Synthesis and Reactivity of the Silylated Triphosphites $[(R^1O)_2PO]_3SiR^2$ (R^1 = Me or Et; R^2 = Me, Ph or $CH{=}CH_2$). Crystal Structure of *fac*-$[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$†

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The silylated triphosphites $[(R^1O)_2PO]_3SiR^2$ (R^1 = Me or Et; R^2 = Me, Ph or $CH{=}CH_2$) have been prepared in high yield by the reactions between SiR^2Cl_3 and $(R^1O)_2P({=}O)H$ in the presence of NEt_3. The compound $[(MeO)_2PO]_3SiMe$ reacts with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) and $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ to afford $[Mo(CO)_4\{P,P\text{-}[P(OMe)_2O]_2SiMe[OP(OMe)_2]\}]$ and *fac*-$[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$ respectively. The crystal structure of *fac*-$[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$ has been determined in the space group $P2_1/c$ with a = 10.1129(8), b = 14.3197(12) and c = 14.9906(11) Å. The metal-co-ordinated triphosphites are significantly less electron-releasing than tertiary phosphine analogues and more closely resemble the η-arenes of $[Mo(CO)_3(\eta^6\text{-}C_6H_{6-n}Me_n)]$ in their electronic character.

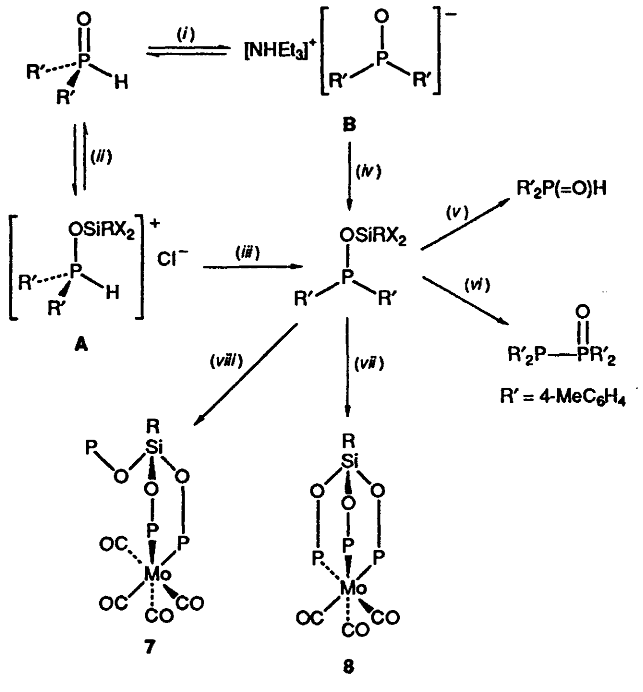
Tripodal polyphosphines such as $(Ph_2PCH_2)_3CMe$ (triphos)[1] have attracted much interest due to their ability to provide a stable yet flexible co-ordination environment for catalytically active transition metals.[2] However, the growing realisation that tertiary phosphites, particularly chelating phosphites, are excellent co-catalysts for many transition-metal-mediated catalytic processes has precipitated a resurgence of interest in metal phosphite chemistry.[3] We have been investigating the chemistry of silylated mono- and di-phosphite compounds[4] and now report the first examples of silylated triphosphites of the form $[(R^1O)_2PO]_3SiR^2$ which are formally analogous to triphos, and aspects of their co-ordination chemistry.

Results and Discussion

Synthesis and Characterisation of the Triphosphites $[(R^1O)_2PO]_3SiR^2$ (R^1 = Me *or* Et; R^2 = Me, Ph *or* $CH{=}CH_2$).—The triphosphites $[(R^1O)_2PO]_3SiR^2$ are readily synthesised by the reaction between SiR^2Cl_3 and $(R^1O)_2P({=}O)H$ in the presence of an excess of NEt_3 in pentane solvent, a procedure analogous to that used in the preparation of silylated mono- and di-phosphites [equation (1) (R^1 = Me or Et; R^2 = Me, Ph, or

$$(R^1O)_2P(O)H + \frac{1}{n}SiR^2_{4-n}Cl_n \xrightarrow{NEt_3} \frac{1}{n}[(R^1O)_2PO]_nSiR^2_{4-n} + NHEt_3Cl \quad (1)$$

$CH{=}CH_2$; n = 3)][4b] Although the stoichiometry requires only 3 equivalents of the secondary phosphite reagent, we have found that the use of 4 equivalents allows the reaction to proceed at a more reasonable rate. Both tetrahydrofuran (thf) and toluene can be used in place of pentane in the above syntheses although with thf the reactions are significantly slower, presumably due to solvation of the chlorosilane reagent which thus impedes access of the secondary phosphites to the silicon atom; similar solvent effects were observed in the syntheses of the diphosphites $[(RO)_2PO]_2SiR_2$.[5] The products **1**–**6** are isolated as clear, mobile liquids in high yields (see Table 1) and are sufficiently pure for synthetic purposes. When the synthesis of **2** is terminated early, $^{31}P\text{-}\{^1H\}$ NMR spectroscopy reveals a resonance at δ 124.8 which we believe to be due to an intermediate species {possibly $[(EtO)_2PO]_2SiMeCl$} since upon further treatment with $(EtO)_2P({=}O)H$ and NEt_3 this species is completely converted into **2**. We presume the mechanism of formation of the triphosphites is similar to that for diphosphites,[5] where the major intermediates are of the type **A** rather than **B** (Scheme 1). Interestingly, the reaction between $SiMeCl_3$ and $(p\text{-}MeC_6H_4)_2P({=}O)H$ (3 equivalents) in the presence of an excess of NEt_3 in toluene solvent at 80 °C (reaction is extremely sluggish at ambient temperature) leads to $(p\text{-}MeC_6H_4)_2PP({=}O)(C_6H_4Me\text{-}p)_2$ as the major product according to $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. It is possible that



Scheme 1 X = Cl or OPR'_2; R′ = MeO or EtO; R = Me, Ph or $CH{=}CH_2$. (*i*) NEt_3; (*ii*) $SiRClX_2$; (*iii*) NEt_3, $-NHEt_3Cl$; (*iv*) $SiRClX_2$, $-NHEt_3Cl$; (*v*) water; (*vi*) heat, 80 °C; (*vii*) $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$, pentane; (*viii*) $[Mo(CO)_4(nbd)]$, pentane

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Spectroscopic data for compounds **1**–**10**

Compound	Yield (%)	IR[a] (cm^{-1})	NMR[b]
1 $[(MeO)_2PO]_3SiMe$	85	1275s δ(SiMe) 960s (br) ν(POSi)	^{1}H: 3.43 [m, 18 H, J(P–H) 10, CH_3O], 0.34 (s, 3 H, CH_3Si) ^{31}P-{^{1}H}: 125.2 (s) ^{13}C-{^{1}H}: 48.03 [m, J(P-C) 9, CH_3O], −2.69 [q, ^3J(P–C) 1, CH_3Si]
2 $[(EtO)_2PO]_3SiMe$	90	1270s δ(SiMe) 975s (br) ν(POSi)	^{1}H: 3.79 [m, 12 H, ^3J(H–H) 7, $CH_3C\mathit{H}_2O$], 1.16 [t, 18 H, ^3J(H–H) 7, $C\mathit{H}_3CH_2O$], 0.30 (s, 3 H, CH_3Si) ^{31}P-{^{1}H}: 123.9(s) ^{13}C-{^{1}H}: 57.03 [m, J(P–C) 10, $CH_3\mathit{C}H_2O$], 16.60 [m, J(P–C) 5, $\mathit{C}H_3$ CH_2O], −2.41 [q, ^3J(P–C) 1, CH_3Si]
3 $[(MeO)_2PO]_3SiPh$	99	1600w ν(C=C) 920s (br) ν(POSi)	^{1}H: 7.7–7.3 (m, 5 H, Ph), 3.49 [m, 18 H, J(P–H) 10, CH_3O] ^{31}P-{^{1}H}: 125.0 (s) ^{13}C-{^{1}H}: 134.08 (s, C_o of Ph), 130.87 (s, C_p of Ph), 129.80 (s, C_{ipso} of Ph), 127.94 (s, C_m of Ph), 48.27 [m, J(P–C) 9, CH_3O]
4 $[(EtO)_2PO]_3SiPh$	99	1592w ν(C=C) 918s (br) ν(POSi)	^{1}H: 7.7–7.3 (m, 5 H, Ph), 3.85 [m, 12 H, ^3J(H–H) 7, J(P–H) 7, $CH_3C\mathit{H}_2O$], 1.19 [t, 18 H, ^3J(H–H) 7, $C\mathit{H}_3CH_2O$] ^{31}P-{^{1}H}: 123.8 (s) ^{13}C-{^{1}H}: 134.24 (s, C_o of Ph), 130.74 (s, C_p of Ph), 130.51 (s, C_{ipso} of Ph), 127.73 (s, C_m of Ph), 57.36 [m, J(P–C) 10, $CH_3\mathit{C}H_2O$], 16.71 (s, $\mathit{C}H_3CH_2O$)
5 $[(MeO)_2PO]_3Si(CH{=}CH_2)$	82	1600w ν(C=C) 955s (br) ν(POSi)	^{1}H: 5.8–5.5 [m, 3 H, J(H–H) 20.5, 14.4, 3.9, $C\mathit{H}{=}C\mathit{H}_2$], 3.12 [m, 18 H, J(P–H) 10, CH_3O] ^{31}P-{^{1}H}: 124.9 (s) ^{13}C-{^{1}H}: 137.57 (s, $CH{=}\mathit{C}H_2$),[c] 128.83 (s, $\mathit{C}H{=}CH_2$),[c] 48.10 [m, J(P–C) 9, CH_3O]
6 $[(EtO)_2PO]_3Si(CH{=}CH_2)$	91	1598w ν(C=C) 920s (br) ν(POSi)	^{1}H: 6.2–5.9 [m, 3 H, J(H–H) 20.7, 14.0, 4.1, $C\mathit{H}{=}C\mathit{H}_2$], 3.85 [m, 12 H, ^3J(H–H) 7, J(P–H) 7, $CH_3C\mathit{H}_2O$], 1.21 [t, 18 H, ^3J(H–H) 7, $C\mathit{H}_3CH_3O$] ^{31}P-{^{1}H}: 123.8 (s) ^{13}C-{^{1}H}: 137.07 (s, $CH{=}\mathit{C}H_2$),[c] 129.51 (s, $\mathit{C}H{=}CH_2$),[c] 57.25 [m, J(P–C) 9, $CH_3\mathit{C}H_2O$], 16.70 (s, $\mathit{C}H_3CH_2O$)
7 $[Mo(CO)_4\{$*P*,*P*-$[P(OMe)_2O]_2SiMe[OP(OMe)_2]\}]$		2043s (sp) ν(CO) 1950s (sh) ν(CO) 1930s (br) ν(CO)	^{31}P-{^{1}H}: 149.8 (s, 2 P), 125.5 (s, 1 P)
8 $[Mo(CO)_3\{$*P*,*P*,*P*-$[P(OMe)_2O]_3SiMe\}]$	70	1980s (sp) ν(CO) 1890s (br) ν(CO)	^{1}H: 3.63 [m, 18 H, J(P–H) 12, CH_3O], 0.42 (s, 3 H, CH_3Si) ^{31}P-{^{1}H}: 153.5 (s) ^{13}C-{^{1}H}: 215.07 (m, CO), 50.68 (s, CH_3O), −5.20 (s, CH_3Si)
9 $[Mo(CO)_3\{$*P*,*P*,*P*-$[P(OMe)_2O]_3SiPh\}]$		1980s (sp) ν(CO) 1890s (br) ν(CO)	^{31}P-{^{1}H}: 153.7 (s)
10 $[Mo(CO)_3\{$*P*,*P*,*P*-$[P(OMe)_2O]_3Si(CH{=}CH_2)\}]$		1980s (sp) ν(CO) 1890s (br) ν(CO)	^{31}P-{^{1}H}: 153.5 (s)

[a] w = Weak, s = strong, sp = sharp, sh = shoulder, br = broad. Data collected as thin films (**1**–**6**) or as solutions in CH_2Cl_2 (**7**–**10**). [b] Given as: chemical shift (δ) [multiplicity, relative intensity, *J* in Hz, assignment]. All data collected at r.t. in $CDCl_3$. [c] Assigned by attached proton test.

this diphosphine monoxide compound is formed from the decomposition of intermediate $[(p\text{-}MeC_6H_4)_2PO]_3SiMe$, which is presumably thermally unstable under the experimental conditions.

The spectroscopic data for compounds **1**–**6** are, as expected, similar to those for the mono- and di-phosphites $[(R^1O)_2PO]_{4-n}SiR^2{}_n$ ($n = 3$ and 2 respectively) reported previously.[5] In particular, the high-frequency ^{31}P NMR chemical shifts (Table 1) are in the region typical of tertiary phosphites[6] and the resonances for the derivatives with R^1 = Et are consistently lower in frequency than those for R^1 = Me, as found for the diphosphites.[5] The presence of three equivalent phosphite groups attached to silicon is confirmed by the observation of quartet signals [^3J(P–C) 1 Hz] for the carbon atoms of the silicon-bonded methyl groups in the ^{13}C-{^{1}H} NMR spectra of both **1** and **2**, but coupling to the methyl hydrogens was too small to be resolved in the ^{1}H NMR spectra. Coupling between phosphorus and the *ipso*-carbons of **3** and **4** or the methine carbons of **5** and **6** was not resolved. Infrared spectroscopy located the ν(POSi) vibrations as strong, broad absorptions in the range 918–975 cm^{-1} and no bands assignable to ν(P–O) vibrations were observed.

All the triphosphites hydrolyse to the corresponding secondary phosphites upon exposure to moist air over several hours at room temperature, the methysilyl derivatives being more sensitive than the vinyl and phenyl analogues as found also in the diphosphite series.[5]

Co-ordination of Silylated Triphosphites to Transition Metals.—The triphosphite **1** reacted readily with $[Mo(CO)_4(nbd)]$ {nbd = norbornadiene(η^4-bicyclo[2.2.1]hepta-2,5-diene)} at −78 °C to afford a single species which we believe to be $[Mo(CO)_4\{$*P*,*P*-$[P(OMe)_2O]_2SiMe[OP(OMe)_2]\}]$ **7** containing two, metal-co-ordinated phosphite moieties and one pendant phosphite group (Scheme 1). This is supported by ^{31}P-{^{1}H} NMR spectroscopy which shows two singlet resonances in a 2:1 ratio at δ 149.8 and 125.5 due to the co-ordinated and unco-ordinated phosphite phosphorus atoms respectively. Infrared spectroscopy is consistent with a tetracarbonyl structure (Table 1). Unfortunately, we were unable to isolate this compound as a solid. Heating a toluene solution of **7** to 85 °C for 20 h afforded a number of products as evidenced by the observation of several new ^{31}P NMR resonances in the range δ 154–150: we presume these to be mainly polynuclear

Table 2 Selected IR and NMR data for several $Mo(CO)_3L_3$ and $Mo(CO)_3(\eta\text{-arene})$ compounds

Compound	$\nu(CO)/cm^{-1}$	$\delta(CO)^a$
$[Mo(CO)_3(C_6H_6)]$	1985, 1912^b	
8 $[Mo(CO)_3\{[P(OMe)_2O]_3SiMe\}]$	1980, 1890^c	215.07
9 $[Mo(CO)_3\{P(OMe)_2O]_3SiPh\}]$	1980, 1890^c	214.63
10 $[Mo(CO)_3\{[P(OMe)_2O]_3Si(CH{=}CH_2)\}]$	1980, 1890^c	214.62
$[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$	1981, 1910, 1877	220.6^d
$[Mo(CO)_3(C_6H_4Me_2\text{-}1,4)]$	1975, 1901^b	
$[Mo(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$	1972, 1900^b	223.7^d
$[Mo(CO)_3(C_6H_2Me_4)]$	1964, 1891^b	224.4^d
$[Mo(CO)_3(C_6Me_6)]$	1958, 1882^b	225.9^d
$[Mo(CO)_3\{(PPh_2CH_2CH_2)_3P\}]$	1940, 1850^e	
$[Mo(CO)_3\{(PPh_2CH_2)_3CMe\}]$	1930, 1834^f	

[a] In $CDCl_3$ at room temperature unless stated otherwise. [b] In cyclohexane.[7] [c] In dichloromethane. [d] Ref. 8. [e] In dichloromethane.[9] [f] In 1,2-dichloroethane.[10]

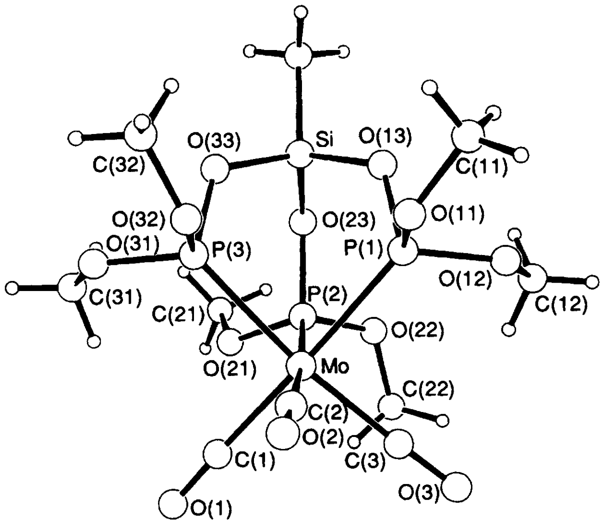

Fig. 1 An ORTEP drawing of the molecular structure of compound **8**

phosphite-bridged species but a resonance at δ 153.1 may be due to the tridentate complex $[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$ **8** which we have independently synthesised and characterised (see below).

Compound **8** was isolated in *ca.* 70% yield *via* the dropwise addition of a pentane solution of $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ to $[(MeO)_2PO]_3SiMe$ at −78 °C. When less than 2 equivalents of triphosphite were used or the order of addition of the reagents was reversed the yield of **8** decreased and a second product precipitated which displayed a single, broad resonance in the ^{31}P NMR spectrum at δ 151.3. We presume that this complex is a polynuclear species in which the triphosphite acts as a bridging ligand. Complex **8** displays two ν(CO) vibrations (A_1 + E) as expected for a tricarbonyl with C_{3v} point symmetry.[7] The ν(CO) vibrational frequencies for **8** suggest that the $[(MeO)_2PO]_3SiMe$ ligand is significantly less electron-releasing than the triphosphine ligands in the formally isoelectronic complexes $[Mo(CO)_3\{P,P,P\text{-}(PPh_2CH_2)_3CMe\}]$ and $[Mo(CO)_3\{P,P,P\text{-}(PPh_2CH_2CH_2)_3P\}]$ and more closely resembles the electronic properties of arene ligands in $[Mo(CO)_3(\eta^6\text{-arene})]$ systems (Table 2). This observation receives support from $^{13}C\text{-}\{^1H\}$ NMR spectroscopy: the carbon monoxide carbon resonance is sensitive to the electron-releasing nature of the ancillary ligands, shifting to higher frequencies as these ligands become more electron-releasing.[11] Thus it can be seen from Table 2 that the triphosphite $[(MeO)_2PO]_3SiMe$ supports a relatively electrophilic metal centre in complex **8**.

Table 3 Atom coordinates (× 10^4) for compound **8** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Mo	949.9(2)	1 672.42(14)	2 345.63(13)
Si	−2 607.0(7)	1 930.0(5)	2 577.8(5)
P(1)	−199.8(6)	2 545.4(5)	3 483.9(4)
P(2)	−661.9(6)	2 265.7(5)	1 247.4(4)
P(3)	−647.7(6)	449.1(5)	2 697.3(4)
O(11)	−15(2)	2 1633(2)	4 472.5(12)
C(11)	−705(5)	2 5544(4)	5 214(2)
O(12)	68(2)	3 628.2(15)	3 677(2)
C(12)	−143(4)	4 331(2)	3 008(3)
O(13)	−1 807(2)	2 549.1(13)	3 337.8(12)
O(21)	−802(2)	1 676.5(13)	350.5(12)
C(21)	−1 855(4)	1 848(3)	−304(2)
O(22)	−656(2)	3 327.6(13)	897.7(14)
C(22)	447(4)	3 652(3)	407(2)
O(23)	−2 164(2)	2 293.2(14)	1 591.3(12)
O(31)	−857(2)	−502.3(13)	2 154.4(13)
C(31)	−1 139(4)	−490(2)	1 210(2)
O(32)	−460(2)	45.0(14)	3 674.7(12)
C(32)	−1 448(4)	−492(3)	4 115(3)
O(33)	−2 166(2)	832.3(12)	2 687.2(13)
Me	−4 387(3)	2 055(2)	2 688(2)
C(1)	1 837(3)	940(2)	1 391(2)
O(1)	2 364(3)	530(2)	851(2)
C(2)	2 186(3)	1 094(2)	3 262(2)
O(2)	2 905(2)	753(2)	3 767(2)
C(3)	2 190(3)	2 752(2)	2 212(2)
O(3)	2 894(2)	3 375(2)	2 175(2)

Table 4 Bond lengths (Å) for compound **8** with e.s.d.s in parentheses

Mo–C(1)	2.006(3)	P(2)–O(22)	1.609(2)
Mo–C(2)	2.010(3)	P(2)–O(23)	1.618(2)
Mo–C(3)	2.005(3)	P(3)–O(31)	1.598(2)
Mo–P(1)	2.4367(8)	P(3)–O(32)	1.582(2)
Mo–P(2)	2.4369(7)	P(3)–O(33)	1.630(2)
Mo–P(3)	2.4504(8)	O(11)–C(11)	1.443(4)
Si–O(13)	1.639(2)	O(21)–C(21)	1.449(3)
Si–O(23)	1.642(2)	O(31)–C(31)	1.436(4)
Si–O(33)	1.641(2)	O(12)–C(12)	1.433(4)
Si–Me	1.821(3)	O(22)–C(22)	1.431(4)
P(1)–O(11)	1.586(2)	O(32)–C(32)	1.436(4)
P(1)–O(12)	1.599(2)	C(1)–O(1)	1.144(3)
P(1)–O(13)	1.634(2)	C(2)–O(2)	1.143(3)
P(2)–O(21)	1.590(2)	C(3)–O(3)	1.144(3)

Both $[(MeO)_2PO]_3SiPh$ **3** and $[(MeO)_2PO]_3Si(CH{=}CH_2)$ **5** form analogous complexes with molybdenum but the yields were significantly lower due to difficulties in separating the products from the excess of triphosphite. Again, with a stoichiometric quantity of triphosphite, polynuclear species were produced which also hindered purification. The complexes have thus been characterised spectroscopically (**9** and **10** in Table 1). As found for **8**, IR and NMR spectroscopies show **9** and **10** to possess relatively electrophilic metal centres (Table 2) and as with the diphosphites[5] the more electron-releasing substituents on silicon appear to result in a slightly more electron-rich metal centre.

The Crystal Structure of *fac*-$[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$ **8**.—Crystals suitable for X-ray diffraction study were grown from a saturated pentane solution cooled to 4 °C. The crystal consists of discrete, distorted-octahedral molecules in which the triphosphite ligand co-ordinates to molybdenum through all three of the phosphorus atoms (Fig. 1). Atomic coordinates are reproduced in Table 3, selected bond distances and angles in Tables 4 and 5 respectively.

The Mo–P distances range from 2.4367(8) to 2.4504(8) Å,

Table 5 Bond angles (°) for compound **8** with e.s.d.s in parentheses

C(1)–Mo–C(2)	89.44(11)	C(3)–Mo–C(1)	92.21(11)	C(3)–Mo–C(2)	90.41(11)
P(2)–Mo–P(1)	88.34(2)	P(1)–Mo–P(3)	83.44(2)	P(2)–Mo–P(3)	87.83(2)
C(1)–Mo–P(1)	178.05(8)	C(2)–Mo–P(1)	91.88(8)	C(3)–Mo–P(1)	89.21(8)
C(1)–Mo–P(2)	90.23(8)	C(2)–Mo–P(2)	175.45(8)	C(3)–Mo–P(2)	94.14(8)
C(1)–Mo–P(3)	95.19(8)	C(2)–Mo–P(3)	87.68(8)	C(3)–Mo–P(3)	172.34(8)
O(33)–Si–O(13)	108.73(10)	O(33)–Si–O(23)	108.25(10)	O(23)–Si–O(13)	108.23(10)
O(13)–Si–Me	110.72(12)	O(23)–Si–Me	110.24(12)	O(33)–Si–Me	110.59(13)
O(11)–P(1)–O(12)	98.69(12)	O(21)–P(2)–O(22)	103.13(11)	O(31)–P(3)–O(32)	99.83(11)
O(11)–P(1)–O(13)	102.54(11)	O(21)–P(2)–O(23)	102.72(11)	O(31)–P(3)–O(33)	99.86(10)
O(12)–P(1)–O(13)	100.59(11)	O(22)–P(2)–O(23)	95.33(11)	O(32)–P(3)–O(33)	102.72(11)
O(11)–P(1)–Mo	115.53(8)	O(21)–P(2)–Mo	115.35(7)	O(31)–P(3)–Mo	125.34(8)
O(12)–P(1)–Mo	122.85(9)	O(22)–P(2)–Mo	122.77(8)	O(32)–P(3)–Mo	113.46(8)
O(13)–P(1)–Mo	113.59(7)	O(23)–P(2)–Mo	114.16(7)	O(33)–P(3)–Mo	112.57(7)
P(1)–O(13)–Si	124.14(11)	P(2)–O(23)–Si	124.16(11)	P(3)–O(33)–Si	125.23(11)
C(11)–O(11)–P(1)	122.6(2)	C(21)–O(21)–P(2)	121.9(2)	C(31)–O(31)–P(3)	120.8(2)
C(12)–O(12)–P(1)	122.3(2)	C(22)–O(22)–P(2)	119.0(2)	C(32)–O(32)–P(3)	123.7(2)
O(1)–C(1)–Mo	178.7(3)	O(2)–C(2)–Mo	178.3(3)	O(3)–C(3)–Mo	177.0(3)

within the range found for molybdenum complexes containing diphosphite ligands, $[P(OMe)_2O]_2SiPhR$ (R = Ph or Me).[5] The Mo–C distances extend from 2.005(3) to 2.010(3) Å and also compare favourably with analogous distances in diphosphite complexes.[5]

In the diphosphite complexes $[Mo(CO)_4\{[P(OMe)_2O]_2SiPhR\}]$ (R = Ph or Me), the chelate rings adopt twist-boat conformations presumably in part due to the flexibility of the phosphite ligands. Much of this flexibility is lost in **8** and the six-membered chelate rings are constrained to boat conformations. Thus, the silicon and molybdenum atoms are disposed on the same side of the best-fit planes connecting the atoms (*i*) P(3)O(33)P(2)O(23), (*ii*) P(2)O(23)P(1)O(13) and (*iii*) P(1)O(13)P(3)O(33), by (*i*) 0.705(2) (Si), 1.084(2) (Mo), (*ii*) 0.721(2) (Si), 1.034(2) (Mo) and (*iii*) 0.645(2) (Si), 1.308(1) (Mo) Å respectively, thus demonstrating the greater degree of boat character in the triphosphite ligand complexes over the diphosphite analogues.[5] The other internal parameters of the triphosphite ligand are not significantly different to those in the diphosphite systems.

The combination of IR and NMR spectroscopies (see above) suggests the molybdenum atom to possess a similar electronic environment to that found in $Mo(CO)_3(\eta\text{-arene})$ systems, and from Table 2 the relative electron-releasing properties fall in the order $(C_6Me_6) > (C_6H_3Me_3\text{-}1,3,5) > [(MeO)_2PO]_3SiMe$. Indeed, crystallographic data support this order: the average Mo–CO and [C–O] distances for $[Mo(CO)_3(C_6Me_6)]$, $[Mo(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$ and **8** are 1.943(2) [1.153(6)], 1.964(5) [1.153(6)] and 2.007(2) [1.144(1)] Å respectively showing that the more electron-releasing ligands have shorter Mo–C and longer C–O distances.[12]

Experimental

All syntheses and manipulations were performed under an atmosphere of dry dinitrogen using Schlenk and cannula techniques. Solvents were pre-dried over either sodium wire, calcium chloride or 4Å molecular sieves before reflux and subsequent distillation, under dinitrogen, from a suitable drying agent (given in parentheses); thf and pentane (sodium diphenylketyl), toluene (sodium metal) and dichloromethane (calcium hydride). Deuteriated solvents were dried by passage down a column of basic alumina (Brockmann Grade I). All solvents were deoxygenated before use. Elemental analyses were performed by the Microanalytical Laboratory of this department. Infrared spectra were recorded between KBr windows on a Perkin Elmer 257 grating spectrophotometer, all NMR spectra on JEOL FX90Q, FX100 and Bruker AM 400 instruments and mass spectra in the electron-impact (EI) mode on a VG Autospec instrument with 8 kV acceleration. The compounds $(R^1O)_2P({=}O)H$ (R^1 = Me or Et), SiR^2Cl_3 (R^2 = Me, Ph or $CH{=}CH_2$) and NEt_3 were purchased from commercial sources and were distilled prior to use. Triethylamine was further purified by passage down a short column of basic alumina (Brockmann Grade I). The compounds $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ and $[Mo(CO)_4(nbd)]$ were prepared and purified using published procedures.[13,14]

General Syntheses of $[(R^1O)_2PO]_3SiR^2$ (R^1 = Me *or* Et; R^2 = Me, Ph *or* $CH{=}CH_2$).—The compound SiR^2Cl_3 (1.81 mmol) was added dropwise at room temperature to a stirred mixture of $(R^1O)_2P({=}O)H$ (7.26 mmol) and NEt_3 (9.11 mmol) in pentane solvent (30 cm^3). The initially clear solutions became cloudy within seconds of adding the silicon reagent due to the precipitation of $NHEt_3Cl$. After stirring for 72 h (96 h for R^1 = Et), the mixture was filtered, the residue washed with pentane (10 cm^3) and all volatiles removed under reduced pressure to leave a colourless liquid in which was suspended a small amount of $NHEt_3Cl$. Subsequent extraction with pentane (15 cm^3), refiltration and removal of the volatiles *in vacuo* afforded the products as clear, mobile liquids. Yields are given in Table 1.

Attempted Synthesis of $[(p\text{-}MeC_6H_4)_2PO]_3SiMe$.—A mixture of $(p\text{-}MeC_6H_4)_2P({=}O)H$ (0.84 g, 3.65 mmol), $SiMeCl_3$ (0.18 g, 1.22 mmol) and NEt_3 (0.51 g, 5.0 mmol) in toluene solvent was stirred at ambient temperature for 24 h and then heated at 90 °C for 40 h. Subsequent work-up as described above afforded an oily, white, toluene-soluble solid which was shown to be a mixture, the major component of which was assigned as $(p\text{-}MeC_6H_4)_2(O{=})PP(C_6H_4Me\text{-}p)_2$ on the basis of the similarity of its $^{31}P\text{-}\{^1H\}$ NMR spectral data to that of $Ph_2(O{=})PPPh_2$. $\delta_P(CDCl_3)$: δ 36.4 [d, ^1J(P–P) 224 Hz, $Ph_2(O{=})P$-], −24.8 [d, ^1J(P–P) 224 Hz, -PPh_2].

Reaction between $[(MeO)_2PO]_3SiMe$ *and* $[Mo(CO)_4(nbd)]$.—A solution of $[Mo(CO)_4(nbd)]$ (0.1 g, 0.34 mmol) in pentane (10 cm^3) was added dropwise to $[(MeO)_2PO]_3SiMe$ (0.24 g, 0.68 mmol) in pentane (10 cm^3) at −78 °C. Upon warming to room temperature (r.t.) the initial yellow colour was rapidly discharged. After stirring at r.t. for 2 h, the solution was filtered and the volatiles removed to afford a yellow-brown oil which was examined by IR and NMR spectroscopy (Table 1).

Synthesis of *fac*-$[Mo(CO)_3\{P,P,P\text{-}[P(OMe)_2O]_3SiMe\}]$ **8**.—The compound $[Mo(CO)_3(\eta^6\text{-}C_7H_8)]$ (0.2 g, 0.74 mmol) in pentane (20 cm^3) was added dropwise to a pentane solution of

$[(MeO)_2PO]_3SiMe$ (0.54 g, 1.47 mmol in 10 cm^3 solvent) at −78 °C and was allowed to warm to room temperature slowly. The initial orange-red colour of the solution was slowly discharged over a period of 4 h after which time the reaction mixture was filtered and the filtrate concentrated and cooled to −35 °C whereupon the product crystallised as colourless crystals (0.28 g, 70%) (Found: C, 21.65; H, 3.90. $C_{10}H_{21}MoO_{12}P_3Si$ requires C, 21.85; H, 3.85%). *m/z* 555–546, M^+; 526–515, $[M - OMe]^+$; 499–487, $[M - 2CO]^+$; 471–459, $[M - 3CO]^+$.

Complexes **9** and **10** were synthesised in an analogous manner but were not isolated as solids due to the difficulties of removing the excess of triphosphite.

Single-crystal X-Ray Diffraction Analysis of Compound **8**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using an on-line profile-fitting method[15] and graphite-monochromated Mo-Kα X-radiation (λ = 0.710 69 Å). The data set was corrected for absorption using azimuthal ψ scans.

The positions of the heavy atoms (Mo, P and Si) were determined from a Patterson synthesis using the program SHELXS 86.[16] The remaining non-hydrogen atoms were located by difference techniques and the structure was refined by full-matrix least squares (based on F^2) using the SHELXL 92 program system.[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions (C–H 97 pm) and were assigned fixed, isotropic thermal parameters ($1.5U_{equiv}$ of the parent carbon atom). The weighting scheme $w = [\sigma^2(F_o) + (0.0377P)^2 + 1.0382P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used. An ORTEP[18] diagram of the structure is shown in Fig. 1.

Crystal data. $C_{10}H_{21}MoO_{12}P_3Si$, $M = 550.17$, monoclinic, space group $P2_1/c$, $a = 10.1129(8)$, $b = 14.3197(12)$, $c = 14.9906(11)$ Å, $\beta = 91.608(6)°$, $U = 2170.0(3)$ $Å^3$, $Z = 4$, $D_c = 1.684$ Mg m^{-3}, $\mu = 0.932$ mm^{-1}, $F(000) = 1112$.

Data collection. $4.0 < 2\theta < 50.0°$. 7976 Data (2 equivalents) were collected, 3816 unique ($R_{int} = 0.0188$, $R_{sig} = 0.0225$) all of which were used in refinement. 3530 Data with $F > 4.0\sigma(F)$ were used to calculate R $[=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ which is listed below for comparison with refinements based on F, $T = 290$ K.

Structure refinement. Number of parameters = 251, $R' = 0.0673$ ($R = 0.0250$).

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

Acknowledgements

We thank the SERC and BP Chemicals Ltd. (CASE award to N. G.) for supporting this work and Professor G. M. Sheldrick of the University of Göttingen for permission to use crystallographic software (SHELXL 92) prior to general release.

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Received 28*th October* 1992; *Paper* 2/05757C