Chromium and molybdenum complexes of tertiary alkyl and pendant donor triphosphamacrocycles†

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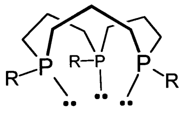
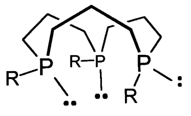
The first tritertiary (1,5,9-triphosphacyclododecane)chromium(0) complexes have been prepared from the secondary phosphine macrocycle precursor complex tricarbonyl(1,5,9-stiphosphacyclododecane)chromium(0), and the range of molybdenum(0) complexes with tritertiary 1,5,9-triphosphacyclododecane ligands has been extended. The synthetic routes involve either deprotonation of the secondary phosphine precursor followed by alkylation with alkyl halide or by radical-catalysed hydrophosphination of selected alkenes. These routes are general and allow access to a range of macrocyclic triphosphines with alkyl functions or with alkyl arms containing pendant donor functions (N, P, O, S) attached to phosphorus for both chromium and molybdenum. All compounds have been spectroscopically and analytically characterised.

There are few examples in the literature of macrocyclic phosphines, most notably those reported by Kyba and co-workers,[1] and by Norman and co-workers[2] who reported the elegant metal template synthesis of the molybdenum tricarbonyl complex of 1,5,9-triphosphacyclododecane (H_3L). In addition to the co-ordination properties of triphosphamacrocycles, we are also interested in the application of potentially hemi-labile phosphines[3] containing oxygen and other small p-block donors especially in applications of metals to catalysis. Compounds of this nature have been shown to be of value in this field and it has been suggested that the relatively enhanced lability of the 'hard' donor may well improve the availability of vacant co-ordination sites in solution whilst the chelate effect maintains their potential ability to stabilise catalytically active species.[4] During our investigation of routes to free triphosphorus macrocycles we have recently reported the formation of the first tritertiary complexes of 1,5,9-triphosphacyclododecane with molybdenum and tungsten,[5] and the oxidation of these compounds with halogens.[6] In order to improve our understanding of the behaviour of these ligand systems as well as to further investigate efficient preparative routes, we have expanded our study to chromium including the high-yield synthesis and structural characterisation of the first chromium trisecondary 1,5,9-triphosphacyclododecane complex, tricarbonyl(1,5,9-triphosphacyclododecane)chromium(0) **1**.[7] This complex is a potentially useful precursor to P-functionalised macrocycles and two synthetic strategies for the formation of tertiary phosphine macrocycles have been investigated. The tritertiary macrocycle complexes may be prepared from the trisecondary (H_3L) precursor complex by either deprotonation of the co-ordinated PH function followed by alkylation using alkyl halide, or by radical-initiated coupling of alkenes to the secondary PH function. The latter procedure readily allows the incorporation of pendant donors into the macrocycle. We have also recently reported the stereoselective liberation of the free unco-ordinated tritertiary triphosphamacrocycle, 1,5,9-tris(2-propyl)-triphosphacyclododecane[8] from the metal template and this method is general for a number of alkyl-substituted, tritertiary triphosphamacrocycles from the molybdenum template; the secondary macrocycle H_3L may be liberated in a similar fashion from the chromium template.[9] We have shown, however, that alkylation of the free secondary macrocycle forms the thermodynamically more stable *syn-anti* stereoisomer **b** as the only product (detected by NMR spectroscopy) by either of the routes investigated herein. This is in contrast to the stereospecific (for the *syn-syn* isomer) liberation of the template-co-ordinated tertiary macrocycles. Also, liberation of the secondary macrocycle proceeds in a far lower yield than that of the tertiary macrocycles (40 *vs.* 60–90%). In the synthesis of selectively functionalised macrocycles these two points clearly demonstrate the advantages of alkylation of phosphorus in the template complex prior to liberation.



a

syn-syn



b

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In this paper we describe the application of these alkylation routes to the synthesis of new tritertiary 1,5,9-triphosphacyclododecane complexes with both molybdenum and chromium, including a range of complexes incorporating pendant donor functions.

Results and Discussion

For all the new complexes discussed below, NMR spectroscopic data are collected in Table 1; IR, mass spectrometry and some experimental synthetic data are collected in Table 2. Synthetic transformations are summarised in Scheme 1.

Chromium complexes

Tricarbonyl(1,5,9-triphosphacyclododecane)chromium [Cr(CO)$_3$(H$_3$L)] **1** was prepared in good yield by our previously described method.[6] Our approach to the synthesis of the tritertiary derivatives was based on that previously described by us for the preparation of related molybdenum complexes (*i.e.* either by the well precedented[10] deprotonation of co-ordinated secondary phosphines followed by alkylation, or by coupling of alkene groups with the secondary PH function).[4] The first method, however, was only partially successful. Whereas for the reactions of [Mo(CO)$_3$(H$_3$L)][5] a range of alkyl halides can be used in the preparation of the corresponding tritertiary complexes [Mo(CO)$_3$L^{R}] (R = Me, C_3H_5, Pr^i or Me$_3$SiCH$_2$), this approach only gave the expected tritertiary product for the reaction of **1** with LiBu^n–MeI to give [Cr(CO)$_3$L^{Me}] **2** as a white powder for which satisfactory analytical data were obtained. Complex **2** is characterised by its NMR spectra. In the ^{31}P

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 The NMR spectroscopic data for chromium and molybdenum complexes[a]

Complex	$\delta(^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\})$[b]	$\delta(^1\mathrm{H})$,[c] J/Hz	$\delta(^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\})$,[d] J/Hz
2 $[\mathrm{Cr(CO)_3L^{Me}}]$	16.4 (s)	1.72 (m, 4 H, $\mathrm{PCH_2}$) 1.44 (br m, 2 H, $\mathrm{PCH_2C}H_2$) 0.89 (br s, 3 H, $\mathrm{CH_3}$)	230.5 (m, CO) 31.9 (dd, separation of inner and outer peaks, 10 and 16 Hz, $\mathrm{PCH_2}$) 20.3 (cm, $\mathrm{PH_2}C\mathrm{H_2}$) 13.8 (d, $^1J_{\mathrm{PC}} = 18$, $\mathrm{CH_3}$)
3 $[\mathrm{Cr(CO)_3L^{Et}}]$	23.6 (s)	1.78 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.70 (m, 2 H, $\mathrm{PC}H_2\mathrm{CH_3}$) 1.52 (br m, 2 H, $\mathrm{PCH_2C}H_2$) 1.09 (m, 3 H, $\mathrm{PCH_2C}H_3$)	231.0 (m, CO) 29.6 (br m, $\mathrm{P}C\mathrm{H_2CH_2}$) 26.9 (d, $^1J_{\mathrm{CP}} = 17$, $\mathrm{P}C\mathrm{H_2CH_3}$) 19.9(m, $\mathrm{PCH_2}C\mathrm{H_2}$) 8.0 (d, $^2J_{\mathrm{CP}} = 10$, $\mathrm{CH_3}$)
4 $[\mathrm{Cr(CO_3L^{C_2H_4OEt}}]$	20.9 (s)	3.72 (m, 2 H, $\mathrm{OC}H_2\mathrm{CH_2}$) 3.42 (q, $^2J_{\mathrm{HH}} = 7$, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$) 1.97 (br m, 2 H, $\mathrm{PC}H_2\mathrm{CH_2O}$) 1.67 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.46 (br m, 2 H, $\mathrm{PCH_2C}H_2$) 1.10 (t, $^2J_{\mathrm{HH}} = 7$, 3 H, $\mathrm{OCH_2C}H_3$)	231.6 (m, CO) 65.4 (s, $\mathrm{O}C\mathrm{H_2CH_2}$) 64.9 (s, $\mathrm{O}C\mathrm{H_2CH_3}$) 33.3 (cm, $\mathrm{OCH_2}C\mathrm{H_2}$) 28.6 (dd, separation of inner and outer peaks, 8 and 12 Hz, $\mathrm{P}C\mathrm{H_2CH_2}$) 18.9 (cm, $\mathrm{PCH_2}C\mathrm{H_2}$) 14.3 (s, $\mathrm{OCH_2}C\mathrm{H_3}$)
5 $[\mathrm{Cr(CO)_3L^{C_3H_6OMe}}]$	22.2 (s)	3.36 (t, $^2J_{\mathrm{HH}} = 7$, 2 H, $\mathrm{OC}H_2\mathrm{CH_2}$) 3.27 (s, 3 H, $\mathrm{OCH_3}$) 1.73 (br m, 6 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.50 (br m, 4 H, $\mathrm{PCH_2C}H_2$, $\mathrm{PCH_2C}H_2\mathrm{CH_2O}$)	231.5 (m, CO) 73.5 (d, $^3J_{\mathrm{PC}} = 7$, $\mathrm{O}C\mathrm{H_2CH_2}$) 58.5 (s, $\mathrm{OCH_3}$) 30.8 (cm, $\mathrm{P}C\mathrm{H_2CH_2CH_2O}$) 28.6 (dd, separation of inner and outer peaks, 8 and 12 Hz, $\mathrm{P}C\mathrm{H_2CH_2}$) 23.8 (br m, $\mathrm{PCH_2}C\mathrm{H_2CH_2O}$) 19.9 (br, $\mathrm{PCH_2}C\mathrm{H_2}$)
6 $[\mathrm{Cr(CO)_3L^{C_3H_6NH_2}}]$	22.1 (s)	2.69 (m, 2 H, $\mathrm{NH_2}$) 1.67 (m, 8 H, $\mathrm{PCH_2}$, $\mathrm{NH_2C}H_2$) 1.48 (m, 4 H, $\mathrm{PCH_2C}H_2$, $\mathrm{NH_2CH_2C}H_2$	231.7 (m, CO) 68.1 (d, $^3J_{\mathrm{CP}} = 8$, $\mathrm{CH_2NH_2}$) 43.5 (br m, $\mathrm{P}C\mathrm{H_2CH_2CH_2NH_2}$) 31.6 (m, $\mathrm{P}C\mathrm{H_2CH_2}$) 28.5 (br m, $\mathrm{NH_2CH_2}C\mathrm{H_2}$) 19.8 (br m, $\mathrm{PCH_2}C\mathrm{H_2}$)
7 $[\mathrm{Cr(CO)_3L^{C_3H_6SMe}}]$	22.3 (s)	2.64 (br m, 2 H, $\mathrm{SCH_2}$) 2.36 (s, 3 H, $\mathrm{SCH_3}$) 1.79 (m, 6 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.47 (br m, 4 H, $\mathrm{PCH_2C}H_2$, $\mathrm{SCH_2C}H_2$)	231.2 (m, CO) 39.2 (d, $^3J_{\mathrm{CP}}$ 11, = $\mathrm{S}C\mathrm{H_2CH_2CH_2}$) 31.9 (m, $\mathrm{P}C\mathrm{H_2CH_2CH_2S}$) 29.7 (br m, $\mathrm{P}C\mathrm{H_2CH_2}$) 27.7 (d, $^2J_{\mathrm{CP}} = 7$, $\mathrm{SCH_2}C\mathrm{H_2}$) 19.8 (br m, $\mathrm{PCH_2}C\mathrm{H_2}$) 14.1 (s, $\mathrm{SCH_3}$)
8 $[\mathrm{Cr(CO)_3L^{C_3H_6PPh_2}}]$	22.5 (s) −17.4 (s)	7.70 (m), 7.43 (m), 7.30 (m) (aromatic, 10 H) 2.61 (m, 2 H, $\mathrm{Ph_2PC}H_2$) 1.85 (m, 2 H, $\mathrm{Ph_2PCH_2CH_2C}H_2$) 1.67 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.45 (m, 2 H, $\mathrm{PCH_2C}H_2$) 1.26 (m, 2 H, $\mathrm{Ph_2PCH_2C}H_2$)	231.5 (m, CO) 138.7 (m), 131.8 (m), 128.6 (m) (aromatic) 39.2 (m, $\mathrm{Ph_2P}C\mathrm{H_2}$) 27.8 (t, $^1J_{\mathrm{CP}} = 9$, $\mathrm{P}C\mathrm{H_2CH_2}$) 23.4 (m, $\mathrm{Ph_2PCH_2CH_2}C\mathrm{H_2}$) 21.4 (m, $\mathrm{Ph_2PCH_2}C\mathrm{H_2}$) 19.8 (m, $\mathrm{PCH_2}C\mathrm{H_2}$)
10 $[\mathrm{Mo(CO)_3L^{CH_2Ph}}]$	2.6 (s)	7.40 (m), 7.32 (m), 7.12 (m) (aromatic, 5 H) 1.85 (br, 4 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.65 (m, 2 H, $\mathrm{PCH_2C}H_2$) 1.34 (m, 2 H, $\mathrm{PC}H_2\mathrm{Ph}$)	219.8 (m, CO) 132.1, 128.6, 124.1, 120.2 (aromatic) 41.3 (m, $\mathrm{P}C\mathrm{H_2C}$) 27.5 (m, $\mathrm{P}C\mathrm{H_2CH_2}$) 19.8 (m, $\mathrm{PCH_2}C\mathrm{H_2}$)
11 $[\mathrm{Mo(CO)_3L^{Et}}]$	4.4 (s)	1.82 (br m, 4 H, $\mathrm{PC}H_2\mathrm{CH_2}$) 1.67 (m, 2 H, $\mathrm{PC}H_2\mathrm{CH_3}$) 1.52 (br m, 2 H, $\mathrm{PCH_2C}H_2$) 1.10 (dt, $^2J_{\mathrm{HH}}$ 8, $^3J_{\mathrm{PH}}$ 15, 3 H, $\mathrm{PCH_2C}H_3$)	221.1 (m, CO) 29.1 (m, $\mathrm{P}C\mathrm{H_2CH_2}$) 27.6 (m, $\mathrm{P}C\mathrm{H_2CH_3}$) 20.9 (m, $\mathrm{PCH_2}C\mathrm{H_2}$) 8.1 (m, $\mathrm{PCH_2}C\mathrm{H_3}$)

[a] In $\mathrm{CDCl_3}$ solution. [b] Chemical shifts relative to $\mathrm{H_3PO_4}$. [c] Chemical shifts relative to $\mathrm{CDCl_3}$ (δ 7.27). [d] Chemical shifts relative to $\mathrm{CDCl_3}$ (δ 77.0).

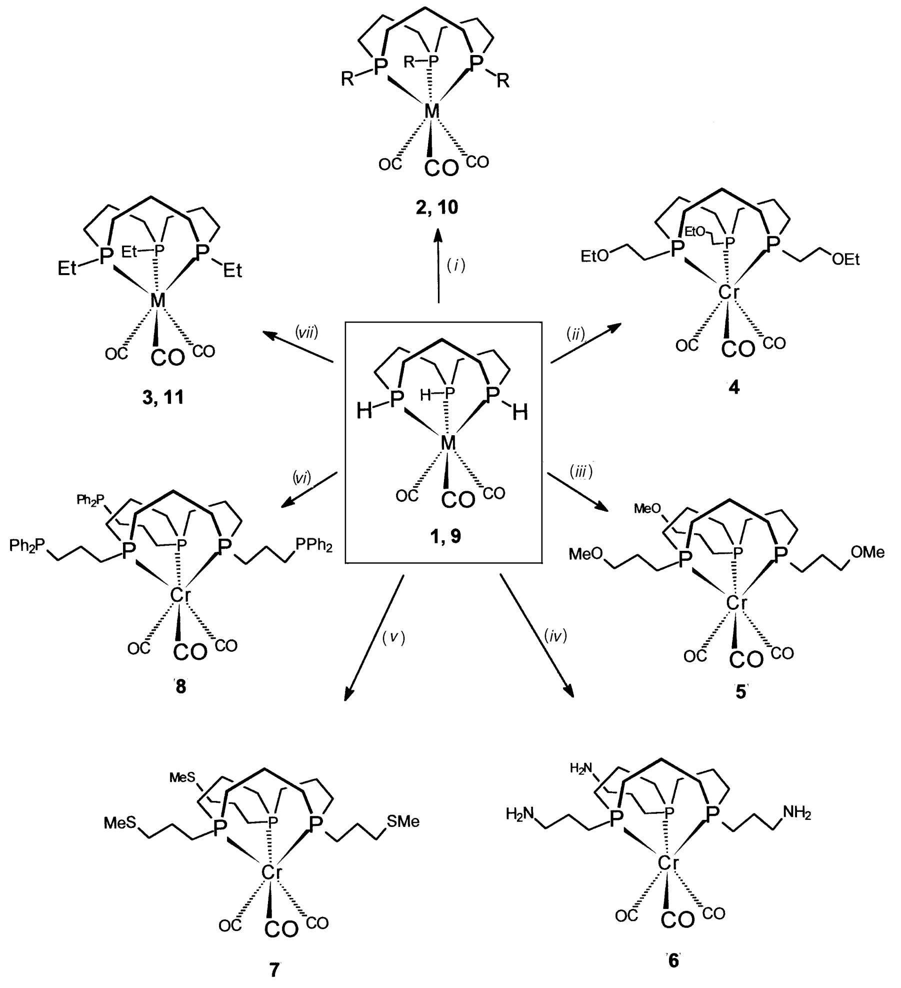
NMR spectrum a singlet is observed in the region expected (δ 16.4) for co-ordinated tertiary phosphines of this type.[5] A broadened singlet is observed in the ^{1}H NMR spectrum which may be assigned to the methyl protons (*i.e.* $^2J_{\mathrm{PH}}$ is small). Two other multiplets (δ 1.72 and 1.44) may be assigned to the ring α($\mathrm{PCH_2}$) and β($\mathrm{PCH_2C}H_2$) protons respectively on the basis of intensity. As well as resonances due to the ring carbons, the methyl carbon appears as a doublet ($^1J_{\mathrm{PC}} = 18$ Hz) at δ 13.8 in the ^{13}C-{^{1}H} NMR spectrum.

In all other cases the addition of 3 equivalents of LiBu$^{\mathrm{n}}$

Table 2 Selected infrared, analytical and mass spectrometry data

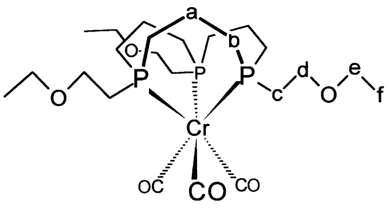
Complex	IR[a] ν(CO)/ cm^{-1}	Analysis (%)[b] C	H	Mass spectrum,[c] *m/z*	Method[d]	Yield (%)
2	1911	45.0	6.75	M^+ 400 [100],	A	75
	1813	(45.1)	(6.9)	$M - 3CO^+$ 316 (60)		
3	1911	48.9	7.45	M^+ 442 (30),	B	82
	1813	(48.2)	(7.05)	$M - 3CO^+$ 353 (50)		
4	1908	50.2	7.85	M^+ 574 (55)	B	80
	1813	(50.2)	(7.85)	$M - 3CO^+$ 490 (100)		
5	1911	50.2	7.85	M^+ 574 (100)	B	90
	1806[e]	(49.8)	(8.1)	$M - 3CO^+$ 490 (20)		
6	1911	47.6	7.95[f]	M^+ 529 (30),	B	80
	1806[e]	(47.2)	(7.85)	$M - 3CO^+$ 445 (100)		
7	1904	46.3	7.55	M^+ 662 (20)	B	75
	1813	(46.5)	(7.25)	$M - 3(CH_3SC_3H_6)^+$ 355 (60)		
8	1918	66.0	6.35	M^+ 1036 (10)[g]	B	70
	1822	(66.3)	(6.60)	$M - 3CO^+$ 952 (15)		
10	1922	58.2	6.0	M^+ 672 (30),	A	71
	1821	(58.9)	(5.85)	$M - 3CO^+$ 588 (100)		
11 [Mo(CO)$_3$L^{Et}]	1918	45.0	7.5	M^+ 488 (70)	B	82
	1815	(44.9)	(6.8)	$M - 3CO^+$ 402 (100)		

[a] All spectra recorded as Nujol mulls. [b] Calculated values in parentheses. [c] Relative intensities in %. [d] See Experimental section. [e] ν(ether) 1103 cm^{-1}. [f] N, 7.95 (7.5%). [g] Electrospray.



Scheme 1 M = Cr or Mo. (*i*) (*a*) 3LiBu, tetrahydrofuran (thf), −78 °C; (*b*) 3 RX (X = halide), −20 °C, R = Me or PhCH$_2$; (*ii*) 3EtOC$_2$H$_3$, azobis(isobutyronitrile) (aibn), 80 °C; (*iii*) 3MeOC$_3$H$_5$, aibn, 80 °C; (*iv*) H$_2$NC$_3$H$_5$, aibn, 80 °C; (*v*) 3MeSC$_3$H$_5$, aibn, 80 °C; (*vi*) Ph$_2$PC$_3$H$_5$, aibn, 80 °C; (*vii*) 3C$_2$H$_4$, aibn, 80 °C, 6 atm (*ca.* 6 × 10^5 Pa)

followed by 3 equivalents of alkyl halide (*e.g.* Pr^{i}Br, PhCH$_2$Cl, Me$_3$SiCH$_2$Cl or C$_3$H$_5$Br) gave mixtures of what were presumed to be partially alkylated species (^{31}P NMR spectroscopy) and only very poor yields of the expected tritertiary phosphine complexes. Addition of further equivalents of LiBu^n and alkyl halide still did not give rise to the tritertiary species in appreciable yields and separation of the products was difficult. It appears that proton-abstraction reactions compete with nucleophilic substitutions in these reactions as secondary phosphines can be detected (NMR spectroscopy) in the product mixtures,



Scheme 2

thus the nucleophilicity (relative to basicity) of the intermediate phosphides in the chromium system is less than for the molybdenum analogues. This supposition is plausible on steric grounds since the P−Cr bond length will be significantly shorter than P−Mo thus effectively increasing the steric influence of the $Cr(CO)_3$ unit [in a series of *fac*-tricarbonyltris(phosphine) complexes of Cr including **1** the Cr−P bond is 0.13 Å shorter than Mo−P in the analogous molybdenum complexes[5]]. The poor solubility of the intermediate chromium phosphide complex under the reaction conditions in thf may also contribute to the restricted utility of these reactions.

The second approach (radical-initiated addition of alkenes) was more successful. In all cases, reaction of **1** with an excess of alkene gave rise to the expected tritertiary complex, $[Cr(CO)_3(L^R)]$ [R = Et **3**, $EtOCH_2CH_2$ **4**, $MeO(CH_2)_3$ **5**, $NH_2(CH_2)_3$ **6**, $MeS(CH_2)_3$ **7** or $Ph_2P(CH_2)_3$ **8**] in good yield. The excess of alkene was generally kept to a minimum in order to minimise polymerisation by-products which in some cases were removable only by chromatography. All complexes were readily characterised spectroscopically, molecular ions were observed in their mass spectra and satisfactory elemental analyses were obtained. Complexes **2**–**8** were surprisingly air-sensitive in comparison to **1** and rapidly change from yellow to blue-green in air.

The exact nature of the products formed by aerial oxidation was not ascertained although oxidation of the metal is indicated by the paramagnetism of the green product formed from the trimethyl complex **2** ($\mu_{eff} = 2.68\ \mu_B$ based upon **2**), and oxidation of the macrocycle is apparent from the IR spectrum in which new stretching frequencies at 3423 (br) and 1630s (indicating the presence of hydroxy groups) and 1152 cm^{-1} (indicating the presence of phosphine oxide) appear. Anti-Markovnikov addition of alkene is confirmed for complexes **3**–**8** and **11** by ^1H and $^{13}C-\{^1H\}$ NMR spectroscopy. Although the acid-catalysed addition of alkenes (*via* a carbonium ion) to pH functions leads to the Markovnikov product, it is well established that radical-catalysed addition of alkenes to PH functions leads to the formation of the anti-Markovnikov product.[11]

Complexes **4**–**8** are of particular interest as in addition to containing a triphosphamacrocyclic ring they also possess pendant donor groups (oxygen, nitrogen, sulfur and phosphorus respectively) which potentially could be utilised in the formation of bimetallic systems or as ligands with denticities up to hexadentate.

All complexes exhibit singlets in their ^{31}P NMR spectra, 20–25 ppm downfield from that of the parent complex **1**. As for the molybdenum counterparts,[5] the methylated complex **2** gives the lowest chemical shift and there is only a slight difference between the values of the chemical shifts of the other complexes. There is a downfield chemical shift of 18–24 ppm for the chromium complexes relative to their molybdenum analogues but this difference is smaller than that observed for the differences in the ^{31}P NMR chemical shifts for the two secondary complexes **1** and **9**, which is *ca.* 30 ppm. It is not surprising that the chemical shift values for **5**–**8**, which contain C_3H_6X side-arms (X = heteroatom), show very little variation. Also $^4J_{PP}$ coupling is not observed for **8**, which shows two relatively sharp singlets ($\nu_{\frac{1}{2}}$ *ca.* 8 Hz) in the $^{31}P-\{^1H\}$ NMR spectrum.

In their ^1H NMR spectra the resonances attributable to the PCH_2 ring protons for all the complexes fall in the region δ 1.79–1.67 and those assigned to the ring PCH_2CH_2 protons fall in the region δ 1.52–1.44. In the $^{13}C-\{^1H\}$ NMR spectra the resonances assigned to ring PCH_2 carbons fall in the region δ 31.9–28.6 and those due to the central ring $PCH_2\mathit{C}H_2$ carbons are in the range δ 20.3–19.8; there are no significant variations in these shifts between the chromium and molybdenum complexes. However, complexes **4**–**8** also contain $P(CH_2)_nX$ units in the alkyl side-arms ($n = 2$ for **4**, $n = 3$ for **5**–**8**, X = heteroatom). With the exception of **4** it was not possible to distinguish between the ring and side-arm protons by ^1H NMR spectroscopy in those compounds with heteroatoms in the pendant alkyl chains due to chemical shift coincidences (Table 1). For **4**, however, all proton environments (Scheme 2) may be clearly assigned from the ^1H and two-dimensional correlation (COSY) $^1H-^1H$ NMR spectra.

In the ^1H NMR spectrum of complex **4** the resonances attributed to protons in the two OCH_2, environments and the CH_3 group are observed with typical chemical shift values. Resonances due to protons in the two PCH_2 and in the $PCH_2C\mathit{H}_2$ groups are also observed in the expected region (between δ 1.4 and 2.0) but appear as broadened peaks, presumably due to complex coupling. The two-dimensional COSY $^1H-^1H$ NMR spectrum allows peak assignments to be made, and clearly shows that CH_2^e is coupled to CH_3^f and which also appear as a quartet and triplet respectively ($^3J_{HH} = 7$ Hz) as would be anticipated. Similarly CH_2^d is coupled to CH_2^c, the former being readily assigned to the OCH_2 protons on the basis of chemical shift. The two remaining broad peaks are also coupled to each other and are assigned to CH_2^a and CH_2^b, *i.e.* the ring $\alpha(PCH_2)$ and $\beta(PCH_2C\mathit{H}_2)$ protons respectively and again on the basis of chemical shift as well as intensity. The remaining intensity in the aliphatic region between peaks b and c, as well as those between a and f, is assigned to impurities including poly(vinyl ethyl ether), traces of which are not readily removed upon recrystallisation. In a similar fashion, all carbon environments can be assigned for **4** using $^{13}C-\{^1H\}$ and two-dimensional COSY $^{13}C-^1H$ NMR spectroscopy. It is reasonable to assume that the chemical shifts of the ring carbons change little upon changing the side-arm and thus the complete assignment for **4** is of use in establishing assignments of the ring carbons in the other complexes.

Molybdenum complexes

Unlike complex **1** described above, reaction of $[Mo(CO)_3(H_3L)]$ **9** with 3 equivalents of $LiBu^n$ followed by 3 equivalents of benzyl chloride results in the formation of the expected tritertiary complex $[Mo(CO)_3L^{CH_2Ph}]$ **10** in reasonable yield. This reaction is similar to those previously described for the formation of other molybdenum tritertiary 1,5,9-triphosphacyclododecane complexes.[5] As with the chromium complexes, the radical-catalysed reaction of **9** with alkenes (*i.e.* ethene) results in the formation of the expected tritertiary complexes $[Mo(CO)_3L^{Et}]$ **11**.

All the complexes reported here show two ν(C−O) stretching vibrations in their IR spectra consistent with the A_1 and E modes expected for a facial C_{3v} X_3MY_3 co-ordination structure.[12] For the molybdenum complexes the lower-frequency ν(CO) absorption decreases as the substituents on phosphorus vary in the order H > C_3H_5 > Me ≈ Me_3SiCH_2 > $PhCH_2$ ≈ Et ≈ Me_2CH ≈ $NH_2C_3H_6$. This trend is similar to that previously observed in related molybdenum triphosphamacrocycle complexes (R = H,[2] Me, Me_3SiCH_2, C_3H_5 or $C_3H_6NH_2$[5]). Whether these trends infer a similar order of π-bonding ability in these ligands or σ-donor abilities (or a combination of the two) is unclear.

The same comparison for the chromium complexes shows that the lower-frequency ν(CO) absorption decreases in the order $C_3H_6PPh_2$ > H > Me ≈ Et ≈ $MeSC_2H_5$ ≈ $EtOC_2H_4$ > $MeOC_3H_6$ ≈ $NH_2C_3H_6$. This order is similar to that observed for the molybdenum analogues; the secondary phosphine complexes tend to have higher ν(CO) absorptions than the tertiary phosphine complexes. Further insight into the bonding in these compounds is not readily obtained by ^{13}C-{^1H} NMR spectroscopy; chemical shifts attributed to the carbonyl carbons of these complexes indicate little variation in M−C bonding as the difference across all eight chromium complexes is less than 2 ppm and hence not a significant variation. Variation in δ(^{13}C) is also small between the molybdenum compounds (1.1 ppm), although this value is routinely *ca.* 10 ppm upfield of the equivalent resonance of their chromium counterparts.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by boiling under reflux over standard drying agents. The compounds $[Mo(CO)_3(H_3L)]$[2] and $[Cr(CO)_3(H_3L)]$[7] were prepared by literature methods. All other chemicals were obtained from the Aldrich Chemical Company and dried over molecular sieves and deoxygenated by freeze–thaw degassing with the exception of aibn which was used directly. The NMR spectra were recorded on a Bruker WM360 instrument operating at 360.13 (^1H), 90.53 (^{13}C) MHz or a JEOL FX-90 instrument operating at 36.23 MHz (^{31}P). The COSY-45 ^1H–^1H two-dimensional NMR spectroscopy was carried out on a Bruker DPX400 instrument using the program COSY from the standard Bruker software suite. In the F2 dimension 1024 data points were collected over 4084 Hz, and in F1 128 data points over 4084 Hz. The COSY-45 ^{13}C–^1H two-dimensional carbon–proton correlation NMR spectroscopy was carried out on the same instrument using standard Bruker software. In the F2 dimension, 4096 data points were collected over 3019 Hz, and in F1 200 data points over 15 527 Hz. All NMR spectra were recorded in $CDCl_3$ solution, with the ^1H and ^{13}C NMR chemical shifts quoted in δ relative to solvent resonances and ^{31}P NMR chemical shifts quoted in δ relative to 85% external H_3PO_4 ($\delta = 0$ ppm). Infrared spectra were recorded in Nujol on a Nicolet 510 Fourier-IR spectrometer, mass spectra (EI & ES) on a VG Platform II Fisons spectrometer. Microanalyses were obtained from within this department.

Preparations

Method A: $[M(CO)_3L^R]$ (M = Cr, R = Me 2; M = Mo, R = $PhCH_2$ 10). To a cooled (−78 °C) solution of $[M(CO)_3(H_3L)]$ (0.50 mmol) dissolved in tetrahydrofuran (thf) (20 cm^3) was added dropwise a solution of $LiBu^n$ (1.5 mmol) in hexane (1 cm^3) and the mixture allowed to warm slowly to −20 °C. The mixture was then recooled (−78 °C) and RX (1.5 mmol, RX = MeI **2**, $PhCH_2Cl$ **10**) was added dropwise. The mixture was allowed to warm slowly to room temperature and then stirred for 30 min following which the solvent was removed *in vacuo* to give a pale product. This was extracted into CH_2Cl_2 (30 cm^3) and passed through a (15 cm) silica column with CH_2Cl_2 as eluent. Evaporation *in vacuo* gave the desired product which was then recrystallised from toluene solution at −20 °C.

Method B(*i*): $[Cr(CO)_3L^R]$ (R = $EtOC_2H_4$ 4, $MeOC_3H_6$ 5, $NH_2C_3H_6$ 6, $MeSC_3H_6$ 7 or $Ph_2PC_3H_6$ 8). To a solution of $[M(CO)_3(H_3L)]$ (0.50 mmol) and aibn (*ca.* 1%) in toluene (20 cm^3) was added alkene (*i.e.* $EtOCHCH_2$ for **4**, $MeOC_3H_5$ for **5**, $NH_2C_3H_5$ for **6**, $MeSC_3H_5$ for **7**, $Ph_2PC_3H_5$ for **8**; 1.60 mmol) and the mixture heated under reflux to 80 °C for 3 h. The resultant yellow-brown mixture was allowed to cool to room temperature and filtered through a short (4 cm) Celite column to give a pale yellow solution. The solvent was removed *in vacuo*, the residue extracted into CH_2Cl_2 (30 cm^3) and passed through a (15 cm) silica column with CH_2Cl_2 as eluent. Evaporation *in vacuo* gave the desired products as yellow oils.

Method B(*ii*): $[M(CO)_3L^{Et}]$ (M = Cr 3 or Mo 11). A solution of $[M(CO)_3(H_3L)]$ (0.50 mmol) and aibn (*ca.* 1%) in toluene (20 cm^3) in a glass pressure reaction flask was frozen at −196 °C. A large excess (>2.0 g) of ethene was added, the flask was sealed and the mixture heated to 80 °C for 3 h. The mixture was then allowed to cool and the product isolated as above. The chromium complex **3** was obtained as a yellow oil by evaporation of the CH_2Cl_2; **11** was obtained as colourless prisms by recrystallisation from toluene solution at −20 °C.

Acknowledgements

We thank the EPSRC for a research grant (to J. S. F.) and the Association of Commonwealth Universities and University of Sri Jayewardenepura of Sri Lanka for a scholarship (to S. S. L.).

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Received 19*th August* 1996; *Paper* 6/05749G