46, 85 | s | ss |
| **7** | $[Mo(CO)_3\{(Me_3SiCH_2PC_3H_6)_3\}]$ (0.66, 1.0) | $CH_2Cl_2$ (60) | $Br_2$ (0.16, 1.0) | 0.5 | −78 | $CH_2Cl_2$–$Et_2O$ | 0.56, 68 | ss | i |
| **8** | $[MoBr(CO)_3\{(Me_3SiCH_2PC_3H_6)_3\}]Br$ (0.56, 0.68) | $CH_2Cl_2$ (200) | — | 168 | 25 | $CH_2Cl_2$–$Et_2O$ | 0.39, 72 | s | ss |
| **9** | $[Mo(CO)_3\{(Pr^iPC_3H_6)_3\}]$ (0.53, 1.0) | $CH_2Cl_2$ (60) | $Cl_2$ | 0.5 | 0 | $CH_2Cl_2$–$Et_2O$ | 0.52, 83 | s | ss |
| **10** | $[MoCl(CO)_3\{(Pr^iPC_3H_6)_3\}]Cl$ (0.52, 0.83) | $CH_2Cl_2$ (200) | — | 168 | 25 | $CH_2Cl_2$–$Et_2O$ | 0.39, 83 | s | ss |
| **11** | $[Mo(CO)_3\{(HPC_3H_6)_3\}]$ (0.40, 1.0) | $CH_2Cl_2$ (60) | $Br_2$ (0.16, 1.0) | 0.5 | −78 | Washed with $Et_2O$ | ≈50[c] | ss | i |
| **12** | $[MoBr(CO)_3\{(HPC_3H_6)_3\}]Br$ (0.50, 0.89) | $CH_2Cl_2$ (50) | — | 4 | 25 | Washed with $CH_2Cl_2$ | 0.44, 93 | i | i |
| **13** | $[Mo(CO)_3\{(HPC_3H_6)_3\}]$ (0.40, 1.0) | $CH_2Cl_2$ (60) | $I_2$ (0.25, 1.0) | 0.5 | −78 | Washed with $Et_2O$ | ≈60[c] | ss | i |
| **14** | $[Mo(CO)_3I\{(HPC_3H_6)_3\}]I$ (0.50, 0.79) | $CH_2Cl_2$ (50) | — | 4 | 25 | Washed with $CH_2Cl_2$ | 0.44, 88 | i | i |
| **15** | $[W(CO)_3\{(HPC_3H_6)_3\}]$ (0.49, 1.0) | $CH_2Cl_2$ (60) | $Br_2$ (0.16, 1.0) | 0.5 | −78 | Washed with $Et_2O$ | ≈75[c] | ss | i |
| **16** | $[WBr(CO)_3\{(HPC_3H_6)_3\}]Br$ (0.50, 0.77) | $CH_2Cl_2$ (50) | — | 84 | 25 | Washed with $CH_2Cl_2$ | 0.35, 73 | i | i |
| **17** | $[W(CO)_3\{(HPC_3H_6)_3\}]$ (0.49, 1.0) | $CH_2Cl_2$ (60) | $I_2$ (0.25, 1.0) | 0.5 | −78 | Washed with $Et_2O$ | ≈80[c] | ss | i |
| **18** | $[W(CO)_3I\{(HPC_3H_6)_3\}]I$ (0.50, 0.69) | $CH_2Cl_2$ (50) | — | 84 | 25 | Washed with $CH_2Cl_2$ | 0.36, 73 | i | i |

[a] In $CH_2Cl_2$ (25 cm$^3$) in all cases except for complex **9** where $Cl_2$ gas was bubbled through the solution. [b] At room temperature: s = soluble; ss = slightly soluble; i = insoluble. [c] Product contaminated with the dihalogeno derivative into which it readily converts. The overall chemical yield of the mixture was quantitative; the yields were estimated from the relative intensities of ν(CO) in the IR spectrum.

spectra were recorded in $CDCl_3$ solution on a JEOL FX-90 instrument operating at 36.23 MHz, chemical shifts being quoted in ppm relative to 85% external $H_3PO_4$, infrared spectra in Nujol on a Nicolet 510 FT-IR spectrometer. Mass spectra and microanalyses were obtained from within this department.

*Preparations*.—The procedures for the halogenohalide complexes **1**, **4**, **7**, **9**, **11**, **13**, **15** and **17** are similar; a representative is given for **1**. Likewise, the dihalogeno complexes **3**, **6**, **8**, **10**, **12**, **14**, **16** and **18** were also prepared by the same method which is given in detail for **3**. Complexes **11**, **13**, **15** and **17** were all contaminated with the corresponding dihalogeno derivative into which they convert under the reaction conditions. In all these cases the overall chemical yield (based on metal) was virtually quantitative and the actual yield of the halogenohalide complex was estimated by IR spectroscopy. Other experimental details for complexes **4**, and **6**–**18** are collected in Table 5.

$[MoBr(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]Br$ **1**. To a cooled (−78 °C) solution of $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ (0.53 g, 1.00 mmol) in $CH_2Cl_2$ (60 $cm^3$) was added a solution of $Br_2$ (0.16 g, 1.00 mmol) in $CH_2Cl_2$ (40 $cm^3$) dropwise over 30 min. The solvent was removed *in vacuo* to give a yellow, oily residue which was recrystallised from $CH_2Cl_2$–$Et_2O$ to give **1** as a yellow solid (0.52 g, 75%) which was slightly soluble in chlorinated hydrocarbons and insoluble in hydrocarbons and aliphatic ethers.

$[MoBr(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]BPh_4$ **2**. To a cooled (− 78 °C) solution of $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ (0.53 g, 1.00 mmol) in $CH_2Cl_2$ (60 $cm^3$) was added a solution of $Br_2$ (0.16 g, 1.00 mmol) in $CH_2Cl_2$ (40 $cm^3$) dropwise over 30 min. A solution of $NaBPh_4$ (1.8 g, 5.26 mmol) in EtOH (50 $cm^3$) was added, followed by EtOH (50 $cm^3$), causing the precipitation of a yellow solid. The mixture was allowed to settle and the supernatant decanted from the solid residue. The residue was washed with EtOH and recrystallised from $CH_2Cl_2$–EtOH to give **2** as a pale yellow solid (0.73 g, 70%) which was soluble in dichloromethane and sparingly soluble in toluene.

$[MoBr_2(CO)_2\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ **3**. A solution of complex **1** (0.52 g, 0.75 mmol) in $CH_2Cl_2$ (50 $cm^3$) was stirred at room temperature for 7 d. The solvent was removed *in vacuo* to give a yellow, oily product which was recrystallised from $CH_2Cl_2$–$Et_2O$ to give **3** as a yellow solid (yield = 0.45 g, 92%) which was soluble in dichloromethane and sparingly soluble in toluene.

$[Mo(CO)_3I\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]BPh_4$ **5**. To a cooled (− 78 °C) solution of $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ (0.53 g, 1.00 mmol) in $CH_2Cl_2$ (60 $cm^3$) was added a solution of $I_2$ (0.26 g, 1.00 mmol) in $CH_2Cl_2$ (40 $cm^3$) dropwise over 30 min. A solution of $NaBPh_4$ (1.8 g, 5.26 mmol) in EtOH (50 $cm^3$) was then added, followed by $Et_2O$ (50 $cm^3$), at which point a bright orange solid precipitated. The mixture was allowed to settle and the supernatant decanted from the solid residue. The residue was washed with EtOH and recrystallised from $CH_2Cl_2$–EtOH to give **5** as an orange solid (yield = 72%) which was soluble in dichloromethane and sparingly soluble in toluene.

*Crystallography*.—Crystals of complex **2** suitable for X-ray crystallography were grown from a saturated dichloromethane solution by cooling to −20 °C. An orange prism of approximate dimensions 0.14 × 0.14 × 0.21 mm was selected for data collection and mounted in silicone oil.

*Crystal data*. $C_{45}H_{59}BBrMoO_3P_3$, $M_r = 927.49$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.469(5)$, $b = 12.496(5)$, $c = 16.544(8)$ Å, $\alpha = 78.84(9)$, $\beta = 79.01(9)$, $\gamma = 72.5(3)°$ (by least-squares analysis of 50 reflections), $U = 2196(2)$ Å$^3$, $Z = 2$, $D_c = 1.403$ g $cm^{-3}$, $F(000) = 960$, $\mu = 1.356$ $mm^{-1}$, $T = 150$ K.

*Data collection and processing*.[20] Data were collected on a Delft Instruments FAST TV area detector at the window of a rotating-anode generator (50 kV, 45 mA), with a molybdenum target [$\lambda$(Mo-K$\alpha$) = 0.710 69 Å], controlled by a Micro Vax 3200 computer and driven by MADNES[21] software. 9537 Reflections were collected ($1.88 < \theta < 25.02°$), index ranges $-13 < h < 13$, $14 < k < 14$, $-18 < l < 18$, producing 6162 unique data ($R_{int} = 0.0651$ after absorption correction, DIFABS[22]). Data reduction was performed using the program ABSMAD.[23]

*Structure analysis and refinement*. The structure was solved by the Patterson heavy-atom method (SHELXS[24]) and the remaining non-hydrogen atoms were located by successive Fourier-difference syntheses, and then subjected to full-matrix least-squares refinement based on $F_o^2$ (SHELXL 93[25]). Non-hydrogen atoms were refined anisotropically with all hydrogens fixed in idealised positions and isotropic thermal parameters tied to the value of the parent atom. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$ which gave satisfactory agreement analyses.

Final $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ and $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$ values were 0.1288 and 0.0698 respectively, for all 6162 data and 493 parameters ($\rho_{max}$, $\rho_{min}$ 1.028, −0.769 e Å$^{-3}$). The corresponding $wR_2$ and $R_1$ values for 4341 data with $F_o > 4\sigma(F_o)$ were 0.1231 and 0.0513 respectively. Some carbon atoms had noticeably large anisotropic values of $U_{ij}$ [especially C(5) and C(8)]. However, the structure could not be satisfactorily refined on the assumption that they were disordered with two alternative positions. We presume that the large thermal anisotropy is linked with the expected freedom of these atoms to undergo chair ⟷ boat conformational conversions.

Diagrams were drawn with SNOOPI.[26] Sources of scattering factor data are given in ref. 25.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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