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Synthesis, characterization and crystal structures of $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$TPTA (TPTA = 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane)

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Abstract

Pentacarbonyl complexes of molybdenum and tungsten with 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) have been prepared and characterized. The compounds possess four $M(CO)_5$ units per ligand, with an octahedral coordination environment for each metal atom, all bound to the phosphorus donors from the pendant arms.

Keywords: Molybdenum; Tungsten; Carbonyl; Crystal structure

1. Introduction

The fact that macrocyclic ligand complexes are involved in a number of fundamental biological systems has been known for a long time and has provided a driving force for development of the coordination chemistry of macrocyclic multidentate ligands [1,2].

In the search for metal ion selective ligands, much interest has centered on metal complexes with functionalized polyamine macrocycles that have pendant functional groups. The resulting metal complexes exhibit a considerable range of structure and stability depending substantially on the nature of the pendant arms [3].

1,4,8,11-Tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) is one of the rare functionalized tetraaza macrocycles with phosphorus donor atoms in the side chains [4]. It possesses four NCH_2P units and shows a great variety of coordination modes. However, mostly due to the rather high sensitivity of the ligand, information about its ability in complex formation is still lacking, except for very recent work in our laboratory [5]. In that work, as a part of an integrated study on metal carbonyl chemistry with polydentate ligands [5–7], we synthesized and characterized two binuclear tetracarbonyl complexes of molybdenum and tungsten with TPTA, which appear to be the first reported coordination compounds with this ligand [5].

In an extension of our study, we describe below the preparation and spectral and structural characterization of the two new, tetranuclear, molybdenum and tungsten complexes with 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane.

2. Results and discussion

2.1. Preparation and properties

Treatment of molybdenum and tungsten hexacarbonyls with 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane under carefully chosen reaction conditions resulted in isolation of two crystalline products, which analysed as $[Mo(CO)_5]_4$TPTA (**1**) and $[W(CO)_5]_4$TPTA (**2**). The compounds were formed according to Scheme 1.

The reactions were carried out in n-butanol, in a

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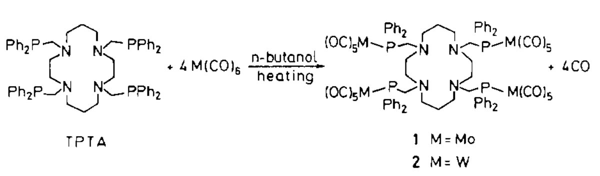

Scheme 1.

sealed tube that was kept for a prolonged period at the appropriate temperature (ca. 100°C for molybdenum and ca. 130°C for tungsten). Even small changes in the experimental conditions were found to change the course of the reaction. For example, an inadequate metal to ligand ratio leads to the formation of the binuclear complexes, $[M(CO)_4]_2$TPTA, described in our previous paper [5], or to a mixture of $[M(CO)_4]_2$TPTA and $[M\text{-}(CO)_5]_4$TPTA, while a little too high temperature causes the decomposition of the ligand. A higher metal to ligand ratio does not change the course of the reaction.

It is to be noted that a subsequent reaction of the tetranuclear complexes, $[M(CO)_5]_4$TPTA (M = Mo, W), with additional ligand in CH_2Cl_2 yields binuclear complexes with the loss of carbon monoxide:

$$[M(CO)_5]_4\text{TPTA} + \text{TPTA} \longrightarrow$$
$$2[M(CO)_4]_2\text{TPTA} + 4\text{CO}$$

It thus appears that the easily affected balance between binuclear and tetranuclear complexes lies slightly on the side of the binuclear species.

The complexes $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$-TPTA are diamagnetic, yellow crystalline substances. They are moderately stable in air. The unusually high molecular weight for monomeric coordination compounds, with four metal atoms per ligand, renders the complexes only slightly soluble, in a limited number of solvents (aliphatic alcohols, CH_2Cl_2, $CHCl_3$). This prevented us from obtaining some spectroscopic data, such as ^{31}P NMR parameters.

The complexes were characterized by elemental analyses, IR and ^{1}H NMR spectral data and by single-crystal X-ray diffraction studies. X-ray quality crystals of **1** and **2** were grown from the more dilute solutions where the reactants, TPTA and the respective metal hexacarbonyl in n-butanol, were gradually warmed and then kept at ca. 90°C for the molybdenum and at ca. 110°C for the tungsten complex.

In previously described binuclear complexes of molybdenum and tungsten with this ligand, two phosphorus atoms from the two pendant arms are coordinated to the same metal atom to produce a 9-membered chelate ring, instead of a 4-membered chelate ring with one phosphorus and one nitrogen atom [5]. The strong preference of these metals to bind with the soft phosphine donor atoms rather than with the harder nitrogen is evident. In complexes described here, $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$TPTA, the same tendency has been revealed. Phosphorus to metal bonding in **1** and **2** was unambiguously established by the crystal structure determinations, but spectroscopic data aided in the structural assignments.

Table 1
IR spectral data (cm^{-1}) for **1** and **2** [1]

	1	**2**
ν(CO)	2070s, sp (2065) 1995w (1990) 1925vs (1945)	2068s, sp (2070) 1988sh (1975) 1917vs (1940)
δ(M–CO)	608s 582s	596s 572s
ν(M–C)	373s	378s

[1] Spectra run as KBr pellets. Values in parentheses obtained from CH_2Cl_2.

2.2. *Infrared and ^{1}H NMR spectral studies*

The infrared and ^{1}H NMR spectral data (summarized in Tables 1 and 2) are consistent with phosphorus to metal bonding in $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$TPTA.

The most dominant absorption bands in the IR spectra of **1** and **2** are those from the CO group vibrations. In the case of the $M(CO)_5$ moiety, the isolated complexes have local C_{4v} symmetry, which leads to three infrared active carbonyl stretching modes (two A_1 and an E) [8]. Three absorption bands are indeed observed in the ν(CO) region of the spectra of $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$TPTA (Table 1). The frequencies of the CO stretching vibrations correlate with those for the analogous phosphine ligand complexes, and are higher than the frequencies found for the corresponding complexes with nitrogen.

The ^{1}H NMR spectrum of the ligand, in addition to the phenyl proton resonances, exhibits in the range of $\delta = 4$ to $\delta = 1$ ppm, four resonances with relative intensities of 2:2:2:1. These resonances correspond respectively to a doublet from the CH_2 protons outside the ring, to a singlet from the NCH_2CH_2N protons, to a triplet from the methylene protons α to the ring

Table 2
^{1}H NMR data for TPTA and $[Mo(CO)_5]_4$ TPTA [1]

H-atoms	δ (ppm)	
	TPTA	$[Mo(CO)_5]_4$TPTA
$P\text{–}C_6H_5$	7.31 (40 H)	7.39 (40 H)
NCH_2P	3.25 (d, 8H)	3.18 (s, 8H)
NCH_2CH_2N	2.57 (s, 8H)	2.08 (s, 8H)
$NCH_2CH_2CH_2N$	2.50 (t, 8H)	1.91 (t, 8H)
$NCH_2CH_2CH_2N$	1.42 (m, 4H)	1.08 (m, 4H)

[1] Spectra recorded in $CDCl_3$ at 22°C and referenced to TMS; s, singlet; d, doublet; t, triplet; m, multiplet.

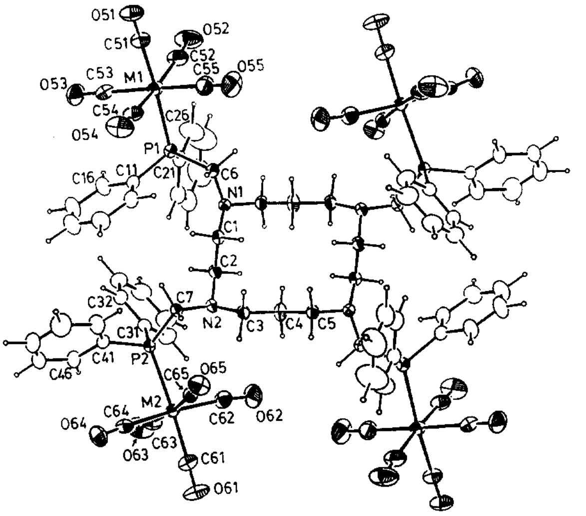

Fig. 1. ORTEP drawing of $[M(CO)_5]_4$TPTA (M = Mo in **1**, M = W in **2**) with the atom numbering scheme.

nitrogens in $NCH_2CH_2CH_2N$ units and to a multiplet from the bridging CH_2 protons in the same units (Table 2). In keeping with the diamagnetism of the complex, $[Mo(CO)_5]_4$TPTA also gives a well-resolved proton NMR spectrum. The resonances originating from the protons inside the ring exhibit large upfield chemical shift upon coordination of the ligand. This is attributed to the shielding effect due to the negative charge provided by the metal bound to phosphorus. If coordination were through nitrogen, deshielding would be expected. At the same time, there is only a small upfield shift for the NCH_2P protons and a decreased shielding of the phenyl protons, indicating charge removal from the phosphorus atoms.

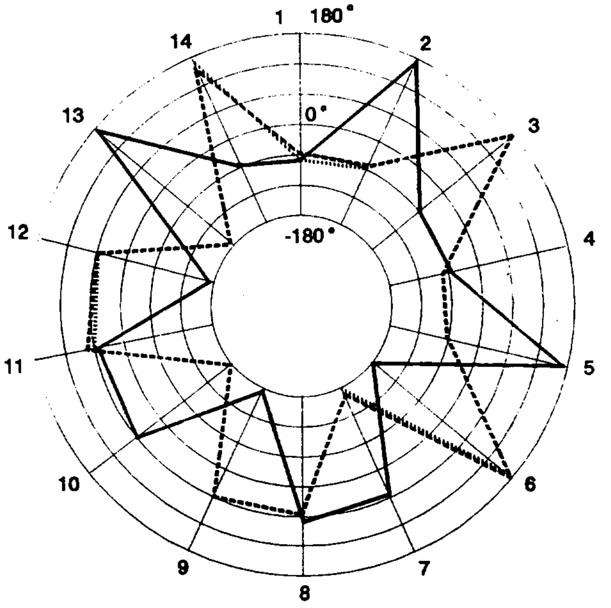

Fig. 2. Polar diagram illustrating the conformation of the macrocyclic ring in TPTA (dashed lines), $[M(CO)_4]_2$TPTA (dotted lines, only where different from TPTA) and **1** and **2** (full lines). The values of torsion angles are plotted for the ring bond sequence starting with bond N1–Cl for $[M(CO)_4]_2$TPTA and $N1^i$–Cl^i for **1** and **2**.

It should be noted that the PCH_2N methylene protons in the complex exhibit a slightly broadened singlet with no resolvable P–H coupling observed (Table 2). This is rather unexpected, since protons on carbons α to phosphorus in diamagnetic coordination compounds usually exhibit a detectable coupling to phosphorus. However, this decoupling effect has been observed previously [9,10].

Table 3
Bond lengths (Å) with e.s.d.s in parentheses for **1** and **2**

	M = Mo	M = W
M1–P1	2.544(2)	2.532(2)
M1–C51	2.002(7)	2.009(8)
M1–C52	2.067(8)	2.066(8)
M1–C53	2.038(8)	2.040(8)
M1–C54	2.018(8)	2.008(8)
M1–C55	2.069(7)	2.055(7)
M2–P2	2.535(2)	2.520(2)
M2–C61	2.008(6)	1.991(7)
M2–C62	2.039(7)	2.040(7)
M2–C63	2.044(7)	2.031(7)
M2–C64	2.059(9)	2.057(9)
M2–C65	2.044(7)	2.033(7)
C51–O51	1.143(8)	1.132(10)
C52–O52	1.137(10)	1.121(11)
C53–O53	1.144(10)	1.130(10)
C54–O54	1.140(9)	1.142(11)
C55–O55	1.130(8)	1.130(9)
C61–O61	1.136(8)	1.148(9)
C62–O62	1.128(9)	1.125(9)
C63–O63	1.133(8)	1.145(9)
C64–O64	1.127(11)	1.129(12)
C65–O65	1.140(9)	1.139(9)
P1–C6	1.880(5)	1.873(6)
P1–C11	1.837(5)	1.829(5)
P1–C21	1.821(7)	1.823(8)
P2–C7	1.856(5)	1.854(5)
P2–C31	1.833(6)	1.832(6)
P2–C41	1.837(5)	1.833(5)
C6–N1	1.442(7)	1.452(8)
C7–N2	1.472(6)	1.462(7)
N1–C1	1.474(6)	1.461(8)
C1–C2	1.530(8)	1.520(10)
C2–N2	1.484(6)	1.477(7)
N2–C3	1.479(6)	1.473(7)
C3–C4	1.530(8)	1.517(9)
C4–C5	1.537(7)	1.530(8)
$C5–N1^1$	1.471(7)	1.465(8)
Average bond lengths within the phenyl rings (*n* = 1, 2, 3, 4)		
Cn1–Cn2 Cn1–Cn6	1.386(3)	1.389(4)
Cn2–Cn3 Cn5–Cn6	1.390(5)	1.390(4)
Cn3–Cn4 Cn4–Cn5	1.364(3)	1.363(4)

[1] Symmetry code: (i) $1-x$, $1-y$, $1-z$.

Table 4
Bond angles (°) with e.s.d.s in parentheses for **1** and **2**

	M = Mo	M = W
C54–M1–C55	86.8(3)	86.8(3)
C53–M1–C55	176.8(3)	176.4(3)
C53–M1–C54	89.9(3)	89.6(3)
C52–M1–C55	93.7(3)	93.6(3)
C52–M1–C54	174.9(4)	175.1(3)
C52–M1–C53	89.6(3)	89.9(4)
C51–M1–C55	89.7(3)	89.1(3)
C51–M1–C54	88.9(3)	88.6(3)
C51–M1–C53	90.3(3)	90.6(3)
C51–M1–C52	86.0(3)	86.5(3)
P1–M1–C55	88.4(2)	88.6(2)
P1–M1–C54	87.2(2)	87.4(2)
P1–M1–C53	91.4(2)	91.4(3)
P1–M1–C52	97.8(2)	97.4(3)
P1–M1–C51	175.8(2)	175.6(2)
C64–M2–C65	91.0(3)	91.6(3)
C63–M2–C65	173.7(3)	173.9(3)
C63–M2–C64	92.0(3)	91.1(3)
C62–M2–C65	87.6(3)	87.7(3)
C62–M2–C64	175.5(3)	175.0(3)
C62–M2–C63	89.8(3)	90.0(3)
C61–M2–C65	85.6(3)	85.6(3)
C61–M2–C64	91.6(3)	91.5(3)
C61–M2–C63	88.7(3)	88.9(3)
C61–M2–C62	92.6(3)	93.4(3)
P2–M2–C65	90.5(2)	90.6(2)
P2–M2–C64	89.5(2)	89.8(2)
P2–M2–C63	95.1(2)	94.8(2)
P2–M2–C62	86.3(2)	85.3(2)
P2–M2–C61	176.0(2)	176.1(2)
M1–P1–C21	123.1(2)	122.8(2)
M1–P1–C11	109.5(2)	109.5(2)
M1–P1–C6	111.9(2)	111.8(2)
C11–P1–C21	104.3(3)	104.2(3)
C6–P1–C21	101.2(3)	101.5(3)
C6–P1–C11	105.1(3)	105.4(3)
M2–P2–C41	110.5(2)	110.7(2)
M2–P2–C31	120.0(2)	119.6(2)
M2–P2–C7	117.2(2)	116.5(2)
C31–P2–C41	103.4(2)	103.6(3)
C7–P2–C41	103.3(3)	103.4(3)
C7–P2–C31	100.4(2)	101.0(2)
P1–C6–N1	114.5(4)	114.5(4)
P2–C7–N2	109.4(4)	109.3(4)
C6–N1–C5$^{\mathrm{i}}$	113.3(4)	113.2(5)
C1–N1–C5$^{\mathrm{i}}$	115.1(4)	115.2(5)
C6–N1–C1	115.2(4)	115.1(5)
N1–C1–C2	111.2(4)	111.3(5)
C1–C2–N2	114.4(4)	115.2(5)
C7–N2–C2	112.7(4)	113.5(5)
C2–N2–C3	115.3(4)	114.7(5)
C7–N2–C3	112.3(4)	112.0(5)
N2–C3–C4	112.0(4)	112.9(5)
C3–C4–C5	111.0(5)	112.0(5)
C4–C5–N1^{1}	113.7(4)	114.4(5)
M1–C51–O51	177.5(6)	178.7(6)
M1–C52–O52	175.1(7)	175.7(8)
M1–C53–O53	176.3(7)	177.6(8)
M1–C54–O54	177.5(7)	178.1(7)
M1–C55–O55	175.6(6)	176.8(7)
M2–C61–O61	179.1(6)	179.2(7)
M2–C62–O62	176.6(6)	177.3(6)
M2–C63–O63	175.0(6)	173.8(7)
M2–C64–O64	178.8(7)	177.5(8)
M2–C65–O65	175.1(6)	175.7(6)
P1–C11–C16	120.0(4)	120.2(5)
P1–C11–C12	121.1(4)	121.1(5)
P1–C21–C26	120.5(5)	120.3(6)
P1–C21–C22	122.2(5)	121.1(5)
P2–C31–C36	119.7(4)	120.2(5)
P2–C31–C32	121.4(4)	121.2(5)
P2–C41–C46	118.0(5)	118.1(5)
P2–C41–C42	122.0(4)	122.3(5)
Average bond angles within the phenyl rings (n = 1, 2, 3, 4)		
Cn2–Cn1–Cn3	118.5(5)	118.5(3)
Cn1–Cn2–Cn3 Cn1–Cn6–Cn5	120.3(3)	120.3(2)
Cn2–Cn3–Cn4 Cn4–Cn5–Cn6	120.3(3)	120.2(2)
Cn3–Cn4–Cn5	120.3(2)	120.5(2)

[1] Symmetry code: (i) $1-x$, $1-y$, $1-z$.

2.3. *X-ray structures of complexes 1 and 2*

The X-ray study confirmed that the tetranuclear complexes $[Mo(CO)_5]_4$TPTA and $[W(CO)_5]_4$TPTA are formed by coordination to the metal atoms of phosphorus atoms from the four methyldiphenylphosphino groups of the TPTA macrocycle. The molecular structure of $[M(CO)_5]_4$TPTA (M = Mo in **1** and M = W in **2**) is shown in Fig. 1. Bond distances and angles for both complexes are listed in Tables 3 and 4.

Compounds **1** and **2** are isomorphous and isostructural. The molecules have a crystallographically imposed center of symmetry. Comparison of the corresponding distances and angles in the two complexes shows that there is a close similarity which is consistent with the fact that Mo and W are chemically very similar and have a similar radius. Each of the metal atoms is coordinated by a phosphorus atom and five carbon atoms from the carbonyl groups, forming a slightly deformed octahedron. The octahedron around M1 is deformed to a greater degree as a result of the steric repulsion of phenyl C21–C26 which is at an angle of 74.2(2)° in **1** and 73.9(2)° in **2** to the equatorial carbonyl plane, with the hydrogen atom on C26 approaching C52 at a distance of 2.39(1) and 2.36(1) Å in **1** and **2**, respectively. This results in the increase of the M1–P1–C21 angle from the ideal tetrahedral to 123.1(2)° in **1** and 122.8(2)° in **2**. In order to minimize repulsions, the carbonyl CO(52) moves away from the phenyl, resulting in the P1–M1–C52 angle of 97.8(2)° in **1** and 97.4(3)° in **2**, which represents the greatest deviation from an ideal octahedron. The other phenyl (C11–C16) is almost parallel to the equatorial carbonyl plane (10.2(2)° in **1** and 10.4(2)° in **2**) and has no effect on the octahedral geometry. The steric effects on the M2 octahedron are less pronounced.

Such an orientation of the phenyl C21–C26 probably causes the bond M1–P1 (2.544(2) Å in **1** and 2.532(2) Å in **2**) to be longer than M2–P2 (2.535(2) Å in **1** and 2.520(2) Å in **2**). The Mo–P bonds are longer than in the structures of $Mo(CO)_5Ph_2PNSO$ [12], $Mo(CO)_5P(CH_2CH_2CN)_3$ [13] or $Mo(CO)_5PPh_2P(O)(OEt)_2$ [14] where these values are 2.484(2), 2.506(1) and 2.524(1) Å, respectively. The unstrained distance of Mo2–P2 is similar to the value of 2.534(1) Å in $Mo(CO)_5PPh_2P(O)Ph_2$ [15], but both Mo–P values in **1** are shorter than in $Mo(CO)_5PPh_3$ [13] where the distance is 2.560(1) Å. The W–P bonds in **2** are longer than in $W(CO)_5P(CH_3)_3$ (d(W–P) = 2.516(2) Å) [16], comparable to the value of 2.535(2) Å in $W(CO)_5(P^iPr)_3$ [17], but shorter than in $W(CO)_5P(^tBu)_3$ [18] (d(W–P) = 2.686(4) Å). The weakening of the Mo–P and W–P bond has been discussed in terms of the steric effects of bulkier ligands [14,17], which is in agreement with the above discussion.

The carbonyls *trans* to phosphorus have significantly shorter M–C distances than those that lie in the equatorial plane because of the greater degree of M–C π-back bonding. This is due to the lower π acidity of the ligand compared with that of the carbonyl group. The average distance $M{-}CO_{ax}$ is 2.005(3) Å in **1** and 2.000(9) Å in **2**, while the average $M{-}CO_{eq}$ distances are 2.048(6) and 2.041(6) Å for **1** and **2**, respectively.

The bond lengths and angles within the TPTA macrocycle are within the normal ranges and there are no significant differences of the corresponding values in the free TPTA and the four complexes **1**, **2** and $[M(CO)_4]_2$TPTA (M = Mo, W). The conformations of the macrocyclic ring in TPTA [4] and in the binuclear complexes $[M(CO)_4]_2$TPTA [5] are very similar (the maximum difference between the values of the torsion angles is 13°). The bonding of the two phosphorus atoms to metal in the binuclear complexes is achieved by rotation of the methyldiphenylphosphino groups and by only a small change in the conformation of the ring. This enables a closer approach of the two phosphorus atoms and rotation of the phenyl groups away from the metal. In the tetranuclear complexes **1** and **2**, the four very bulky substituents ($-CH_2PPh_2M(CO)_5$) tend to be separated as far apart as possible. This is achieved not only by rotation of methyldiphenylphosphino groups but also by a change in the conformation

Table 5
Crystal data, data collection parameters and refinement details for **1** and **2**

	1	**2**
Empirical formula	$Mo_4C_{82}H_{68}N_4O_{20}P_4$	$W_4C_{82}H_{68}N_4O_{20}P_4$
Formula weight	1937.1	2288.7
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.260(4)	10.224(4)
b (Å)	13.390(5)	13.334(6)
c (Å)	16.458(6)	16.427(7)
α (°)	84.22(2)	84.19(2)
β (°)	75.10(4)	75.20(4)
γ (°)	78.71(2)	78.46(2)
V (Å^3)	2140(1)	2118(2)
Z	1	1
D_{calc} (g cm^{-3})	1.503	1.794
F(000)	976	1104
Face indices, distances from centroid (mm)	(010), (0 − 10) 0.083; (001), (00 − 1) 0.79; (111), (−1 − 1 − 1) 0.225	(010), (0 − 10) 0.040; (001), (00 − 1) 0.112; (111), (−1 − 1 − 1) 0.218
μ (cm^{-1})	6.3	53.1
Min, max. transmission coefficients	–	0.313, 0.663
Range of collected data (°)	$4 < 2\Theta < 56$	$4 < 2\Theta < 60$
Scan type	ω	ω
No. of collected reflections	5932	7864
No. of significant reflections	4186	5876
n ($I > n\sigma(I)$)	3.0	3.5
No. of parameters refined	519	519
$R = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$	0.032	0.026
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{1/2}$	0.035	0.028
$S = [\Sigma w\Delta^2 / (N_{observations} - N_{parameters})]^{1/2}$	1.56	1.92
Weighting scheme w	1.0	1.0
Largest final shift/e.s.d.	0.003	0.002
Max. final $\Delta\rho$ (e Å^{-3})	0.41 (1.0 Å from Mo)	0.93 (0.8 Å from W)

of the macrocycle. The conformation of the macrocycle in TPTA and those in the four complexes closely approximate to the [3434] conformation of cyclotetradecane [19]. The polar map of the torsional angles in TPTA and the binuclear and tetranuclear complexes is given in Fig. 2 [20]. The macrocycles in $[M(CO)_5]_4$-TPTA and $[M(CO)_4]_2$TPTA can be overlapped by superimposing the heteroatoms $N1^i$ and $N2^i$ from **1** and **2** with the carbon atoms C1 and C3 in the binuclear complexes (the macrocycles in the complexes have the same numbering schemes).

The geometry of the phenyl rings reflects the σ-electron release from P, which results in a decrease in the α endocyclic angle to 118.5(3)° (average for both **1** and **2**) [21].

There are only Van der Waals contacts between the molecules.

In summary, pentacarbonyl complexes of molybdenum and tungsten with 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) are described. The compounds possess four $M(CO)_5$ units per ligand, with an octahedral coordination environment for each metal atom, all of the metals being bound to the phosphorus donors from the pendant arms. This was not surprising in the light of a greater affinity of these soft metals for phosphorus and of the steric requirements of the ligand. Studies on the ability of the ligand to form complexes that also contain coordinated nitrogen atoms are planned.

3. Experimental details

3.1. Materials

The ligand, 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) was synthesized by a published procedure [4]. 1,4,8,11-Tetraazacyclotetradecane (Fluka), diphenylphosphine (Fluka) and formaldehyde (37% aqueous, Kemika) were used as received. Metal hexacarbonyls, obtained from commercial sources (Merck) were resublimed prior to use. The solvents were purified and dried by standard methods and distilled under argon before use.

3.2. Physical measurements

Infrared spectra of dichloromethane solutions and KBr discs were recorded on a Perkin-Elmer Model 580B spectrophotometer, in the region 4000–200 cm^{-1}. Proton NMR spectra were recorded on a Varian Gemini-300 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Magnetic susceptibility measurements were performed at 22°C by the Gouy method, with $CuSO_4 \cdot 5H_2O$ for calibration. The complexes were diamagnetic.

3.3. Preparation of complexes 1 and 2

3.3.1. $[Mo(CO)_5]_4$TPTA (1)

A mixture of 0.118 g (0.45 mmol) of $Mo(CO)_6$, 0.099 g (0.10 mmol) of TPTA and 6 cm^3 of n-butanol was placed in a 20 cm Carius tube. The tube was then thoroughly degassed with argon, sealed and heated in a Carius furnace at 100°C for 3 days then allowed to cool to room temperature. The pale-yellow crystals that separated were filtered off, washed with a few cm^3 of dry n-butanol, and dried in vacuo. The yield was 0.095 g (49%).

Anal. Found: C, 50.94; H, 3.51; N, 2.95; P, 6.45; Mo, 19.53. $C_{82}H_{68}Mo_4N_4O_{20}P_4$ calc.: C, 50.84; H, 3.54; N, 2.89; P, 6.40; Mo, 19.81%.

3.3.2. $[W(CO)_5]_4$TPTA (2)

A mixture of 0.140 g (0.40 mmol) of $W(CO)_6$, 0.099 g (0.10 mmol) of TPTA and 4 cm^3 of n-butanol was placed in a 20 cm Carius tube under argon and the tube was sealed and heated at 130°C for 3 days then allowed to cool to room temperature. The light-yellow crystals were filtered off, washed with a small quantity of dry n-butanol and dried in vacuo. The yield was 0.100 g (44%).

Anal. Found: C, 43.14; H, 3.19; N, 2.60; P, 5.68; W, 31.75. $C_{82}H_{68}N_4O_{20}P_4W_4$ calc.: C, 43.03; H, 2.99; N, 2.45; P, 5.41; W, 32.13%.

3.4. Crystal structure determination

X-Ray diffraction data were collected at room temperature on a Philips PW1100 diffractometer (upgraded by STOE) using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) for both compounds. Unit cell dimensions were obtained by least-squares refinement of 20 reflections ($27.1 < 2\theta < 33.5°$) for both **1** and **2**. The unit cell parameters and details of data collection and refinement are given in Table 5. Standard reflections monitored every 90 min indicated no significant change in intensities for both complexes. The intensities were corrected for Lorentz and polarization effects. Absorption correction was applied only for **2** using program ACXR for a Gaussian correction [22]. R_{int} obtained by merging equivalent reflections was 0.028 in **1**, while in **2** it dropped from 0.070 to 0.032 after the absorption correction.

Positions of W atoms in **2** were determined by the Patterson method. Subsequent full-matrix least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms. Positions of the heavy atoms and the macrocyclic ring atoms from **2** were used as a starting model in **1**. The hydrogen atoms were included in calculated positions (C–H 1.08 Å) with grouped isotropic thermal parameters. All non-H atoms in both structures were refined anisotropically. Atomic scatter-

Table 6
Positional parameters and equivalent isotropic thermal parameters, with e.s.d.s in parentheses for **1**

	x	y	z	U_{eq} [1]
Mo1	−0.25429(5)	0.80657(4)	0.59039(3)	0.0479(2)
Mo2	0.52689(5)	0.13803(4)	0.83333(3)	0.0403(2)
P1	−0.04529(13)	0.72847(11)	0.64603(8)	0.0420(5)
P2	0.32038(12)	0.27525(10)	0.82697(8)	0.0344(5)
N1	0.2228(4)	0.6234(3)	0.5881(3)	0.044(2)
C1	0.2551(5)	0.5117(4)	0.6016(3)	0.045(2)
C2	0.3488(5)	0.4817(4)	0.6622(3)	0.042(2)
N2	0.3974(4)	0.3703(3)	0.6724(2)	0.039(1)
C3	0.4747(5)	0.3200(4)	0.5940(3)	0.045(2)
C4	0.5978(5)	0.3697(5)	0.5485(3)	0.052(2)
C5	0.6618(5)	0.3285(4)	0.4605(3)	0.045(2)
C6	0.0971(5)	0.6614(4)	0.5625(3)	0.046(2)
C7	0.2887(5)	0.3158(4)	0.7215(3)	0.038(2)
C51	−0.4254(6)	0.8596(5)	0.5511(4)	0.061(3)
O51	−0.5257(5)	0.8879(4)	0.5311(3)	0.081(2)
C52	−0.2198(7)	0.9551(6)	0.5715(5)	0.078(3)
O52	−0.2090(6)	1.0385(4)	0.5589(4)	0.120(3)
C53	−0.1474(7)	0.7795(6)	0.4696(5)	0.081(4)
O53	−0.0927(6)	0.7614(6)	0.4015(4)	0.135(4)
C54	−0.3023(7)	0.6657(5)	0.6043(4)	0.067(3)
O54	−0.3342(6)	0.5877(4)	0.6123(4)	0.102(3)
C55	−0.3652(6)	0.8258(5)	0.7137(5)	0.063(3)
O55	−0.4307(6)	0.8320(4)	0.7803(3)	0.098(3)
C11	−0.0898(5)	0.6290(4)	0.7283(3)	0.046(2)
C12	−0.0913(6)	0.5308(4)	0.7078(4)	0.052(2)
C13	−0.1367(6)	0.4582(5)	0.7694(5)	0.070(3)
C14	−0.1848(7)	0.4844(6)	0.8517(5)	0.076(3)
C15	−0.1867(7)	0.5799(6)	0.8724(4)	0.072(3)
C16	−0.1403(6)	0.6542(5)	0.8125(3)	0.056(2)
C21	0.0472(5)	0.8032(5)	0.6906(3)	0.050(2)
C22	0.1370(6)	0.7586(5)	0.7395(4)	0.058(2)
C23	0.2141(7)	0.8142(7)	0.7678(4)	0.076(4)
C24	0.2032(9)	0.9157(8)	0.7478(6)	0.105(5)
C25	0.1156(1)	0.9617(7)	0.7002(7)	0.131(6)
C26	0.0376(8)	0.9068(6)	0.6714(5)	0.090(4)
C61	0.6815(6)	0.0225(5)	0.8414(4)	0.063(3)
O61	0.7679(5)	−0.0437(4)	0.8460(4)	0.101(3)
C62	0.4938(6)	0.0824(4)	0.7309(4)	0.049(2)
O62	0.4690(5)	0.0542(4)	0.6753(3)	0.080(2)
C63	0.6660(7)	0.2171(5)	0.7555(4)	0.065(3)
O63	0.7497(5)	0.2544(4)	0.7117(4)	0.102(3)
C64	0.5449(7)	0.2004(5)	0.9384(5)	0.066(3)
O64	0.5523(7)	0.2349(4)	0.9964(4)	0.111(3)
C65	0.4025(6)	0.0446(5)	0.9066(4)	0.056(2)
O65	0.3393(5)	−0.0132(4)	0.9445(3)	0.095(2)
C31	0.3045(5)	0.3997(4)	0.8693(3)	0.038(2)
C32	0.1785(6)	0.4618(4)	0.8946(3)	0.045(2)
C33	0.1677(7)	0.5588(5)	0.9207(4)	0.060(3)
C34	0.2839(8)	0.5950(5)	0.9207(4)	0.068(3)
C35	0.4104(7)	0.5353(5)	0.8946(5)	0.069(3)
C36	0.4212(6)	0.4370(4)	0.8689(4)	0.054(3)
C41	0.1617(5)	0.2311(4)	0.8850(3)	0.040(2)
C42	0.0727(6)	0.2050(5)	0.8447(4)	0.065(3)
C43	−0.0411(7)	0.1617(6)	0.8924(5)	0.093(4)
C44	−0.0604(7)	0.1472(5)	0.9774(5)	0.082(4)
C45	0.0272(7)	0.1743(5)	1.0180(4)	0.069(3)
C46	0.1381(6)	0.2171(4)	0.9722(3)	0.055(2)

[1] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j$.

Table 7
Positional parameters and equivalent isotropic thermal parameters, with e.s.d.s in parentheses for **2**

	x	y	z	U_{eq} [1]
W1	−0.25623(3)	0.80735(2)	0.59053(2)	0.0440(1)
W2	0.52709(2)	0.13763(2)	0.83337(2)	0.0371(1)
P1	−0.04681(15)	0.72876(12)	0.64585(10)	0.0375(5)
P2	0.32029(14)	0.27466(11)	0.82679(9)	0.0316(5)
C6	0.0952(6)	0.6614(5)	0.5623(4)	0.043(2)
C7	0.2901(5)	0.3140(4)	0.7206(3)	0.036(2)
N1	0.2227(5)	0.6228(4)	0.5879(3)	0.039(2)
C1	0.2554(6)	0.5115(5)	0.6009(4)	0.042(2)
C2	0.3485(6)	0.4808(4)	0.6615(4)	0.040(2)
N2	0.3974(5)	0.3695(4)	0.6726(3)	0.038(2)
C3	0.4762(6)	0.3193(4)	0.5946(4)	0.042(2)
C4	0.5985(7)	0.3684(5)	0.5490(4)	0.050(2)
C5	0.6626(6)	0.3289(4)	0.4607(3)	0.040(2)
C51	−0.4295(7)	0.8611(5)	0.5517(5)	0.057(3)
O51	−0.5282(6)	0.8899(4)	0.5306(4)	0.075(3)
C52	−0.2210(8)	0.9562(6)	0.5720(6)	0.072(4)
O52	−0.2099(7)	1.0388(5)	0.5614(5)	0.114(4)
C53	−0.1495(8)	0.7793(7)	0.4695(5)	0.073(4)
O53	−0.0933(7)	0.7615(7)	0.4024(4)	0.121(4)
C54	−0.3044(7)	0.6668(6)	0.6042(5)	0.059(3)
O54	−0.3354(7)	0.5881(5)	0.6120(4)	0.096(3)
C55	−0.3672(7)	0.8268(5)	0.7130(5)	0.054(3)
O55	−0.4309(6)	0.8337(5)	0.7801(4)	0.086(3)
C11	−0.0911(6)	0.6297(5)	0.7282(4)	0.040(2)
C12	−0.0914(6)	0.5308(5)	0.7080(4)	0.049(2)
C13	−0.1367(8)	0.4586(6)	0.7703(5)	0.066(3)
C14	−0.1848(8)	0.4852(7)	0.8514(5)	0.074(4)
C15	−0.1882(8)	0.5820(7)	0.8734(5)	0.071(3)
C16	−0.1428(7)	0.6552(6)	0.8124(4)	0.056(3)
C21	0.0455(6)	0.8041(5)	0.6906(4)	0.045(2)
C22	0.1358(7)	0.7571(6)	0.7407(4)	0.054(2)
C23	0.2138(8)	0.8155(8)	0.7679(5)	0.071(4)
C24	0.2038(2)	0.9160(0)	0.7473(7)	0.111(6)
C25	0.1164(3)	0.9629(9)	0.6994(8)	0.126(7)
C26	0.0378(0)	0.9064(7)	0.6697(6)	0.086(4)
C61	0.0817(7)	0.0225(6)	0.8411(5)	0.060(3)
O61	0.7698(6)	−0.0445(4)	0.8463(4)	0.093(3)
C62	0.4913(6)	0.0834(5)	0.7308(4)	0.046(2)
O62	0.4663(6)	0.0542(4)	0.6757(3)	0.071(2)
C63	0.6644(7)	0.2173(6)	0.7561(5)	0.058(3)
O63	0.7499(6)	0.2540(5)	0.7116(4)	0.095(3)
C64	0.5472(8)	0.2010(6)	0.9376(5)	0.059(3)
O64	0.5534(8)	0.2373(5)	0.9954(4)	0.105(3)
C65	0.4039(7)	0.0442(5)	0.9065(4)	0.052(2)
O65	0.3400(6)	−0.0131(4)	0.9447(4)	0.088(3)
C31	0.3047(6)	0.3996(4)	0.8691(3)	0.036(2)
C32	0.1772(6)	0.4624(5)	0.8949(4)	0.044(2)
C33	0.1668(7)	0.5589(5)	0.9211(4)	0.054(3)
C34	0.2833(9)	0.5947(5)	0.9216(5)	0.063(3)
C35	0.4110(8)	0.5351(6)	0.8942(5)	0.067(3)
C36	0.4217(7)	0.4374(5)	0.8690(5)	0.053(3)
C41	0.1614(5)	0.2308(4)	0.8845(4)	0.036(2)
C42	0.0718(7)	0.2038(6)	0.8441(5)	0.060(3)
C43	−0.0419(9)	0.1619(7)	0.8917(7)	0.088(5)
C44	−0.0625(8)	0.1474(6)	0.9772(6)	0.073(4)
C45	0.0269(8)	0.1730(5)	1.0176(5)	0.063(3)
C46	0.1375(7)	0.2163(5)	0.9720(4)	0.051(2)

[1] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

ing factors and anomalous dispersion coefficients were taken from International Tables for X-ray Crystallography [23]. No extinction correction was made; only the low angle reflections 100, 110 and 101 were omitted from calculations in the last cycles in both complexes. Computing was carried out on an IBM PC/AT-compatible computer using SHELX76 [24]

Atomic coordinates for **1** and **2** are given in Tables 6 and 7, respectively. Lists of anisotropic thermal parameters, angles, hydrogen atom coordinates, bond lengths and angles in the phenyl rings have been deposited with the Cambridge Crystallographic Data Centre. Tables of torsion angles and least square planar equations are available from the authors.

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