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Primary alkenyl phosphine complexes of chromium and molybdenum; synthesis and characterisation of tricarbonyl(1,5,9-triphosphacyclododecane)chromium(0)

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The reaction of *fac*-[Cr(CO)$_3$(MeCN)$_3$] with primary allyl- and vinyl-phosphines gave rise to the corresponding tris(primary phosphine)chromium tricarbonyl complexes. Radical-catalysed coupling of the allyl functions with PH groups in the tris(allylphosphine) complex led to the chromium tricarbonyl complex of 1,5,9-triphosphacyclododecane. The molybdenum analogue of the chromium prop-2-enylphosphine complex has also been prepared. Radical-catalysed coupling of the vinyl functions with PH groups in these complexes resulted in new complexes with multidentate ligand systems but not in complexes of new macrocycles. The crystal structures of the new 1,5,9-triphosphacyclododecane and prop-2-enylphosphine complexes have been determined and structural implications for these template cyclisation reactions investigated.

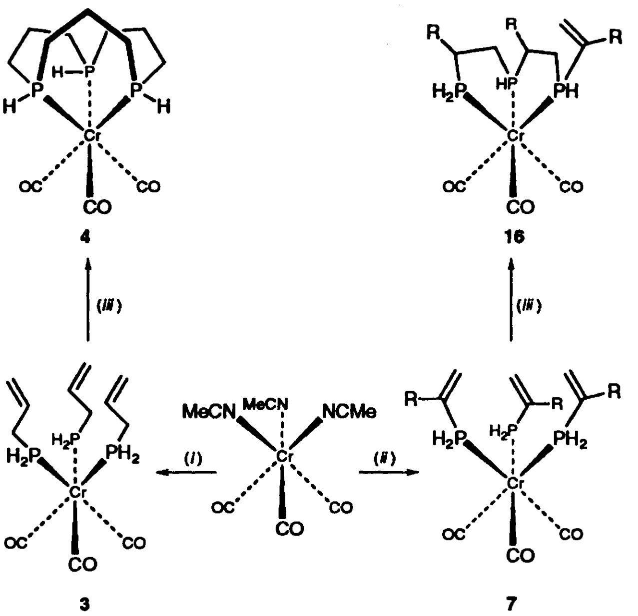
We have an interest in acyclic tridentate systems including linear triphosphines for the following principal reasons. These compounds have the ability kinetically to stabilise unusual chelate complexes which may also exhibit dynamic solution behaviour. As well as forming chelate-stabilised complexes with pendant donors available for further stabilisation of lower-co-ordinate reaction intermediates, they can support bimetallic and polynuclear complexes, acting as bridging ligands. They also have the ability to co-ordinate facially to three mutually *cis* sites on a metal which is of considerable interest in the study of new properties and in applications of transition metals in catalysis. In this last property they act as six-electron ligands and can be considered analogous to the cyclopentadienyl family of ligands. Their co-ordination versatility complicates the study of their complexes however, and restricts their application. In order to achieve a higher degree of control of the co-ordination behaviour of such tridentate systems triphosphorus macrocycles are of interest. Again, in order to simplify the co-ordination chemistry, we have chosen to investigate triphosphorus macrocycles for which mixtures of isomers is restricted and hence where the bridging 'backbone' functions between adjacent phosphorus atoms are identical. Such compounds are very rare; prior to our current study, there was only one example of a 1,5,9-triphosphacyclododecane complex reported by Norman and co-workers[1] who also prepared the 1,6,11-triphosphacyclopentadecane analogue, both of which were prepared by a metal-template route with the added benefit of control over the stereochemistry at phosphorus. We have extended this chemistry to tungsten and have recently reported the syntheses and characterisations of the first complexes of tritertiary derivatives of 1,5,9-triphosphacyclododecane.[2] The free, unco-ordinated macrocycles are currently unknown despite attempts at their liberation from the metal template upon which they were prepared. Since the co-ordination chemistry of phosphorus-containing macrocycles of these types, as well as the reaction chemistry of complexes and organometallic derivatives, will be of interest, we have chosen to extend this study to similar chromium complexes with the aim of broadening our knowledge of these macrocyclic phosphorus systems. In this way we hope to maximise our opportunities for the design of synthetic procedures to the free triphosphorus macrocycles. In addition, since the template cyclisation works well for propenyl- and butenyl-phosphines, generating the corresponding twelve- and fifteen-membered macrocycles, we have also investigated the preparation of similar vinylphosphine complexes and their coupling reactions.

Results and Discussion

Synthetic routes to the new compounds discussed below are collected in Schemes 1–3, NMR data are in Table 1 and IR and analytical data in Table 2.

Chromium allylphosphine and macrocycle complexes

The synthetic approaches to the molybdenum and tungsten cyclo-triphosphine complexes are similar *via* the tris(allylphosphine)tricarbonyl complexes. These were prepared by reaction of the tricarbonyl(mesitylene)metal(0) complexes with allylphosphine (M = Mo **1**; or W **2**). Tris(allylphosphine)tricarbonylchromium(0) **3**, however, could not be prepared from tricarbonyl(mesitylene)chromium(0) cleanly and in good yield. An alternative route (Scheme 1) *via* the substitution of acetonitrile in tris(acetonitrile)tricarbonylchromium(0) by allylphosphine gives rise to the required tris(phosphine) complex in high yield and this route is also applicable to the molybdenum and tungsten analogues. By this reaction, tris(allylphosphine)tricarbonylchromium(0) was obtained as a viscous yellow oil which was characterised spectroscopically. Thus the co-ordination of allylphosphine is clearly indicated by ^{31}P NMR spectroscopy (δ −23.6, t, $^1J_{PH}$ = 320 Hz) where the co-ordination chemical shift ($\Delta^{31}P = \delta_{\text{co-ordinated P}} - \delta_{\text{unco-ordinated P}}$) relative to the free phosphine ligand is *ca.* 111 ppm and $^1J_{PH}$ increases by *ca.* 125 Hz. The increase in $^1J_{PH}$ is similar to that observed for the molybdenum and tungsten analogues **1** and **2** (Table 1), although $\Delta^{31}P$ increases markedly with decreasing atomic number of the metal atom in this series. In the ^{1}H and ^{13}C-{^{1}H} NMR spectra resonances due to allyl functions are observed and the spectra are very similar to those for the analogues **1** and **2**. In the IR spectrum two bands assigned to ν(CO) (1932, 1834 cm^{-1}) confirm the *fac*-octahedral geometry and other expected characteristic ligand absorptions were observed, *i.e.* ν(PH) (2305 cm^{-1}) and ν(C=C) (1630 cm^{-1}). The molecular ion is also observed in the mass spectrum (*m*/*z* 358) as well as fragmentation due to loss of allylphosphine and carbonyl ligands.



Scheme 1 (*i*) Allylphosphine (3 : 1), CH_2Cl_2; (*ii*) vinyl- or prop-2-enylphosphine (3 : 1), CH_2Cl_2; (*iii*) aibn, 80 °C

When solutions of complex **3** in toluene are heated (80–100 °C) with aibn (azobisisobutyronitrile), a new material **4** can be obtained upon work-up as colourless crystals in good yield (*ca.* 80%). Microanalysis indicates the formula $C_9H_{21}P_3$-$Cr(CO)_3$ and spectroscopic data clearly confirm that the allylphosphine functions have coupled to give rise to the new 1,5,9-triphosphacyclododecane chromium complex (Scheme 1). Thus in the ^{31}P NMR spectrum a doublet is observed (δ −3.9, $^1J_{PH}$ = 331 Hz) consistent with a secondary phosphine; the downfield shift upon cyclisation [relative to the tris(alkenylphosphine) precursor] is similar to the behaviour of the molybdenum **5** and tungsten **6** analogues and again a significant (monotonic) increase in δ(^{31}P) occurs as the atomic number of the metal atom decreases. The ^1H and ^{13}C-{^1H} NMR spectra are also very similar to those of **5** and **6**; there is little variation in δ(CO) between the tris(alkenylphosphine) precursors and the corresponding macrocycle complexes. In the mass spectrum an intense molecular ion is observed (M^+, *m*/*z* 358, 62%) along with a fragmentation pattern indicating sequential loss of carbonyls. Two carbonyl stretching absorptions appear in the IR spectrum [ν(CO) 1918, 1820 cm^{-1}] which are consistent with a *fac*-tricarbonyl octahedral structure. A band assigned to ν(PH) (2298 cm^{-1}) and the absence of a band due to ν(C=C) are also consistent with the formation of the macrocycle. The lowering of ν(CO) relative to that of **3** is similar to variations observed in the molybdenum and tungsten analogues and may indicate that the secondary phosphine donors in the macrocyclic ligand are poorer π acceptors than the monodentate primary phosphines, as might be expected.

Vinylphosphine complexes

In order to investigate the viability of this template route to 1,4,7-triphosphacyclononane derivatives, chromium complexes of vinyl- and prop-2-enyl-phosphine were investigated. Since vinylphosphine is commonly contaminated with ethylphosphine when prepared by reduction of vinyl phosphonates, the detailed study was performed with prop-2-enylphosphine.

The reaction of 3 mole equivalents of prop-2-enylphosphine with $[Cr(CO)_3(MeCN)_3]$ gives rise to pale yellow solutions from which colourless crystals may be obtained in high yield by crystallisation from light petroleum. Analytical data for these crystals indicate the composition, $[Cr(CO)_3\{H_2PC(Me)CH_2\}_3]$ **7**. Spectroscopic data are consistent with this formulation. The molecular ion is observed in the mass spectrum (*m*/*z* 358) along with a fragmentation pattern indicating successive loss of carbonyl groups. In the IR spectrum two bands may be assigned to ν(CO) (1940, 1848 cm^{-1}) indicating a *fac*-octahedral arrangement of ligands and bands assigned to ν(PH) (2298 cm^{-1}) and ν(C=C) (1616 cm^{-1}) confirm the presence of prop-2-enylphosphine ligands. The NMR spectra are also consistent with **7** being the *fac*-tris(primary phosphine) isomer since a triplet is observed in the ^{31}P spectrum (δ −12.8, $^1J_{PH}$ = 305 Hz). The ^1H and ^{13}C-{^1H} NMR spectra are also consistent with magnetically equivalent phosphine ligands; resonances assigned to alkene carbons are observed (δ 134.7, 125.0) as are resonances due to the carbonyl (δ 229.0) and methyl carbons (δ 24.8).

The tris(vinylphosphine) analogue of **7**, *i.e.* $[Cr(CO)_3(H_2PCHCH_2)_3]$ **8**, may be prepared in a similar manner by addition of 3 mole equivalents of purified vinylphosphine to a solution of $[Cr(CO)_3(MeCN)_3]$ and may be isolated as a pale yellow solid. Analytical data are consistent with the formulation and a molecular ion is observed in the mass spectrum (*m*/*z* 316). In the IR spectrum bands assigned to ν(CO) (1939, 1841 cm^{-1}), ν(PH) (2305 cm^{-1}) and ν(C=C) (1602 cm^{-1}) are observed and again confirm the presence of alkenylphosphine and a *fac*-octahedral arrangement of carbonyl ligands. In the ^{31}P NMR spectrum the resonance due to co-ordinated primary phosphine appears as a triplet as expected (δ −29.3, $^1J_{PH}$ = 309 Hz) and alkenyl, carbonyl and PH functions are confirmed in the ^1H and ^{13}C-{^1H} NMR spectra.

The molybdenum analogue of complex **7** is readily prepared in the same manner by the addition of prop-2-enylphosphine to $[Mo(CO)_3(C_6H_3Me_3$-1,3,5)] or to $[Mo(CO)_3(MeCN)_3]$ and may be isolated as pale yellow needles by crystallisation from light petroleum (b.p. 40–60 °C). Analytical data are consistent with the formulation $[Mo(CO)_3\{H_2PC(Me)CH_2\}_3]$ and the *fac*-tris(primary phosphine) structure is confirmed by spectroscopic data. The ^{31}P co-ordination chemical shift of the prop-2-enylphosphine ligands relative to free phosphine is much less than observed for the chromium compounds **7** and **8** (Δ = 76.4 *vs.* 108.6 and 107.2 ppm respectively). This effect was also observed for the allylphosphine complexes **1** and **3** and appears to be general for these primary phosphine complexes.

Coupling reactions of tris(vinylphosphine) complexes

Attempts to form triphosphacyclononane derivatives by cyclisation of the tris(prop-2-enylphosphine) complex **7** by thermal, radical or UV activation failed. In each case the reaction was monitored by ^{31}P NMR spectroscopy and coupling was observed to occur although the expected product was not. Thus, heating a toluene solution of **7** in the presence of catalytic quantities of aibn (conditions identical to those for the successful preparation of the triphosphacyclododecane complex **4**) generated a mixture of products with numerous peaks in the ^{31}P-{^1H} NMR spectrum. The predominant resonances were due to secondary phosphines (doublets in the ^{31}P NMR spectrum, $^1J_{PH} \approx 300$ Hz) with poorly resolved fine structure and other peaks due to primary and tertiary phosphines were also present, the latter indicating that intermolecular reactions also take place. These complex mixtures could not be readily separated and no pure components were identified. Further heating caused decomposition and precipitation of intractable, and presumably polymeric, materials. Thus, for the prop-2-enylphosphine complex **7** there appears to be a number of reaction pathways operating under the conditions employed, presumably including intermolecular coupling (giving rise to tertiary phosphines). However, there was no evidence (^{31}P-{^1H} NMR,[3] in the range δ +600 to −200) of vinylphosphine $\longleftrightarrow$ phosphaalkene tautomerism as had been observed for $[W(CO)_5\{Me(H)PCHCH_2\}]$ upon heating under somewhat more vigorous conditions than in the present case.[4] Similar

Table 1 The NMR data for the metal–phosphine complexes **1**–**12**

Complex	δ(^{31}P)[a]	$^1J_{PH}$/Hz	Δ^{31}P	δ(^1H)[b]	δ[$^{13}C-\{^1H\}$][c]
1 *fac*-$[Mo(CO)_3(H_2PC_3H_5)_3]$[d]	−57.5 (t)	295	77	5.90, 5.10, 5.00 C=CH 3.92 PH_2 2.36 PCH_2	217.7 CO 135.4, 117.6 C=C 26.4 PCH_2
2 *fac*-$[W(CO)_3(H_2PC_3H_5)_3]$[e]	−80.1 (t)	319	54.4	5.60, 5.10, 4.90 C=CH 3.50 PH_2 2.20 PCH_2	217.9 (m) CO 135.3 (s), 117.2 (s) C=C 28.4 PCH_2 (d, $^1J_{PC}$ = 59 Hz)
3 *fac*-$[Cr(CO)_3(H_2PC_3H_5)_3]$	−23.6 (t)	320	110.9	5.85, 5.10, 4.95 C=CH 4.05 PH_2 2.56 PCH_2	229 (m) CO 135.2 (s), 117.8 (s) C=C 26.5 (d, $^1J_{PC}$ 59 Hz) PCH_2
4 $[Cr(CO)_3\{$*cyclo*-$(HPC_3H_6)_3\}]$	−3.9 (d)	331	—	4.92 (m) PH 1.95 (m) PCH_2 1.60 (m) $PCH_2C\mathit{H}_2$	230 (m) CO 24.2 (d, $^1J_{PC}$ 25 Hz) PCH_2 21.5 (m) $PCH_2\mathit{C}H_2$
5 $[Mo(CO)_3\{$*cyclo*-$(HPC_3H_6)_3\}]$[d]	−32.1 (d)	318	—	4.70 (m) PH 1.80 (m) CH_2	—
6 $[W(CO)_3\{$*cyclo*-$(HPC_3H_6)_3\}]$[e]	−60.8 (d)	312	—	4.82 (m) PH 1.95 (m) PCH_2 1.70 (m) $PCH_2C\mathit{H}_2$	220 (m) CO 25.0 (d, $^1J_{PC}$ 38 Hz) PCH_2 22.9 $PCH_2\mathit{C}H_2$
7 *fac*-$[Cr(CO)_3\{H_2PC(Me)CH_2\}_3]$	−12.8 (t)	305	108.6	5.50, 5.60 $C=CH_2$ 4.65 PH_2 2.00 CH_3	229 (m) CO 134.7 (m) $P\mathit{C}=C$ 125.0 (m) $PC=\mathit{C}$ 24.8 (s) CH_3
8 *fac*-$[Cr(CO)_3(H_2PC_2H_3)_3]$	−29.3 (t)	309	107.2	6.28, 5.95, 5.80 $C=CH_2$ 4.83 PH_2	229 (m) CO 130.3 (m) $P\mathit{C}=C$ 125.5 (m) $PC=\mathit{C}$
9 *fac*-$[Mo(CO)_3\{H_2PC(Me)CH_2\}_3]$	−45.5 (t)	302	76.4	5.50, 5.60 $C=CH_2$ 4.60 PH_2 2.00 CH_3	218 (m) CO 134.8 (m) $P\mathit{C}=C$ 126.5 (m) $PC=\mathit{C}$ 24.8 (s) CH_3
10 *cis*-$[Cr(CO)_4\{H_2PC(Me)CH_2\}_2]$	−21.6 (t)	321	100.0	5.70, 5.60 $C=CH_2$ 4.75 PH_2 2.10 CH_3	223 (m) CO 134.7 (m) $P\mathit{C}=C$ 126.3 (m) $PC=\mathit{C}$ 23.9 (s) CH_3
11 $[Cr(CO)_4\{H_2PCH(Me)CH_2P(H)C(Me)CH_2\}]$	45.6 (dd),[f] 5.0 (dt)	317, 320	—	5.60, 5.45 $C=CH_2$ 4.65 PH, PH_2 2.12 $C=CCH_3$ 2.00 CH 1.80 CH_2 1.54 CH_3	220.6 (m) CO 135.8 (m) $P\mathit{C}=C$ 127.1 (m) $PC=\mathit{C}$ 24.9 (br m) CH_2, CH 5.4 (br m) CH_3
12 $[Cr(CO)_3(MeCN)(H_2PC_3H_5)_2]$	−30.3 (t)	297	102	5.85, 5.05, 4.95 C=CH 4.10 PH_2 2.60 PCH_2 2.12 CH_3	220.9 (m) CO 135.8 (s) $P\mathit{C}=C$ 125.4 (s) CN 117.2 (m) $PC=\mathit{C}$ 26.8 (m) PCH_2 21.1 (s) CH_3

[a] In $CDCl_3$ solution, relative to external H_3PO_4 (85%). [b] In $CDCl_3$ solution, relative to $SiMe_4$. [c] In $CDCl_3$ solution, relative to solvent. [d] Data from ref. 1. [e] Data from ref. 2. [f] $^2J_{PP}$ = 67 Hz.

Table 2 Infrared spectroscopic[a] and analytical data for complexes **1**–**12**

	IR/cm^{-1}			Analysis (%)[b]	
Complex	ν(CO)	ν(PH)	ν(C=C)	C	H
1[c]	1954, 1864	2299	1633	35.7 (35.8)	5.40 (5.25)
2[d]	1935, 1825	2350	1630	—	—
3	1932, 1834	2305	1630	37.5 (40.2)	5.40 (5.85)
4	1918, 1820	2298	—	39.5 (40.2)	5.95 (5.85)
5[c]	1945, 1844	—	—	36.0 (35.8)	5.40 (5.25)
6[d]	1910, 1825	2305	—	28.5 (29.4)	4.60 (4.30)
7	1940, 1848	2298	1616	39.95 (40.20)	5.80 (5.85)
8	1939, 1841	2305	1602	33.90 (34.15)	4.90 (4.75)
9	1932, 1831	2298	1603	35.75 (35.80)	5.20 (5.10)
10	2066, 2017, 1936, 1876	2305	1623	37.45 (38.45)	4.90 (4.50)
11	2073, 2017, 1946, 1836	2326	1632	37.75 (38.45)	4.70 (4.50)
12[e]	1911, 1883, 1834	2333	1630	35.40 (37.25)	6.20 (5.90)

[a] Recorded in Nujol. [b] Calculated values in parentheses. [c] Data from ref. 1. [d] Data from ref. 2. [e] ν(CN) at 2284 cm^{-1}.

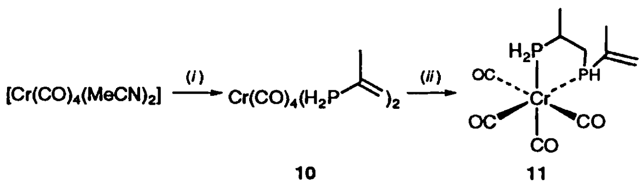
attempts to cyclise the vinylphosphine functions in **8** and the prop-2-enyl functions in **9** resulted in similar observations. Thus heating a solution of **8** in toluene in the presence of aibn again resulted in mixtures that gave rise to complex NMR spectra. Secondary phosphines could again be identified in both cases and continued heating resulted in the precipitation of intractable materials. Again no evidence of vinylphosphine ⟷ phosphaalkene tautomerism was observed.

Although the chromium(0) tris(phosphine) complexes are not substitution labile at ambient temperature, in all these three cases, during the early stages of the attempted cyclisations, free unco-ordinated primary phosphine was generated in solution and this may account for one of the undesirable competing reactions in this system, since any free primary phosphine would readily enter into intermolecular coupling reactions. Thus the lability of phosphine ligands increases with increasing temperature as might be expected and the cyclisation of the allylphosphine groups in **3** is rapid enough that dissociation does not compete detrimentally. No further variable-temperature NMR behaviour was observed although in the formation of the chromium primary phosphine complexes evidence that suggests stepwise substitution of acetonitrile in [$Cr(CO)_3(MeCN)_3$] was obtained from ^{31}P NMR spectra of the reaction solutions where singlets assigned to mono(phosphine)-bis(acetonitrile), bis(phosphine)mono(acetonitrile) and the tris(phosphine) products were observed upon addition of prop-2-enylphosphine and allylphosphine (δ −33.3, −22.6, −12.8 and −38.6, −30.3 and −23.6 respectively). This is in contrast to the formation of the molybdenum tris(phosphine) analogues where only the desired tris(phosphine) complex is formed even when a deficiency of primary phosphine is employed. Although the chromium complexes appear to exhibit enhanced lability (in comparison to the molybdenum analogues), no attempts were made to investigate the liberation of the acyclic phosphine products.

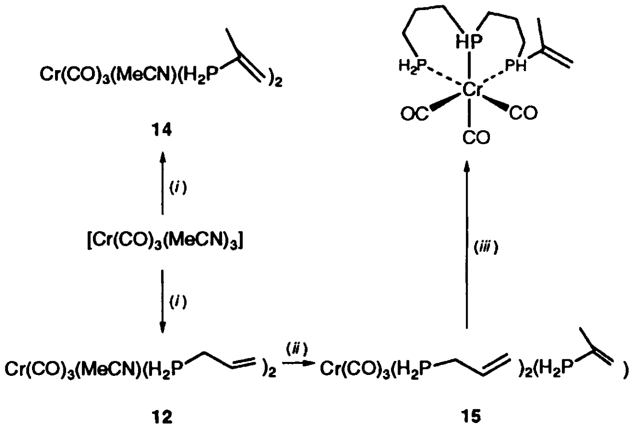
Bis(vinyl) and mixed allylphosphine-vinylphosphine complexes

In an attempt to determine whether intramolecular coupling is intrinsically stubborn in these complexes or other competing reactions render this template approach non-viable, we have studied similar coupling reactions in a bis(prop-2-enylphosphine) model complex where the intramolecular coupling can be limited to one addition between adjacent phosphines. The required tetracarbonylbis(prop-2-enylphosphine)chromium(0) complex was readily prepared from [$Cr(CO)_4(MeCN)_2$] and prop-2-enylphosphine (Scheme 2). The product, [$Cr(CO)_4\{H_2PC(Me)CH_2\}_2$] **10**, was isolated as a yellow oil from hydrocarbon solvent and identified by ^{31}P NMR spectroscopy (δ −21.6, $^1J_{PH}$ = 321 Hz). In addition a molecular ion was observed in the mass spectrum (*m/z* 312) and four absorptions in the IR spectrum due to ν(CO) (2066, 2017, 1936, 1876 cm^{-1}) are consistent with a *cis*-bis(phosphine)tetracarbonyl arrangement of ligands; ν(PH) (2305 cm^{-1}) and ν(C=C) (1623 cm^{-1}) were also observed. Heating a solution of **10** in toluene in the presence of aibn results in rapid reaction to form a new material **11** (Scheme 2), which is identified by an AB pattern in the $^{31}P-\{^1H\}$ NMR spectrum (δ 5.0, d; 45.6, d; $^2J_{PP}$ = 67 Hz). The former resonance appears as broad triplet in the ^{31}P NMR spectrum ($^1J_{PH}$ = 320 Hz) and hence is assigned to a primary phosphine; the latter appears as a broad doublet ($^1J_{PH}$ = 317 Hz) and is assigned to a secondary phosphine indicating that coupling has occurred between adjacent primary phosphines to give a new diphosphine ligand according to Scheme 2. Clearly, for this di(primary phosphine) complex intramolecular coupling is facile.

An alternative reason for the failure of the template triphosphacyclononane synthesis is that the final step to close the macrocycle may be inhibited by geometric constraints imposed by the linear triphosphine (*i.e.* the second intermediate, **16** in Scheme 1) required during the course of the reaction. If the constraints of the two carbon backbones between the coupled phosphorus atoms hold the terminal phosphines too far apart for the macrocycle to be closed easily, then competing intermolecular reactions may predominate resulting in intractable products as was observed. In this case a route to triphosphorus macrocycles with ring sizes intermediate between triphospha-cyclododecane and -cyclononane may be possible with mixed allylphosphine–vinylphosphine complexes analogous to the tris(phosphine) complexes. During the course of the preparation of **3** an intermediate was observed which was believed to be a partially substituted phosphine–acetonitrile complex (see above). This material was prepared selectively (Scheme 3) by the controlled addition of 2 mole equivalents of allylphosphine to [$Cr(CO)_3(MeCN)_3$] and was isolated as a yellow oil which was identified as [$Cr(CO)_3(MeCN)(H_2PCH_2CHCH_2)_2$] **12** spectroscopically. Thus, a singlet was observed in the $^{31}P-\{^1H\}$ NMR spectrum (δ −30.3) and acetonitrile was identified in the IR [ν(C≡N) 2284 cm^{-1}], $^{13}C-\{^1H\}$ NMR [δ(C≡N) 125.4] and ^1H NMR spectra [δ(Me) 2.12]. In addition, the molecular ion (*m/z* 325) was observed in the mass spectrum. In a likewise fashion, the bis(vinylphosphine)-monoacetonitrile complexes could be selectively prepared from [$Cr(CO)_3(MeCN)_3$] by addition of 2 mole equivalents of the appropriate primary phosphine and enabling isolation of [$Cr(CO)_3(MeCN)(H_2PCHCH_2)_2$] **13** and [$Cr(CO)_3(MeCN)\{H_2PC(Me)CH_2\}_2$] **14** as yellow oils and which were identified by their NMR spectra [$\delta(^{31}P)$ −37.0 and −22.6 respectively].



Scheme 2 (*i*) Prop-2-enylphosphine, CH_2Cl_2; (*ii*) aibn, 80 °C



Scheme 3 (*i*) Alkenylphosphine (2:1), CH_2Cl_2; (*ii*) prop-2-enylphosphine, CH_2Cl_2; (*iii*) aibn, 80 °C

Addition of 1 mole equivalent of prop-2-enylphosphine to a solution of complex **12** gave rise to a new triphosphine complex in good yield which was identified as the mixed-phosphine complex, [$Cr(CO)_3(H_2PCH_2CHCH_2)_2\{H_2PC(Me)CH_2\}$] **15** [rather than a mixture of the tris(allylphosphine) and tris(prop-2-enylphosphine) complexes, **3** and **7**, Scheme 3] by $^{31}P-\{^1H\}$ NMR spectroscopy. Thus two new resonances were observed, a triplet (δ −11.7) and a doublet (δ −18.2) in an intensity ratio of 1:2, and conforming to an A_2B spin pattern ($^2J_{PP}$ = 29 Hz). Complex **15** appears to be indefinitely stable in solution at ambient temperature. However, upon heating in the presence of aibn proportionation was indicated by the presence of the triphosphacyclododecane complex **4** as one of the reaction products. The other major product from this reaction gives rise to three broad resonances in the $^{31}P-\{^1H\}$ NMR spectrum (δ 45.8, 24.3, −55.2) of approximately equal intensity and which can be identified as secondary, secondary and primary phosphines respectively on the basis of the ^{31}P NMR spectrum [doublet ($^1J_{PH}$ 324), doublet (324), triplet (335 Hz) respectively]. The presence of this product implies that coupling has occurred and on the basis of the ^{31}P NMR data we propose the formation of a linear triphosphine of the type indicated in Scheme 3 where the two allylphosphine groups have coupled leaving the vinyl function pendant. Further heating causes decomposition and no other products could be characterised. It appears then that the final closing step between the vinyl function and the remaining terminal primary phosphine is again relatively slow resulting in unwanted side reactions.

Structural studies

In order to gain insight into the geometrical properties of the tris(alkenylphosphine) complexes and corresponding influences on these metal-template coupling reactions, the crystal structures of the chromium triphosphacyclododecane complex **4**, and the prop-2-enylphosphine complexes of Cr and Mo (**7** and **9** respectively) were measured. Selected bond angles and lengths are collected in Table 3 and crystal data in Table 4.

The structure of complex **4** (Fig. 1) clearly shows the distorted *fac*-octahedral geometry around Cr. The average Cr–P distance [2.326(2) Å] is similar to that observed in other chromium carbonyl phosphine complexes {*e.g.* 2.346(3) Å in *fac*-[$Cr(CO)_3(PH_3)_3$]}.[5] It is slightly shorter than in other *trans*-[$Cr(CO)_4L(L')$] complexes[6] [2.349(4)–2.364(6) Å, L = PPh_3, L' = PBu_3, $P(OMe)_3$ or $P(OPh)_3$] and is 0.13 Å shorter than that observed in the molybdenun analogue **5**. This relative shortening of the metal–ligand bonds in the chromium relative to the molybdenum complex is expected and agrees well with the reported difference in crystal radii.[7] The average Cr–C distance [1.847(5) Å] also compares favourably with that in *fac*-[$Cr(CO)_3(PH_3)_3$] [1.838(7) Å] and is again 0.13Å shorter than in the molybdenum analogue **5**. The interligand bond angles are close to those for idealised octahedral geometry [average P–Cr–P angle 91.09(5)°] in **4** and are greater than those observed in **5** [average P–Mo–P 88.88(3)°]. The C–Cr–C and *cis*-P–Cr–C angles are also close to 90° in **4** [average C–Cr–C 91.43(2), average *cis*-P–Cr–C 88.7(1)°] and are similar to the corresponding angles in **5** [average C–Mo–C 91.7(1), average *cis*-P–Mo–C 89.7(1)°]. These minor differences reflect the relative sizes of the metal atoms, thus the size of this macrocyclic ligand appears to result in a slight expansion of the P–M–P angles around the smaller chromium relative to those for molybdenum.

The structures of the prop-2-enylphosphine complexes of Cr (**7**, Fig. 2) and Mo (**9**, Fig. 3) also show the *fac*-octahedral geometry around the metal atoms. Since the interligand angles are relatively unrestricted in comparison to the macrocycle complexes **4** and **5** a more regular octahedral geometry is observed for both prop-2-enylphosphine complexes [for M = Cr, average P–M–P 89.35(6), *cis*-P–M–C 90.8(1), C–M–C 89.7(2); for M = Mo, average P–M–P 88.47(4), *cis*-P–M–C 91.0(1), C–M–C 89.6(2)°]. The average M–P [2.345(2) for **7** and 2.501(1) Å for **9**] and M–C distances again reflect a reduction in crystal radius (0.16 Å) for Cr in comparison to Mo in these directly analogous complexes. Other structural features are as expected and the alkene C=C bond [average 1.314(5) for **7** and 1.315(7) Å for **9**] is readily distinguished from the C–C bond to the α-methyl group [average 1.510(5) for **7** and 1.503(7) Å for **9**] in both complexes. A comparison of the non-bonded P···P distances in both **7** and **9** with **4** is of interest [average 3.297(4), 3.487(5) and 3.321(4) Å respectively] since it appears that there is only a slight contraction of the non-bonded P_3 framework upon cyclisation again indicating that 1,5,9-triphosphacyclododecane is well suited to match the steric requirements for octahedral co-ordination in these complexes. Clearly comparison with triphosphacyclononane complexes is not possible as the ligand is still currently unknown, however we have modelled the hypothetical analogue of **4**, *i.e.* (1,4,7-triphosphacyclononane)chromium tricarbonyl* in order to estimate the non-bonded P···P distances and derive a comparison of the relative sizes of the twelve- and nine-membered macrocycles.

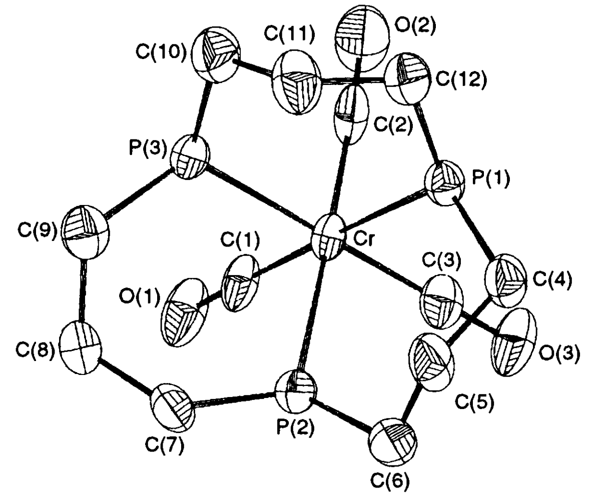


Fig. 1 Molecular structure and atom-labelling scheme of [$Cr(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}$] **4**

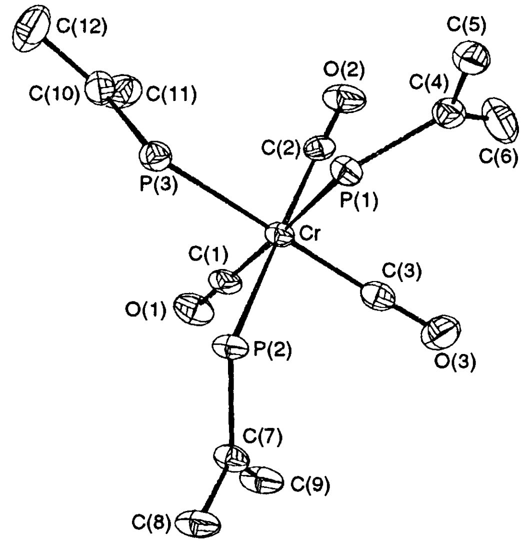


Fig. 2 Molecular structure and atom-labelling scheme of *fac*-[$Cr(CO)_3\{H_2PC(Me)CH_2\}_3$] **7**

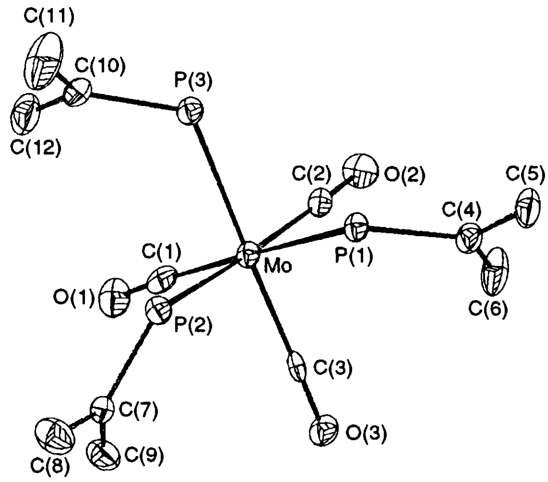


Fig. 3 Molecular structure and atom-labelling scheme of *fac*-[$Mo(CO)_3\{H_2PC(Me)CH_2\}_3$] **9**

Simulation generates a P··· P distance of 2.752 Å and indicates that for cyclisation to occur in the vinylphosphine complexes a considerable compression of the P–M–P angles is required. We suggest that this may be a significant factor in the apparent

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* Using CHEM-X molecular simulation software (Chemical Design, Chipping Norton, UK); bond lengths were restricted to the values observed for complex **4** followed by energy minimisation.

Table 3 Selected bond lengths (Å) and angles (°) for complexes **4**, **7** and **9**

	4	**7**	**9**
M–C(1)	1.829(4)	1.839(4)	1.988(5)
M–C(2)	1.869(5)	1.843(4)	1.990(5)
M–C(3)	1.844(4)	1.844(4)	1.995(5)
M–P(1)	2.342(2)	2.350(2)	2.496(1)
M–P(2)	2.315(2)	2.345(2)	2.496(1)
M–P(3)	2.320(2)	2.340(1)	2.511(1)
O(1)–C(1)	1.172(4)	1.162(4)	1.153(6)
O(2)–C(2)	1.146(5)	1.157(4)	1.146(5)
O(3)–C(3)	1.168(4)	1.166(4)	1.136(5)
C(4)–P(1)	1.821(4)	1.820(4)	1.832(5)
C(7)–P(2)	1.845(4)	1.823(4)	1.827(5)
C(10)–P(3)	1.826(4)	1.825(4)	1.822(5)
C(12)–P(1)	1.847(4)		
C(6)–P(2)	1.831(4)		
C(9)–P(3)	1.839(4)		
C(4)–C(5)	1.525(5)	1.511(5)	1.498(5)
C(4)–C(6)		1.312(5)	1.315(6)
C(7)–C(8)	1.515(5)	1.318(5)	1.508(6)
C(7)–C(9)		1.514(5)	1.310(7)
C(10)–C(11)	1.503(5)	1.312(5)	1.321(6)
C(10)–C(12)		1.506(5)	1.504(7)
C(5)–C(6)	1.520(5)		
C(8)–C(9)	1.530(5)		
C(11)–C(12)	1.487(5)		
C(1)–M–C(2)	90.2(2)	89.9(2)	89.7(2)
C(1)–M–C(3)	91.4(2)	90.5(2)	88.0(2)
C(2)–M–C(3)	92.7(2)	88.8(2)	91.0(2)
C(1)–M–P(1)	178.47(13)	178.40(12)	178.33(13)
C(1)–M–P(2)	88.12(14)	90.58(11)	92.51(13)
C(1)–M–P(3)	90.27(12)	89.81(13)	92.12(12)
C(2)–M–P(1)	90.75(13)	91.82(12)	91.28(13)
C(2)–M–P(2)	178.20(13)	178.06(11)	176.15(12)
C(2)–M–P(3)	87.88(13)	91.51(12)	87.20(12)
C(3)–M–P(1)	87.36(12)	91.05(12)	90.64(12)
C(3)–M–P(2)	88.03(14)	89.98(11)	92.24(12)
C(3)–M–P(3)	178.21(1)1	179.57(11)	178.16(12)
P(1)–M–P(2)	90.92(4)	89.69(5)	86.56(4)
P(1)–M–P(3)	90.95(5)	88.61(6)	89.26(4)
P(2)–M–P(3)	91.41(5)	89.74(5)	89.58(4)
O(1)–C(1)–M	179.2(3)	176.4(3)	176.1(4)
O(2)–C(2)–M	177.4(4)	174.5(3)	178.3(4)
O(3)–C(3)–M	179.4(4)	176.8(3)	176.7(4)
M–P(1)–C(4)	118.87(14)	132.83(14)	123.0(2)
M–P(2)–C(7)	119.76(14)	122.68(13)	123.8(2)
M–P(3)–C(10)	119.8(2)	123.21(14)	122.1(2)

reluctance of our vinylphosphine complexes **7–9** to form triphosphacyclononane complexes.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried and degassed by boiling under reflux over standard drying agents under a nitrogen atmosphere. Light petroleum had b.p. 40–60 °C. The compounds *fac*-[Cr(CO)$_3$(MeCN)$_3$],[8] *fac*-[Mo(CO)$_3$(MeCN)$_3$],[8] [Mo(CO)$_3$(C$_6$H$_3$Me$_3$-1,3,5)],[9] allylphosphine,[1] vinylphosphine and prop-2-enylphosphine[10] were prepared by literature methods. All other chemicals and 'Celite' were obtained from the Aldrich Chemical Company. The NMR spectra were recorded on a Bruker WM360 instrument operating at 360.13 (^{1}H) and 90.53 (^{13}C) MHz or a JEOL FX-90 instrument operating at 36.23 (^{31}P) MHz. All NMR spectra were recorded in CDCl$_3$ solution, with the ^{1}H and ^{13}C chemical shifts quoted in ppm relative to solvent and ^{31}P chemical shifts quoted in ppm relative to 85% external H$_3$PO$_4$ (δ 0); +δ values refer to chemical shifts downfield from the standards. The IR spectra were recorded in Nujol on a Nicolet 510 FT-IR spectrometer. Mass spectra and microanalyses were obtained from within this department.

CAUTION: The organophosphines and some of their complexes described are *highly malodorous* and likely *highly toxic*. Care should be exercised in their handling.

Preparations

Tris(primary phosphine) metal tricarbonyl complexes. The syntheses of complexes **3**, **7**, **8** and **9** were very similar and so a general method is described. To a frozen solution of phosphine [13.5 mmol, allylphosphine (**3**), prop-2-enylphosphine (**7** and **9**), vinylphosphine (**8**)] in toluene (50 cm^3) was added *fac*-[M(CO)$_3$(MeCN)$_3$] (3.3 mmol, M = Cr **3**, **7**, **8** or Mo **9**). The mixture was allowed to warm to room temperature and stirred for 8 h. Following removal of solvent and unreacted phosphine *in vacuo*, the product remained as a yellow oil in almost quantitative yields. Purification was by recrystallisation from light petroleum.

[Cr(CO)$_3${cyclo-(HPC$_3$H$_6$)$_3$}] 4. To a solution of complex **3** (1.07 g, 3.0 mol) in toluene (250 cm^3) was added a catalytic (*ca.* 1% w/w) amount of aibn and the mixture heated to 80–100 °C for 4 h. The mixture was allowed to cool to room temperature and filtered through a short (4 cm) Celite column to give a yellow solution. The solvent was removed *in vacuo* to give a viscous yellow oil which was recrystallised from toluene at − 20 °C to give the product as colourless crystals (yield = 0.87 g, 81%).

***cis*-[Cr(CO)$_4${H$_2$PC(Me)CH$_2$}$_2$] 10.** This complex was prepared (> 90% yield) in an identical manner to **7**, using *cis*-[Cr(CO)$_4$(MeCN)$_2$] as the starting material and giving an oil upon evaporation of the reaction solution *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and passed down a short (2.5 cm) Celite column. The solvent was removed *in vacuo* to give the crude product as a yellow oil which was further purified by recrystallisation from light petroleum.

[Cr(CO)$_4${H$_2$PCH(Me)CH$_2$P(H)C(Me)CH$_2$}] 11. This complex was prepared (85% yield) by an identical method to that for **4**, using **10** as the starting material.

[Cr(CO)$_3$(MeCN)(H$_2$PCH$_2$CHCH$_2$)$_2$] 12. To a frozen solution of allylphosphine (10.0 mmol) in toluene (50 cm^3) was added *fac*-[Cr(CO)$_3$(MeCN)$_3$] (5 mmol). The mixture was allowed to warm to room temperature and stirred for 4 h. Removal of solvent *in vacuo* generated the product as a yellow oil in almost quantitative yields. Purification was by recrystallisation from light petroleum.

[Cr(CO)$_3$(H$_2$PCH$_2$CHCH$_2$)$_2${H$_2$PC(Me)CH$_2$}] 15. To a frozen solution of prop-2-enylphosphine (5.0 mmol) in toluene (50 cm^3) was added a solution of complex **12** (1.63 g, 5 mmol) in toluene (50 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. The solvent was removed *in vacuo* to give the product as a yellow oil in almost quantitative yield. Purification was by recrystallisation from toluene–light petroleum.

Crystallography

Data collection and processing.[11] Data were collected on a Delft Instruments FAST TV area detector diffractometer, X-rays being produced by a rotating-anode generator using a molybdenum target [λ(Mo-Kα) = 0.710 69 Å], and being controlled by a Micro Vax 3200 computer, driven by MADNES[12] software. All data sets were recorded at 120 K using an Oxford Cryostream low-temperature cooling system. Data reduction was performed using the ABSMAD[13] program.

Structure determination and refinement. The structures were solved by heavy-atom methods (SHELXS 86[14]) and subjected

Table 4 Crystal data for compounds **4**, **7** and **9**

	4	**7**	**9**
Empirical formula	$C_{12}H_{21}CrO_3P_3$	$C_{12}H_{21}CrO_3P_3$	$C_{12}H_{21}MoO_3P_3$
M_r	358.2	358.2	402.14
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	12.521(7)	6.651(4)	6.7058(5)
b/Å	8.458(4)	15.292(7)	11.5523(12)
c/Å	15.002(7)	17.308(6)	12.4224(9)
α/°			74.968(13)
β/°	92.96(4)	93.92(7)	75.6(2)
γ/°			78.804(7)
U/Å^3	1586.6(14)	1756(2)	891.53(13)
Z	4	4	2
D_c/g cm^{-3}	1.500	1.355	1.498
F(000)	744	744	408
μ/mm^{-1}	1.023	0.924	1.005
Crystal size/mm	0.25 × 0.145 × 0.07	0.29 × 0.11 × 0.035	0.2 × 0.14 × 0.14
No. reflections collected	6433	4508	3824
θ Range/°	2.72–24.94	1.78–24.91	2.8–24.98
hkl Ranges	−14 to 12, −9 to 9, −17 to 14	−5 to 5, −13 to 16, −18 to 13	−7 to 5, −12 to 13, −14 to 14
No. unique data	2341	2284	2503
R_{int}	0.0517	0.0317	0.0482
$wR_2{}^a$ (all data)	0.0814	0.0786	0.0922
$R_1{}^b$ (all data)	0.0619	0.0489	0.0418
No. parameters	184	199	199
ρ_{max}, ρ_{min}/e Å^{-3}	0.45, −0.271	0.456, −0.298	1.117, −0.531
wR_2 ($F_o > 4\sigma F_o$)	0.074 (1571 data)	0.0766 (1715 data)	0.0902 (2193 data)
R_1 ($F_o > 4\sigma F_o$)	0.0352	0.0332	0.0367

[a] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$. [b] $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$.

to full-matrix least-squares refinement based on $F_o{}^2$ (SHELXL 93[15]). Non-hydrogen atoms were refined anisotropically with all hydrogens included in idealised positions, having isotropic thermal parameters riding on the value of their parent atoms. An absorption correction (DIFABS[16]) was applied to all three structures. The weighting scheme used was $w = 1/[\sigma^2(F_o{}^2)]$.

Diagrams were drawn with SNOOPI.[17] Sources of scattering factor data were from the literature.[16]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request for this material should quote the full literature citation and the reference number 186/17.

Acknowledgements

We thank the EPSRC for a research grant (to J. S. F.) and support for X-ray facilities. We would also like to thank 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 25th *October* 1995; *Paper* 5/07032E