

Comparative investigation of the Group 6 (Cr, Mo or W) metal carbonyl complexes of 1,3,5-triazacyclohexanes

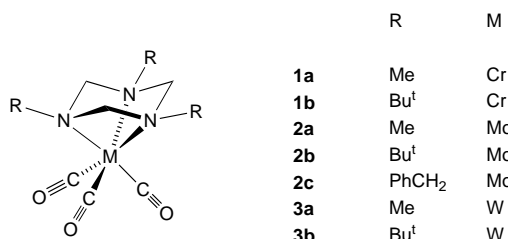
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The preparation and characterisation of 1,3,5-trialkyl-1,3,5-triazacyclohexane complexes of Group 6 metal carbonyls $[M(CO)_3(C_3H_6N_3R_3)]$ ($R = Me$ or Bu^t , $M = Mo$ or W ; $R = CH_2Ph$, $M = Mo$) are reported. The complexes have been characterised by NMR, IR spectroscopy and mass spectrometry. Their spectroscopic properties and reactivity are discussed and compared with those of the corresponding complexes of Cr and analogous 1,4,7-triazacyclononane complexes. The single-crystal structures of the 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane adducts with Mo and W have been determined.

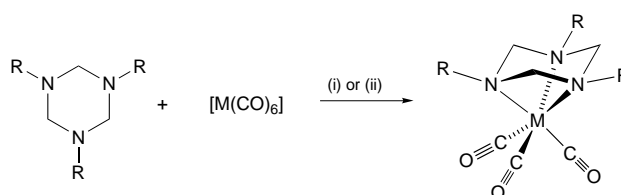
Although 1,3,5-trialkyl-1,3,5-triazacyclohexanes have been well known to organic chemists since the 1920s, their tridentate co-ordination chemistry is only now beginning to be examined in depth.¹⁻⁸ The triazacyclohexane system represents the smallest member of the triazamacrocycle family, and the strain that accompanies tridentate co-ordination of it results in some unique reactivity patterns.

We recently reported the synthesis and characterisation of chromium tricarbonyl complexes of 1,3,5-trialkyl-1,3,5-triazacyclohexanes.¹ In these complexes **1** the triazacyclohexane was tridentate, and the complexes adopted a 'piano-stool' conformation. Both the kinetic and the thermodynamic stabilities of the complexes increased with increase in the size of the alkyl substituent on the triazacyclohexane ring. When the substituent was Me the triazacyclohexane ligand was easily displaced by pyridine, $P(OMe)_3$, and other ligands, but when the substituent was Bu^t the triazacyclohexane ligand was inert toward displacement.



The 1,3,5-trimethyl-1,3,5-triazacyclohexane molybdenum complex $[Mo(CO)_3(tmtach)]$ **2a** was prepared in the 1950s by Lüttringhaus and Kullick² in unspecified yield; more recently, **2a** and its benzyl analogue **2c** were prepared by Schumann.⁸ The molybdenum complexes were poorly characterised in these studies, with infrared spectroscopy providing the only evidence for the presence of a tridentate triazacyclohexane ligand.

In this paper we extend our study of the co-ordination chemistry of 1,3,5-trialkyl-1,3,5-triazacyclohexanes to include tricarbonyl complexes of molybdenum and tungsten. We have examined the properties (1H and ^{13}C NMR, IR and reactivity towards nucleophiles) of these new complexes in comparison to those of the chromium complexes studied previously.¹ The properties will also be compared to those of the well known triazacyclononane (tacn) complexes. The structures of the tri-*tert*-butyl complexes $[Mo(CO)_3(tbtach)]$ **2b** and $[W(CO)_3(tbtach)]$ **3b** have been determined by single-crystal X-ray studies and will be compared with that of the previously structurally characterised $[Cr(CO)_3(tbtach)]$ **1b**.



Scheme 1 (i) Mesitylene, reflux, $M = Cr$ or Mo , $R = Me$ or Bu^t ; (ii) benzene or thf, $h\nu$ (tungsten lamp), $M = Mo$, $R = CH_2Ph$; $M = W$, $R = Me$ or Bu^t

Results and Discussion

Synthesis of complexes

In a procedure similar to our preparation of the chromium adducts **1a** and **1b**,¹ the molybdenum complexes **2a** and **2b** were prepared in yields of up to 98% by simply heating the appropriate triazacyclohexane with $[Mo(CO)_6]$ in mesitylene at reflux (Scheme 1). Attempts to prepare the tungsten complexes using this method resulted in the formation of deep red-black solutions of unknown composition. The tungsten complexes **3a** and **3b** and the molybdenum complex **2c** were instead synthesized in up to 80% yield by irradiation of solutions of $[W(CO)_6]$ or $[Mo(CO)_6]$ and the appropriate triazacyclohexane in benzene or tetrahydrofuran (thf) with tungsten lamps. When prepared according to these procedures, the complexes precipitated from the reaction mixtures as bright yellow powders. In the solid state the tmtach complexes **1a**, **2a** and **3a** were air (oxygen) sensitive, while the tri-*tert*-butyl complexes **1b**, **2b** and **3b** were stable in air indefinitely. The tribenzyl complex **2c** decomposed only after several months exposure to air. The complexes are insoluble in most solvents (benzene, diethyl ether, thf and ethanol) but very slightly soluble in acetone, dichloromethane and other polar solvents {e.g. solubility of $[W(CO)_3(tmtach)]$, 0.05 mg cm^{-3} in acetone}. All the complexes were air-sensitive in solution.

Schumann⁸ reported the synthesis of $[Mo(CO)_3(C_3H_6N_3R_3)]$ ($R = Me$, Pr^i or CH_2Ph) from $[Mo(CO)_3(C_7H_8)]$ in yields of 89–95%. Given that $[Mo(CO)_3(C_7H_8)]$ is itself usually prepared from $[Mo(CO)_6]$ in yields of about 60%,⁹ the synthesis of $[Mo(CO)_3(C_3H_6N_3R_3)]$ directly from the reaction of the appropriate triazacyclohexane and $[Mo(CO)_6]$ compares favourably with Schumann's method. We have not tried to extend Schumann's method to the preparation of $[W(CO)_3(C_3H_6N_3R_3)]$, but note that it would be much less efficient than the synthesis directly from $[W(CO)_6]$ since $[W(CO)_3(C_7H_8)]$ can only be synthesized in about 10% yield from $[W(CO)_6]$.¹⁰

Table 1 Proton and ^{13}C NMR data for $[\text{M}(\text{CO})_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$ complexes^a

Compound	^1H NMR			^{13}C NMR				
	CH_3	$\text{C}(\text{CH}_3)_3$	NCH_2N^b	CH_3	$\text{C}(\text{CH}_3)_3$	$\text{C}(\text{CH}_3)_3$	NCH_2N	CO
1a $[\text{Cr}(\text{CO})_3(\text{tmtach})]$	2.49	—	4.02, 4.66 (8.4)	42.4	—	—	83.2	237.5
1b $[\text{Cr}(\text{CO})_3(\text{tbtach})]$	—	1.36	4.06, 5.16 (8.7)	—	25.6	57.0	73.3	237.5
2a $[\text{Mo}(\text{CO})_3(\text{tmtach})]$	2.51	—	4.08, 4.70 (8.8)	42.4	—	—	83.3	232.5
2b $[\text{Mo}(\text{CO})_3(\text{tbtach})]$	—	1.33	4.26, 5.16 (8.8)	—	25.5	56.5	72.9	232.5
2c $[\text{Mo}(\text{CO})_3(\text{tbntach})]^c$	—	—	3.95, 4.55 (8.2)	—	—	—	83.65	236.1
3a $[\text{W}(\text{CO})_3(\text{tmtach})]$	2.61	—	4.91, 5.06 (8.5)	42.9	—	—	83.5	226.0
3b $[\text{W}(\text{CO})_3(\text{tbtach})]$	—	1.34	5.14, 5.32 (8.9)	—	25.3	57.7	73.4	226.7

^a Spectra recorded from $(\text{CD}_3)_2\text{CO}$ solutions. ^b Apparent doublets, splitting (Hz) in parentheses. ^c Benzyl group resonances: ^1H NMR δ 3.72 (s, CH_2Ph) and 7.3–7.5 (m, Ph); ^{13}C NMR δ 62.93 (CH_2Ph), 133.66 [$\text{Ph}(\text{C}2)$], 133.78 [$\text{Ph}(\text{C}4)$], 135.51 [$\text{Ph}(\text{C}3)$] and 138.10 [$\text{Ph}(\text{C}1)$].

NMR Spectroscopy

The ^1H and ^{13}C NMR data for the $[\text{M}(\text{CO})_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$ complexes are summarised in Table 1. The ^1H NMR spectra in $(\text{CD}_3)_2\text{CO}$ solution confirm the facial co-ordination of the ligand. For each complex the methylene protons of the triazacyclohexane ring give rise to two sets of apparent doublets, corresponding to the non-equivalent axial and equatorial set of protons. The positions and chemical shift separation between these doublets varies depending on the alkyl substituent on the triazacyclohexane ligand and the co-ordinating metal (Table 1). The ^{13}C NMR spectrum for each complex shows the resonances expected for a tridentate triazacyclohexane ligand, along with a signal due to the CO groups in the region δ 226–238.

Reactivity of complexes

When $[\text{Mo}(\text{CO})_3(\text{tmtach})]$ was dissolved in $(\text{CD}_3)_2\text{SO}$ the ^1H NMR spectrum of the resulting solution showed a broad signal centred at δ 3.10 and a sharp singlet at δ 2.16, attributed to the tmtach methylene and methyl protons respectively. Significantly, the methylene protons did not appear as the pair of apparent doublets as expected for methylene protons in a complex in which the tmtach ligand is tridentate (Table 1), and the ^1H and ^{13}C chemical shifts observed for both the methylene and methyl groups matched those observed for a solution of tmtach in $(\text{CD}_3)_2\text{SO}$. These observations suggest that a solvolysis reaction occurred to produce free tmtach and $[\text{Mo}(\text{CO})_3\{(\text{CD}_3)_2\text{SO}\}_3]$. Similar solvolysis reactions occurred when $[\text{Mo}(\text{CO})_3(\text{tbtach})]$ **2c** and $[\text{W}(\text{CO})_3(\text{tmtach})]$ **3a** were dissolved in $(\text{CD}_3)_2\text{SO}$. The molybdenum and tungsten complexes of tmtach and tbtach are more labile than the analogous chromium complexes; $[\text{Cr}(\text{CO})_3(\text{tmtach})]$ dissolves in dmsO and acetonitrile without solvolysis.¹ Solvolysis reactions were not observed for the tbtach complexes **1b**, **2b** and **3b**.

Schumann⁸ has reported ^1H , ^{13}C and ^{95}Mo NMR data for $(\text{CD}_3)_2\text{SO}$ solutions of $[\text{Mo}(\text{CO})_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$ ($\text{R} = \text{Me}$, CH_2Ph or Pr^i). In view of the solvolysis reactions of **2a** and **2c** described above, it appears that Schumann's NMR data correspond to the free triazacyclohexane ligands and $[\text{Mo}(\text{CO})_3\{(\text{CD}_3)_2\text{SO}\}_3]$ in $(\text{CD}_3)_2\text{SO}$ solutions. We note that solutions of **2a** or **2c** in $(\text{CD}_3)_2\text{SO}$ both exhibit a ^{95}Mo signal at δ -933, which we attribute to the $[\text{Mo}(\text{CO})_3\{(\text{CD}_3)_2\text{SO}\}_3]$ solvate. For comparison, $[\text{Mo}(\text{CO})_3(\text{tbtach})]$ **2b**, which does not undergo solvolysis, exhibits a ^{95}Mo signal at δ -796 in $(\text{CD}_3)_2\text{SO}$ solution.[†] Furthermore, solutions of **2a** or **2c** in $(\text{CD}_3)_2\text{SO}$ both exhibit a ^{13}C signal at δ 228.1 (which we attribute to the carbonyl carbons of the $[\text{Mo}(\text{CO})_3\{(\text{CD}_3)_2\text{SO}\}_3]$ solvate), whereas those of **2b** in $(\text{CD}_3)_2\text{SO}$, or **2a–2c** in $(\text{CD}_3)_2\text{CO}$, show a carbonyl signal in the range δ 232–236 (Table 1).

As suggested by the solvolysis results described above, the kinetic stability of the triazacyclohexane complexes of Mo

and W increases as R becomes larger. Thus, $\text{P}(\text{OMe})_3$ displaced tmtach from **2a** and **3a** rapidly at room temperature in acetone to afford *fac*- $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OMe})_3\}_3]$ and *fac*- $[\text{W}(\text{CO})_3\{\text{P}(\text{OMe})_3\}_3]$ respectively, whereas the tbtach complexes **2b** and **3b** did not react with $\text{P}(\text{OMe})_3$ even after 30 min at 80 °C. A similar trend in reactivity was observed previously for chromium triazacyclohexane complexes.¹

Both complexes **2a** and **3a** decompose on exposure to air to produce dark brown solids and $[\text{M}(\text{CO})_6]$. For example, when a sample of $[\text{Mo}(\text{CO})_3(\text{tmtach})]$ in an incompletely sealed ampoule was exposed to air the initially yellow solid became dark brown over a period of weeks, and crystals of $[\text{Mo}(\text{CO})_6]$ (identified by its infrared spectrum) had grown on the walls of the ampoule. The decomposition presumably involves reaction of some $[\text{Mo}(\text{CO})_3(\text{tmtach})]$ with O_2 to form oxides of Mo or W and CO, with the liberated CO subsequently displacing tmtach from remaining $[\text{Mo}(\text{CO})_3(\text{tmtach})]$ to form $[\text{Mo}(\text{CO})_6]$. Lüttringhaus and Kullick² have previously observed formation of $[\text{Mo}(\text{CO})_6]$ from $[\text{Mo}(\text{CO})_3(\text{tmtach})]$ under an atmosphere of CO, and the formation of $[\text{Mo}(\text{CO})_6]$ in solutions of $[\text{Mo}(\text{CO})_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$ complexes exposed to air has been reported by Schumann.⁸

Infrared spectroscopy

The carbonyl stretching frequencies for triazacyclohexane complexes **1a–3b**, and for related complexes of 1,4,7-triazacyclononane (tacn) derivatives^{11,12} are summarised in Table 2. For **1a–3b** the carbonyl region of the infrared spectra show two bands centred near 1900 (A_1 mode) and 1760 cm^{-1} (E mode), as expected for facial tricarbonyl complexes of approximate C_{3v} symmetry.^{13–15} The lower-energy band is broadened or split, presumably because of lower site symmetry in the crystal.¹² The carbonyl stretches for **1a–3b** have consistently higher frequencies than the analogous stretches for similar 1,4,7-triazacyclononane complexes (Table 2). These differences do not correlate with any significant change in M–CO bond distances (Tables 3 and 4), nor can they be explained in terms of differences in the π -acceptor ability of the respective triazacycloalkane ligands, since both ligands should be pure σ donors.¹² The differences in $\tilde{\nu}_{\text{max}}(\text{CO})$ may be a consequence of differences in the effectiveness of the two types of ligand to act as σ donors; σ donation by a triazacyclononane is presumably more efficient than that by a triazacyclohexane because of the larger strain inherent in co-ordination of the latter (*cf.* N–M–N bond angles in Tables 3 and 4). Increased electron density at the metal centre in triazacyclononane complexes should weaken the C–O bond (*i.e.* lower CO stretching frequencies) through increased metal-to-CO back bonding.¹⁸ The variation of CO stretching frequencies with strain in the triazacycloalkane–metal bonding is apparent in related systems. For example, $[\text{Mo}(\text{CO})_3(\text{Htam})]$ ¹⁶ (Htam = 1,5,9-triazacyclo[7.3.1.0^{5,13}]tridecane), which has strained Mo–Htam bonding, shows $\tilde{\nu}_{\text{max}}(\text{CO})$ at 1905, 1780 (sh), and 1745 cm^{-1} (similar to **2a** and **2b**), whereas $[\text{Mo}(\text{CO})_3(\text{tet } a)]$ ¹⁷ (tet *a* = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo-

[†] The low solubility of all the $[\text{Mo}(\text{CO})_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$ complexes in $(\text{CD}_3)_2\text{CO}$ prevented us from obtaining ^{95}Mo NMR data in that solvent.

Table 2 $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CO) for complexes **1a–3b** and $\text{M}(\text{CO})_3$ -triazacyclononane adducts

	[M(CO) ₃ (C ₃ H ₆ N ₃ R ₃)]		[M(CO) ₃ (C ₆ H ₁₂ N ₃ R ₃)]	
	R = Me	R = Bu ^t	R = H ¹¹	R = Pr ⁱ¹²
Cr	1907, 1760 (br)	1901, 1771, 1756	1880, 1740–1700	1886, 1750, 1720
Mo	1900, 1785 (sh), 1750*	1902, 1778, 1760	1850, 1740–1700	1892, 1741, 1720
W	1895, 1772 (sh), 1740	1890, 1764 (sh), 1746	1840, 1730–1690	1881, 1740, 1720

* Ref. 8 gives $\tilde{\nu}_{\max}(\text{CO})$ 1906, 1782 (sh) and 1748 cm^{-1} (KBr).

Table 3 Selected comparative mean geometries (distances in Å, angles in °) for the [M(CO)₃(tbtach)] complexes

	Cr, 1b ¹	Mo, 2b	W, 3b
M–CO	1.80(1)	1.919(7)	1.916(8)
M–N	2.210(7)	2.347(8)	2.332(3)
N–C	1.468(6)	1.471(7)	1.474(7)
N–C(R)	1.507(6)	1.509(5)	1.516(8)
N–M–N	63.3(2)	59.5(1)	59.8(1)
CO–M–CO	85.6(9)	85(1)	86.1(9)
N–M–CO _(trans)	165(1)	163.5(6)	163.0(8)
N–M–CO _(cis)	104.8(9)	107(1)	106(1)
M–N–C(R)	131.4(6)	129.7(2)	129.6(4)
M–N–C	92.1(4)	93.4(4)	93.5(1)
C–N–C	108.0(1)	107.6(3)	107.7(2)
C–N–C(R)	114.5(8)	114.5(8)	114.3(5)
M–C–O	176.1(3)	178.2(6)	178.3(5)
Torsion angles ($\langle \tau \rangle$)			
C–N–C–N	67.5(3)	67.4(4)	67.9(5)

Table 4 Selected comparative mean geometries (distances in Å, angles in °) for *fac*-[Mo(CO)₃L] complexes

	tbtach	Htam ¹⁶	tiptacn ^{12,*}	tet <i>a</i> ¹⁷
Mo–CO	1.919(7)	1.929(8)	1.918(4)	1.903(9)
Mo–N	2.347(8)	2.40(1)	2.369(8)	2.37(3)
N–Mo–N	59.5(1)	57.9(1)	76.9(3)	79(4)
CO–Mo–CO	85(1)	84(1)	84(2)	83(2)
N–Mo–CO _(trans)	163.5(6)	163.5(5)	172(1)	174(2)
N–Mo–CO	107(1)	108.2(6)	100(5)	99(5)

* tiptacn = 1,4,7-Tri(isopropyl)-1,4,7-triazacyclononane.

tetradecane), which has less-strained Mo–tet *a* bonding, shows $\tilde{\nu}_{\max}(\text{CO})$ at 1886 and 1743 cm^{-1} , similar to the [Mo(CO)₃(C₆H₁₂N₃R₃)] complexes in Table 2.

X-Ray studies

The molybdenum and tungsten (Fig. 1) analogues of [Cr(CO)₃(tbtach)] are isomorphous with that structure and were refined in the same setting. Having regard to the caveat concerning twinning problems in the derivatives of Cr and Mo, which appear to have little systematic effect on the bonding parameters, the consequences of the change in the central metal atom are largely as might be expected on the basis of an increase in its radius on passing from chromium to molybdenum, that of tungsten being similar to that of molybdenum (Table 3). In respect of the latter, changes in $\langle\text{M–C}\rangle$ and $\langle\text{M–N}\rangle$ are parallel, indicative of no significant difference in behaviour at this level between the interaction of the two metals with the two different classes of ligand bonding types. The most significant change evident overall is in the M–C–O angles; in the chromium derivative these deviate further from linearity than is the case with the molybdenum and tungsten counterparts, suggestive of relaxation of intramolecular *tert*-butyl/carbonyl interactions with increase in metal radius.

Structural details for [Mo(CO)₃(tbtach)] **2b** and several related [Mo(CO)₃L] complexes are presented in Table 4. The most significant feature of these data is the large distortion

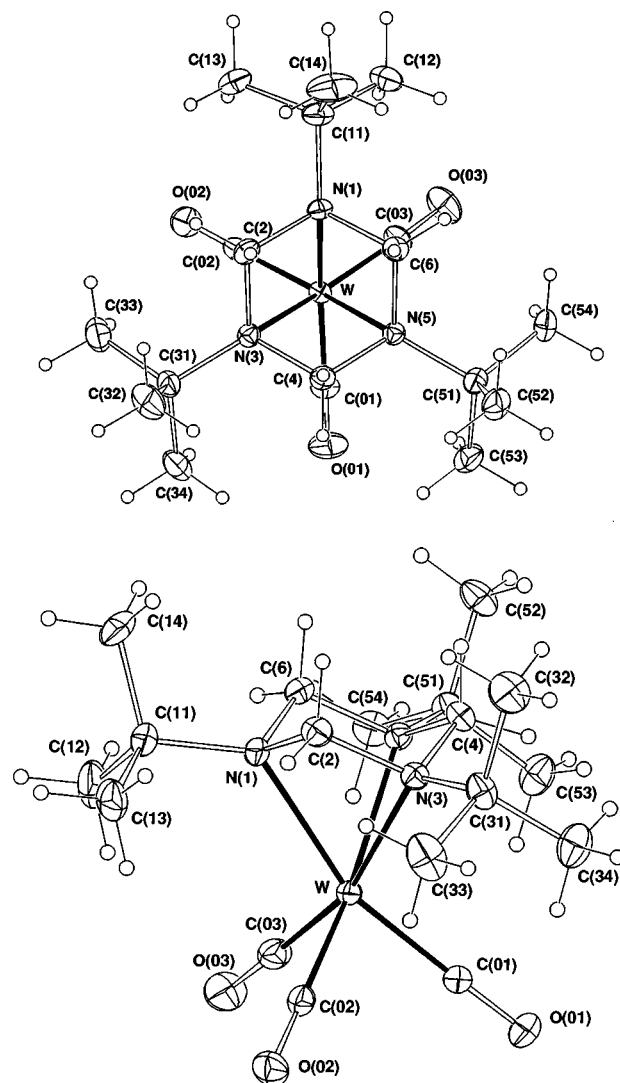


Fig. 1 Projections of [W(CO)₃(tbtach)] **3b** down and normal to its quasi-three-fold axis, showing atom labelling and 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

of the molybdenum octahedron in **2b** and [Mo(CO)₃(Htam)] (N–Mo–N bond angle $\approx 59^\circ$) compared to those of [Mo(CO)₃(tiptacn)] and [Mo(CO)₃(tet *a*)] (N–Mo–N $\approx 78^\circ$).

Experimental

Nuclear magnetic resonance spectra were recorded using a Bruker ARX-500 spectrometer (500.1 MHz for ¹H, 202.5 MHz for ³¹P, 125.8 MHz for ¹³C and 32.6 MHz for ⁹⁵Mo) at ambient temperatures (*ca.* 295 K) and were referenced with respect to the solvent resonances, external 85% H₃PO₄, or external 2 M sodium molybdate solution at pH 11. Infrared spectra were recorded using a Bio-Rad FTS-45 FTIR spectrophotometer from KBr discs, mass spectra by Dr. A. Reeder using a VG Autospec mass spectrometer using fast atom bombardment

(FAB) with a caesium ion source and *m*-nitrobenzyl alcohol as the matrix. Melting points were determined in sealed capillaries under nitrogen using an Electrothermal apparatus. Microanalyses were performed by either the Chemistry Centre of Western Australia or CMAS, Victoria, Australia. Manipulations of air-sensitive compounds or solutions were performed under nitrogen using standard Schlenk techniques or in a nitrogen-filled dry-box. All solvents were distilled and deoxygenated prior to use. Deoxygenation of solvents and reagents was carried out either by distillation under nitrogen or by at least three freeze-pump-thaw cycles. The ligands tmtach,¹⁹ tbtach²⁰ and tbntach²¹ were prepared according to literature methods. Complexes **1a** and **1b** have been reported previously.¹

Synthesis of tricarbonyl(1,3,5-trialkyl-1,3,5-triazacyclohexane)-molybdenum(0) and -tungsten(0) complexes

[Mo(CO)₃(tmtach)] 2a. A mixture of tmtach (3.5 cm³, 20 mmol) and [Mo(CO)₆] (2.0 g, 7.6 mmol) was heated in mesitylene (30 cm³) at reflux for 2 h. During this time a yellow precipitate formed. The mixture was allowed to cool to room temperature and the yellow solid collected and washed with hexane to afford complex **2a** as a fine yellow powder (2.08 g, 88%), m.p. >200 °C (decomp.) (Found: C, 34.9; H, 5.1; N, 13.7. C₉H₁₅MoN₃O₃ requires C, 34.9; H, 4.9; N, 13.6%); *m/z* 311 (*M*, ⁹⁸Mo) and 309 (*M*, ⁹⁶Mo).

[Mo(CO)₃(tbtach)] 2b. This compound was prepared in the same way as **2a**. Yield 98%; m.p. >240 °C (decomp.) (Found: C, 49.7; H, 7.6; N, 9.7. C₁₈H₃₃MoN₃O₃ requires C, 49.7; H, 7.6; N, 9.6%); *m/z* 437 (*M*, ⁹⁸Mo) and 435 (*M*, ⁹⁶Mo).

[Mo(CO)₃(tbntach)] 2c. A mixture of tbntach (2.0 g, 5.6 mmol) and [Mo(CO)₆] (1.5 g, 5.7 mmol) in benzene (30 cm³) was irradiated with two 150 W tungsten filament lamps for 24 h. The irradiation heated the benzene to reflux, and a yellow precipitate formed slowly. The mixture was filtered whilst hot and the solid washed with hexane before drying *in vacuo* to afford [Mo(CO)₃(tbntach)] **2c** as a fine yellow powder (0.57 g, 19%), m.p. >200 °C (decomp.) (Found: C, 60.2; H, 5.1; N, 8.1. C₂₇H₂₇MoN₃O₃ requires C, 60.3; H, 5.1; N, 7.8%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CO) 1908s and 1775s (br); *m/z* 539 (*M*, ⁹⁸Mo) and 537 (*M*, ⁹⁶Mo). The yield, after allowing for unchanged [Mo(CO)₆] recovered from the reaction, was 33%.

[W(CO)₃(tmtach)] 3a. A mixture of tmtach (1.5 cm³, 11 mmol) and [W(CO)₆] (1.4 g, 4.0 mmol) in a mixture of benzene (30 cm³) and thf (20 cm³) was heated at reflux by irradiation with two 150 W tungsten filament lamps for 30 h. The mixture was filtered whilst hot and the yellow precipitate collected. The filtrate was irradiated for 12 h to produce more yellow precipitate, the mixture again filtered whilst hot, and the filtrate irradiated once more (12 h). The combined yellow solids obtained after the three irradiations were washed with hexane, and dried *in vacuo* to afford **3a** as a fine yellow powder (1.27 g, 80%), m.p. >190 °C (decomp.) (Found: C, 26.8; H, 3.8; N, 10.8. C₉H₁₅N₃O₃W requires C, 27.2; H, 3.8; N, 10.6%); *m/z* 399 (*M*, ¹⁸⁶W), 397 (*M*, ¹⁸⁴W), 371 (*M* - CO, ¹⁸⁶W) and 369 (*M* - CO, ¹⁸⁴W).

[W(CO)₃(tbtach)] 3b. This was prepared in a similar fashion to **3a**, but using thf as the solvent. Yield (68%), m.p. >250 °C (decomp.) (Found: C, 41.3; H, 6.4; N, 8.0. C₁₈H₃₃N₃O₃W requires C, 41.7; H, 6.3; N, 8.0%); *m/z* 525 (*M*, ¹⁸⁶W) and 523 (*M*, ¹⁸⁴W).

Displacement of tmtach from [M(CO)₃(tmtach)] by trimethyl phosphite

Trimethyl phosphite (1 mm³, 8.5 μmol) was added *via* syringe to a solution of [Mo(CO)₃(tmtach)] **2a** (0.06 mg, 0.6 μmol) in

(CD₃)₂CO (1 cm³) in a 5 mm NMR tube fitted with a rubber septum. The NMR spectrum indicated that *fac*-[Mo(CO)₃{P(OMe)₃}₃] had been formed in quantitative yield. $\delta_{\text{p}}[(\text{CD}_3)_2\text{CO}]$ 166.1 [lit.,²² 165 (benzene)]; $\delta_{\text{Mo-95}}[(\text{CD}_3)_2\text{CO}]$ -1745.3 (q, *J*_{MoP} 213) [lit.,²³ ([Mo(CO)₃{P(OEt)₃}₃)] -1721.1 (q, *J*_{MoP} 210)-(CH₂Cl₂)]. Use of [W(CO)₃(tmtach)] **3a** in place of **2a** produced *fac*-[W(CO)₃{P(OMe)₃}₃]. $\delta_{\text{p}}[(\text{CD}_3)_2\text{CO}]$ 145.3 [lit.,²² 145.2 (benzene)].

X-Ray crystallography

Crystals of [Mo(CO)₃(tbtach)] **2b** and [W(CO)₃(tbtach)] **3b** suitable for X-ray diffraction studies were grown by slow evaporation of acetonitrile solutions.

Structure determinations. Unique, room-temperature, four-circle diffractometer data sets (2θ-θ scan mode, monochromatic Mo-Kα radiation, λ = 0.7107₃ Å) were measured, yielding *N* independent reflections, *N*_o of these with *I* > 3σ(*I*) being considered 'observed' and used in the full-matrix least-squares refinements, after analytical absorption correction; both complexes were isomorphous with the M = Cr analogue and were refined in that cell and coordinate setting. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*_{iso})_H were included constrained at estimated values. Conventional residuals *R*, *R'* on |*F*| are quoted at convergence, statistical weights derivative of σ²(*I*) = σ²(*I*_{diff}) + 0.0004 σ⁴(*I*_{diff}) being employed. Neutral-atom complex scattering factors were employed; computation used the XTAL 3.2 program system.²⁴

Crystal/refinement data. [M(CO)₃(tbtach)], C₁₈H₃₃MN₃O₃, monoclinic, space group *P*2₁/*c* (*C*_{2h}, no. 14), *Z* = 4.

M = Mo **2b**, *M* = 435.4, *a* = 8.472(3), *b* = 16.582(3), *c* = 16.056(7) Å, β = 110.03(3)°, *U* = 2119(1) Å³, *D*_c = 1.36₅ g cm⁻³, *F*(000) = 912, μ_{Mo} = 6.4 cm⁻¹, specimen 0.68 × 0.10 × 0.50 mm, *A*_{min,max}^{*} = 1.07, 1.29, 2θ_{max} = 60°, *N* = 6058, *N*_o = 4217, *R* = 0.047, *R'* 0.058.

M = W **3b**, *M* = 523.3, *a* = 8.439(3), *b* = 16.646(7), *c* = 15.824(4) Å, β = 109.54(2)°, *U* = 2095(1) Å³, *D*_c = 1.65₉ g cm⁻³, *F*(000) = 1040, μ_{Mo} = 55 cm⁻¹, specimen 0.40 × 0.35 × 0.47 mm, *A*_{min,max}^{*} = 4.1, 6.7, 2θ_{max} = 65°, *N* = 7562, *N*_o = 5718, *R* = 0.037, *R'* 0.041.

Abnormal features/variations in procedure. Like the chromium analogue, the M = Mo complex **2b** exhibited a serious propensity to twinning. No satisfactory single specimen was obtained and data were measured on a specimen cleaved along the plane, albeit not totally successfully, for one of the two reciprocal lattice components. Zones (0,1*kl*) were refined with separate scale factors. For the tungsten complex a satisfactory single specimen was obtained.

CCDC reference number 186/888.

See <http://www.rsc.org/suppdata/dt/1998/1145/> for crystallographic files in .cif format.

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