Pendant Functionalised Triphosphamacrocycles

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The selective functionalisation of a single phosphorus atom in the parent $[Mo(CO)_3(12aneP_3H_3)]$, where $12aneP_3H_3$ is 1,5,9-triphosphacyclododecane, has been achieved by deprotonation and subsequent reaction with an ether containing an alkyl halide group. Yields of the monosubstituted products are very sensitive to the reaction conditions, which must be carefully controlled in order to achieve reasonable selectivity. In addition, trisubstitution of $[M(CO)_3(12aneP_3H_3)]$ with carbon chains containing pendant donors such as ethers, thioethers, amines and phosphanes has been achieved by both deprotonation/addition ($M = Mo^0$) and hydrophosphination ($M = Cr^0$) protocols. The new compounds have been characterised by spectroscopic and analytical techniques, including X-ray crystallography, and a selection of the P_3 macrocycles released from their templates by oxidation and base digestion.

Introduction

We have previously reported the template synthesis and P-atom functionalisation of 1,5,9-triphosphacyclododecane to give a number of tritertiary derivatives ($12aneP_3R_3$), which can be liberated from their Mo^0 and Cr^0 templates by oxidation of the metal centre followed by base digestion.[1] Unlike the only other triphosphorus macrocycle known as the free ligand,[2] our synthetic procedure is stereospecific (for the *syn-syn* isomer) producing ligands with identical bridging backbone functions and hence achiral phosphorus atoms. A feature of these ligands is that they are ideally suited to coordinating a trigonal face in metal coordination polyhedra; the phosphorus atoms are clearly restricted to a mutually all *cis* arrangement which in turn locates the remaining active sites at the metal to also be mutually *cis* (at least for coordination numbers of six or less). Although a number of complexes which approximate to octahedral and tetrahedral geometries are now known for the $12aneP_3R_3$ ligand, there are others which show considerable distortions from idealised geometries as noted for the four coordinate Ni^0 [3] and five-coordinate Co^{II} systems.[4]

The enhanced stability of the metal-ligand unit formed by these macrocycles is in itself of value in the stabilisation of lower coordinate transients formed during reactions (e.g. resulting from a reductive elimination). Such reduced species might not prefer facially capping ligands and it is of interest in this context to study ligand systems that may be able to further stabilise transition states or intermediates by temporary coordination of an intrinsically labile donor, i.e. hemilabile ligands. We have previously studied acyclic phosphanes containing pendant ethers[5] and are interested to extend this approach to strongly bound ligands with a macrocyclic core, such that a section of the ligand will be bound tightly with reduced lability whilst an intrinsically labile function may provide freedom for reaction at the remaining sites and transient stabilisation. Within this theme, it is desirable to be able to selectively synthesise ligands with a chosen number of pendant functions; in this paper, we present the selective stereospecific synthesis of functionalised 1,5,9-triphosphacyclododecanes having one or three pendant ether functions, as well as related trisubstituted pendant thioether, amine or phosphane macrocycles.

Results and Discussion

Following our previous work[6] on the synthesis of tritertiary 1,5,9-triphosphacyclododecane ligands, the introduction of one ether function may be performed by the deprotonation of one secondary phosphane by a strong base (*n*BuLi), followed by the reaction of the resultant coordinated phosphide with the corresponding ether-functionalised alkyl halides (Scheme 1). The temperature at which the deprotonation is performed is critical for success in the synthesis of the mono-substituted derivative **3a**. Thus, when the reaction of the coordinated phosphide (generated in situ) with 2-bromoethyl methyl ether is performed at −78 °C the desired $[Mo(CO)_3\{12aneP_3H_2(CH_2CH_2OCH_3)\}]$ (**3a**) is formed in low yield and is difficult to isolate pure from the reaction mixture. However, when the reaction is performed at −30 °C, **3a** can be obtained in good yield (70%). Monitoring (by ^{31}P NMR spectroscopy) of the reaction mixture after addition of the alkyl halide shows resonances assignable to mono-, di- and trisubstituted macrocycles, with the undesired di- and tri- by-products being far more prevalent in the mixture at −78 °C than at −30 °C.

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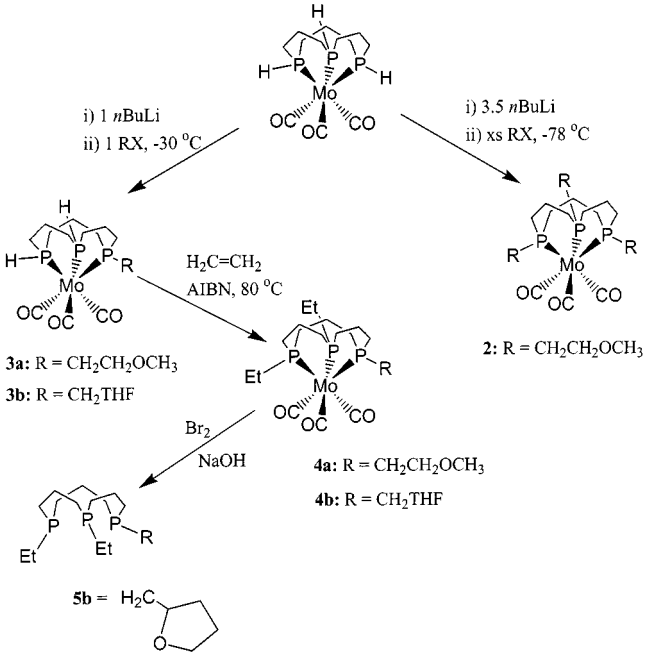
This may reflect incomplete solubility of the lithiated complex at the lower temperature. It should be noted that these yields (70%) are only obtainable with very careful control of the stoichiometry and the reaction temperature. Indeed, reproducibility is a problem and in a series of repeat reactions, yields of less than 20% were typical. Hydrophosphination of the monoether **3a** with ethene in the presence of AIBN gave the diethyl analogue **4a**. The related reaction with tetrahydrofurfuryl chloride was less successful, and although complex **3b** could be characterised by ^{31}P NMR spectroscopy and mass spectrometry, it proved impossible to isolate the complex in a pure form — the compound was invariably contaminated with unsubstituted starting material and/or further substitution (bi- and tri-) products — and it was convenient to prepare the crude diethyl derivative (**4b**) and liberate the free macrocycle **5b**, which could then be isolated pure.



Scheme 1

The $^{31}P\{^1H\}$ NMR spectrum of **3a** appears as a first order AX_2 pattern with the two equivalent secondary phosphorus centres resonating at $\delta_P = -32$ (t, $J = 32.0$ Hz) and the unique tertiary phosphorus at $\delta_P = 3$ (d, $J = 32.0$ Hz). When the two secondary phosphanes are converted into tertiary centres on ethylation to give **4a**, the $^{31}P\{^1H\}$ NMR spectrum approximates to an AM_2 pattern with signals at $\delta_P = 5.9$ (d, $J = 31.0$ Hz, $2 \times R_2PEt$) and 4.3 (t, $J = 31.0$ Hz, $R_2PCH_2CH_2OCH_3$). A similar AM_2 pattern is observed for the tetrahydrofurfuryl macrocycle complex **4b** with $\delta_P = 5.0$ (d, $J = 30.0$ Hz, $2 \times R_2PEt$) and 4.5 (t, $J = 30.0$ Hz, R_2PCH_2THF).

In the infrared spectrum of **3a** there are two bands assignable to P−H stretches at 2355 and 2323 cm^{-1} and two bands with a shoulder for the ν(C−O) stretches reflecting the lower symmetry of **3a**.

The molecular structure of **3a** is shown in Figure 1, with significant bond lengths and angles presented in Table 1. The geometry about the Mo^0 centre is octahedral, with the major source of distortion from ideal being the disparate metal−donor bond lengths [$Mo-P_{av} = 2.491(2)$ and $Mo-C_{av} = 1.989(4)$ Å]. The average Mo−P bond length is closer to that in $[Mo(12aneP_3H_3)(CO)_3]$ [2.476(1) Å][7] than in $[Mo(12aneP_3iPr_3)(CO)_3]$ [2.527(1) Å].[8] There are no significant differences in the Mo−P bond lengths for the secondary and tertiary phosphorus donors; the $M-P_{tert}$ bond being just 0.01 Å longer than the $M-P_{sec}$ bonds. Indeed, comparison with the related C_{3v} complexes above reveals less Mo−P and Mo−C bond variation in **3a** than in these higher symmetry systems. The methoxyethyl pendant group projects over one of the carbonyl groups (C3−O3) with the result that the P1−Mo−C3 angle is expanded significantly [95.99(13)°] compared to the other *cis* angles. As is typical for $12aneP_3$ complexes of Mo^0, the P−Mo−P angles are close to, but slightly less than, 90°. This contrasts with comparable Cr^0 complexes[9] and $[CpFe(12aneP_3R_3)]^+$ [10] species, where expanded angles of greater than 90° are observed; this was anticipated as the M−P bond lengths decrease along the series $Mo^0 > Cr^0 > Fe^{II}$. As in all other structurally characterised complexes of $12aneP_3$ macrocycles, two of the chelate rings have a pseudo-chair conformation whilst the third is pseudo-boat. Other deviations from idealised geometry are small and the data are comparable to other Mo^0 complexes of this type.

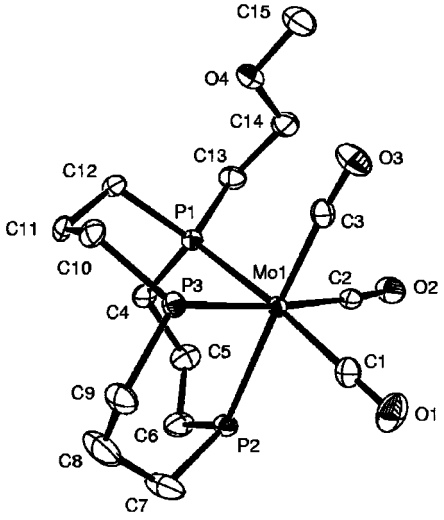


Figure 1. ORTEP representation of complex **3a**

When 3.5 mol equivalents of *n*BuLi are used followed by excess 2-bromoethyl methyl ether, the trisubstituted tertiary derivative **2** is isolated in high yield. As expected, the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at $\delta_P = 3$. The structure of the trisubstituted molybdenum complex **2** is shown in Figure 2 with selected bond lengths and angles presented in Table 2. All the bond lengths are very similar to those for complex **3a**, but, as expected for this higher symmetry complex, the angular distortions about the metal

Table 1. Selected bond lengths (Å) and angles (°) for **3a**

Mo1−C1	1.993(4)	Mo1−C2	1.993(3)	Mo1−C3	1.980(3)
Mo1−P1	2.500(3)	Mo1−P2	2.487(2)	Mo1−P3	2.4852(9)
P1−C13	1.846(4)	P1−C4	1.842(3)	P1−C12	1.839(3)
O1−C1	1.150(4)	O2−C2	1.153(3)	O3−C3	1.158(3)
O4−C15	1.428(3)	O4−C14	1.408(4)		
C2−Mo1−C1	92.34(13)	C2−Mo1−C3	89.37(12)	C1−Mo1−C3	88.9(2)
C2−Mo1−P1	87.44(10)	C1−Mo1−P1	175.12(9)	C3−Mo1−P1	95.99(13)
C2−Mo1−P2	94.37(9)	C1−Mo1−P2	85.81(13)	C3−Mo1−P2	173.63(8)
P1−Mo1−P2	89.34(10)	C2−Mo1−P3	174.65(8)	C1−Mo1−P3	92.11(9)
C3−Mo1−P3	87.75(9)	P1−Mo1−P3	88.37(5)	P2−Mo1−P3	88.91(4)

centre are generally less than those observed in **3a**. Most notably, the large *cis* angle observed in the mono-pendant derivative is not a feature in this C_3 symmetric complex. All the features are similar to those of previously reported structures of this type, including the ubiquitous chair/chair/boat conformation of the three chelate rings.

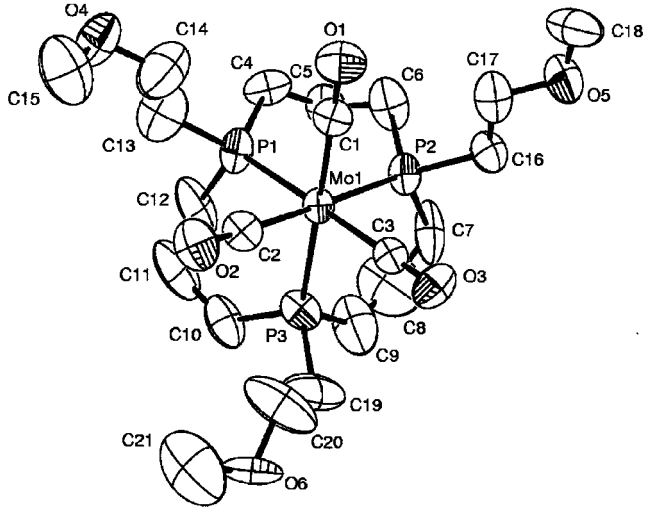


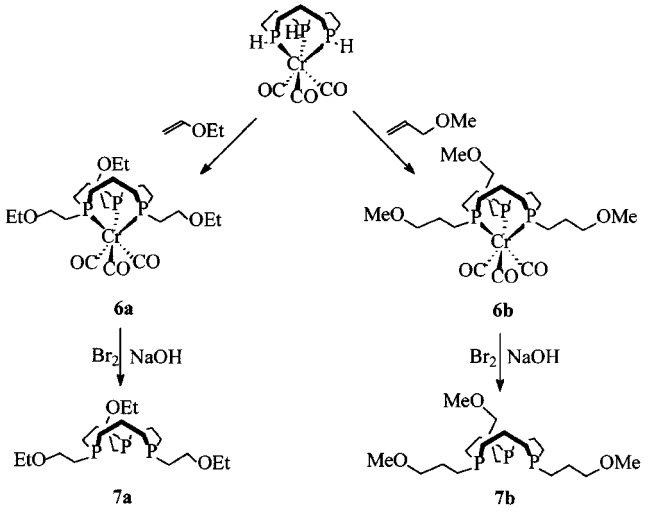
Figure 2. ORTEP representation of complex **2**

The C_3-symmetric trisubstituted macrocycles are also readily formed by radical-initiated hydrophosphinations of appropriate alkenes with $[M(CO)_3(12aneP_3H_3)]$ [M = Mo or Cr]. This method allows the direct incorporation of a range of hydrocarbyl or functionalised substituents including pendant ethers, amines, phosphanes or thioethers in high yield (Scheme 2). We have previously reported the synthesis of these pendant-donor-functionalised chromium compounds[11] although not the synthesis of the free ligands. Thus, the reaction of the coordinated secondary phosphane macrocycle with either vinyl ethyl ether or allyl methyl ether gives rise to the β- or γ-functionalised tris-ether derivatives **6a** and **6b**, respectively. These reactions may be performed readily using either $[Mo(CO)_3(12aneP_3H_3)]$ or $[Cr(CO)_3(12aneP_3H_3)]$, but are generally more efficient with the latter. The reaction of $[Cr(CO)_3(12aneP_3H_3)]$ with excess vinyl ethyl ether in toluene proceeds smoothly to the tritertiary phosphane derivative **6a**. This reaction appears to proceed by a radical-initiated mechanism as might be expected; yields are high when a radical initiator is included but are poor when performed in its absence or in the presence of a base catalyst alone. The same reaction with allyl methyl ether provides the methoxypropyl macrocycle complex, **6b**, in excellent yield.

The tris(methoxyethyl), diethyltetrahydrofurfuryl and tris(methoxypropyl) macrocycles were freed from their Mo and Cr templates by the established procedure of halogen oxidation and base digestion.[1b] As established previously, the liberation proceeds stereoselectively to give the *syn,syn* isomer exclusively; this conclusion is based on the ^{31}P NMR spectra which show singlets for both **7a** and **7b** and is confirmed by the relatively simple ^1H and ^{13}C NMR spectra. The coordination chemistry of these and the other functionalised macrocycles will be explored subsequently and will be reported at a later date. In conclusion, the versatility of the synthetic approaches described in this paper

Table 2. Selected bond lengths (Å) and angles (°) for **2**

Mo1−C2	1.959(7)	Mo1−C1	1.958(8)	Mo1−C3	1.995(7)
Mo1−P1	2.484(2)	Mo1−P2	2.489(2)	Mo1−P3	2.492(2)
P1−C13	1.801(10)	P1−C4	1.855(7)	P1−C12	1.897(9)
O1−C1	1.158(8)	O2−C2	1.148(8)	O3−C3	1.149(7)
O4−C15	1.363(9)	O4−C14	1.453(11)	O5−C17	1.410(9)
O5−C18	1.481(9)	O6−C20	1.382(14)	O6−C21	1.38(2)
C2−Mo1−C1	89.9(3)	C2−Mo1−C3	92.2(3)	C1−Mo1−C3	92.5(3)
C2−Mo1−P1	89.6(2)	C1−Mo1−P1	89.6(2)	C3−Mo1−P1	177.2(2)
C2−Mo1−P2	178.0(2)	C1−Mo1−P2	90.1(2)	C3−Mo1−P2	89.8(2)
P1−Mo1−P2	88.42(6)	C2−Mo1−P3	90.8(2)	C1−Mo1−P3	178.5(2)
C3−Mo1−P3	88.7(2)	P1−Mo1−P3	89.12(8)	P2−Mo1−P3	89.07(7)



Scheme 2

enables access to a range of pendant-donor-functionalised macrocyclic triphosphanes, including selectively functionalised examples.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. All solvents were dried by boiling at reflux over standard drying agents. Petroleum ether had b.p. 40−60 °C. The compounds [Mo(CO)$_3$(12aneP$_3$H$_3$)] and [Cr(CO)$_3$(12aneP$_3$H$_3$)],[2] and **6a** and **6b**[11] were prepared as previously described. All other chemicals were obtained from the Aldrich Chemical Company and used without further purification, except alkyl halide reagents, which were dried over molecular sieves and deoxygenated by freeze-thaw degassing. NMR spectra were recorded on a Bruker WM400 instrument operating at 400 MHz (^{1}H), 100.6 MHz (^{13}C) or a Jeol FX-90Q instrument operating at 36.23 MHz (^{31}P). All NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated, ^{1}H and ^{13}C NMR chemical shifts are quoted in ppm relative to tetramethylsilane ($\delta = 0$), ^{31}P NMR chemical shifts are quoted in ppm relative to external 85% H_3PO_4 ($\delta = 0$). All chemical shifts are positive to low field of the standards. Infrared spectra were recorded in Nujol on a Perkin−Elmer 783 infrared spectrometer. Magnetic susceptibilities were measured by the Gouy method on a Johnson−Matthey magnetic susceptibility balance, an experimental diamagnetic correction was measured for *cyclo*-(HPC$_3$H$_6$)$_3$ and applied. Mass spectra (EI) were recorded on a VG Platform II Fisons mass spectrometer. Melting points were obtained in sealed capillaries and are uncorrected.

[Mo(CO)$_3${12aneP$_3$(CH$_2$CH$_2$OCH$_3$)$_3$}] (2): *n*BuLi (3.5 equiv.) was added dropwise to a cooled (−78 °C) solution of [Mo(CO)$_3$(12aneP$_3$H$_3$)] (**1**; 2.5 g, 5.5 mmol) in THF (35 mL). The reaction mixture was allowed to warm up to −30 °C, whereupon 2-bromoethyl methyl ether (2.5 mL, 26.6 mmol) was added dropwise to the recooled (−78 °C) yellow solution and the whole allowed to warm to 20 °C. The product was purified by chromatography on silica (200 mesh) with dichloromethane as eluent. The solvent was removed to give a white solid which was crystallised from CH_2Cl_2/Et_2O. Yield: 2.63 g (83%) − ^{1}H NMR ($CDCl_3$): δ_H = 1.52 (m, 6 H, PCH$_2$C*H*$_2$CH$_2$P), 1.84 (dt, *J* = 10 and 7 Hz, 6 H, PC*H*$_2$CH$_2$OCH$_3$), 1.91 (m, 12 H, PC*H*$_2$CH$_2$C*H*$_2$P), 3.29 (s, 9 H, PCH$_2$CH$_2$OC*H*$_3$), 3.70 (dt, *J* = 13 and 7 Hz, 6 H, PCH$_2$C*H*$_2$OCH$_3$). − ^{13}C NMR ($CDCl_3$): δ_C = 20.5 (t, *J* = 7 Hz, PCH$_2$*C*H$_2$CH$_2$P), 25.6 (dd, *J* = 8 and 4 Hz, P*C*H$_2$CH$_2$*C*H$_2$P), 30.0 (m, P*C*H$_2$CH$_2$O), 58.4 (s, O*C*H$_3$), 70.2 (d, *J* = 7 Hz, *C*H$_2$O), 231.5 (m, *C*O). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 3 (s). − IR (Nujol): $\tilde{\nu}$ = 1922s, 1825s cm^{-1}. − Positive-ion EI-MS: *m*/*z* = 577 [M$^+$], 549 [M − CO]$^+$. − $C_{21}H_{39}MoO_6P_3$ (576.40): calcd. C 43.75, H 6.83; found C 43.9, H 7.0.

[Mo(CO)$_3${12aneP$_3$H$_2$(CH$_2$CH$_2$OCH$_3$)}] (3a): One equivalent of *n*BuLi was added dropwise to a cooled (−78 °C) solution of [Mo(CO)$_3$(12aneP$_3$H$_3$)] (2.5 g, 5.5 mmol) in THF (35 mL). The reaction mixture was allowed to warm up to −30 °C whereupon 2-bromoethyl methyl ether was added dropwise to the yellow solution and the whole allowed to warm to room temperature (20 °C). The product was purified by chromatography on silica (200 mesh) with toluene as eluent and the resultant white solid crystallised from CH_2Cl_2/Et_2O. Yield: 0.5 g (20%). − ^{1}H NMR ($CDCl_3$): δ_H = 1.52 (m, 4 H, HPCH$_2$CH$_2$C*H*$_2$PR), 1.74 (m, 6 H, PCH$_2$C*H*$_2$CH$_2$P), 1.86 (dt, *J* = 9 and 6 Hz, 2 H, PC*H*$_2$CH$_2$OCH$_3$), 1.93 (m, 8 H, HPC*H*$_2$CH$_2$CH$_2$PR), 3.29 (s, 3 H, PCH$_2$CH$_2$OC*H*$_3$), 3.70 (dt, *J* = 13 and 7 Hz, 2 H, PCH$_2$C*H*$_2$OCH$_3$), 4.86 (d, *J* = 323 Hz, 2 H, P*H*). − ^{13}C NMR ($CDCl_3$): δ_C = 21.8 [d, *J* = 14 Hz, HPCH$_2$-*C*H$_2$CH$_2$P(CH$_2$CH$_2$OCH$_3$)], 22.1 (d, *J* = 11 Hz, HPCH$_2$*C*H$_2$-CH$_2$PH), 24.5 [dd, *J* = 40 and 9 Hz, HP*C*H$_2$CH$_2$-CH$_2$P(CH$_2$CH$_2$OCH$_3$)], 24.6 (d, *J* = 24 Hz, HPCH$_2$*C*H$_2$*C*H$_2$PH), 31.3 [d, *J* = 24 Hz, HPCH$_2$*C*H$_2$CH$_2$P(CH$_2$CH$_2$OCH$_3$)], 35.4 (d, *J* = 26 Hz, P*C*H$_2$CH$_2$OCH$_3$), 58.9 (s, PCH$_2$CH$_2$O*C*H$_3$), 69.6 (d, *J* = 9 Hz, PCH$_2$*C*H$_2$OCH$_3$). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 3 (t, *J* = 32 Hz, R$_3$P), −32 (d, *J* = 32 Hz, 2 × R$_2$PH). − IR (Nujol): ν(P−H) = 2355m, 2323m; ν(C−O) = 1916s, 1831sh, 1821s cm^{-1}. − Positive-ion EI-MS: *m*/*z* = 460 [M$^+$], 432 [M − CO]$^+$. − $C_{15}H_{27}MoO_4P_3$ (460.24): calcd. C 39.14, H 5.92; found C 39.0, H 5.7.

[Mo(CO)$_3${12aneP$_3$H$_2$(CH$_2$THF)}] (3b): The complex was prepared in an analogous fashion to that for **3a** above, with tetrahydrofurfuryl chloride. The complex was not isolated pure and was used as such for the preparation of **4b**.

[Mo(CO)$_3${12aneP$_3$Et$_2$(CH$_2$CH$_2$OCH$_3$)}] (4a): A solution of **3a** (200 mg, 0.43 mmol) was placed in an autoclave with ca. 1% AIBN and the reaction mixture charged with ethene to 90 psi. After 12 h stirring at 90 °C, the autoclave was cooled to 20 °C and the excess of ethene removed. The solution was dried ($MgSO_4$) and the product purified by chromatography column on silica (200 mesh) with CH_2Cl_2 as eluent. Yield: 0.22 g (100%). − ^{1}H NMR ($CDCl_3$): δ_H = 1.08 (m, PCH$_2$*C*H$_3$), 1.7−1.2 (m, 20 H), 1.90 (q, *J* = 8 Hz, 4 H, PC*H*$_2$CH$_3$), 3.28 (s, 3 H, PCH$_2$CH$_2$OC*H*$_3$), 3.69 (dt, *J* = 11 and 7 Hz, 2 H, PCH$_2$C*H*$_2$OCH$_3$). − ^{13}C NMR ($CDCl_3$): δ_C = 8.1 (s, *C*H$_3$), 20.8 (s, PCH$_2$*C*H$_2$CH$_2$P), 23.2 (s, PCH$_2$*C*H$_2$CH$_2$P), 27.6 (dd, *J* = 13 and 9 Hz, P*C*H$_2$CH$_2$*C*H$_2$P), 29.1 (m, P*C*H$_2$CH$_2$*C*H$_2$P), 30.6 (d, *J* = 17 Hz, P*C*H$_2$CH$_3$), 34.8 (d, *J* = 20 Hz, P*C*H$_2$CH$_2$OCH$_3$), 58.3 (s, PCH$_2$CH$_2$O*C*H$_3$), 69.1 (d, *J* = 2 Hz, PCH$_2$*C*H$_2$OCH$_3$). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 4.3 (t, *J* = 32 Hz, R$_2$PCH$_2$CH$_2$OCH$_3$), 5.9 (d, *J* = 32 Hz, 2 × R$_2$PEt). − IR (CH_2Cl_2): ν(C−O) = 1923s, 1825s cm^{-1}. − Positive-ion EI-MS: *m*/*z* = 516 [M$^+$], 488 [M − CO]$^+$. − $C_{19}H_{35}MoO_4P_3$ (516.35): calcd. C 44.18, H 6.84; found C 44.0, H 6.7.

[Mo(CO)$_3${12aneP$_3$Et$_2$(CH$_2$THF)}] (4b): Prepared as for **4a** using crude **3b** (≈70%). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 4.5 (t, *J* = 31 Hz, R$_2$PCH$_2$CH$_2$THF), 5.0 (d, *J* = 31 Hz, 2 × R$_2$PEt). The

resultant material was used directly for the liberation and isolation of **5b**.

12aneP$_3$Et$_2$(CH$_2$THF) (5b): The ligand was released using the method defined previously.[1] It was purified by crystallisation from petroleum ether. Yield: 40%. – ^{1}H NMR ($CDCl_3$): δ_H = 2.0–0.7 (m, 34 H), 3.68 (m, $PCH_2CHCH_2CH_2CH_2O$), 3.83 (m, 2 H, PCH_2THF). – ^{13}C NMR ($CDCl_3$): δ_C = 9.9 (d, J = 12 Hz, CH_3), 19.3 (m, $PCH_2CH_2CH_2P$), 25.8 (s, CH_2-THF), 27.2 (m, $PCH2$), 29.5 (s, CH_2-THF), 33.9 (m, PCH_2CHO), 67.6 (s, $CHOCH_2$), 80.0 (d, J = 16 Hz, $CHOCH_2$). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = –40.4 (t, J = 16 Hz, R_2PCH_2THF), –31.9 (d, J = 16 Hz, 2 × R_2PEt).

7a: Released from the metal as previously described.[1b] Yield = 55%. – ^{1}H NMR ($CDCl_3$): δ_H = 1.10 (t, J = 7 Hz, 9 H, CH_3), 1.46 (br. m, 6 H, $PCH_2CH_2CH_2P$), 1.65 (m, 12 H, $PCH_2CH_2CH_2P$), 1.90 (br. m, 6 H, $PCH_2CH_2OCH_2CH_3$), 3.45 (q, J = 7 Hz, 6 H, $PCH_2CH_2OCH_2CH_3$), 3.72 (t, J = 7 Hz, 6 H, $PCH_2CH_2OCH_2CH_3$). – ^{13}C NMR ($CDCl_3$): δ_C = 14.0 (s, CH_3), 18.4 (m, $PCH_2CH_2CH_2P$), 27.5 (dd, J = 14 and 9 Hz, $PCH_2CH_2CH_2P$), 32.8 (m, PCH_2CH_2O), 64.1 (s, OCH_2CH_3), 65.2 (s, PCH_2CH_2O). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = –42.0 (s). – Positive-ion EI-MS: m/z = 438 [M^+], 365 [$M - EtOC_2H_4]^+$.

7b: Released from the metal as previously described.[1b] Yield = 68%. – ^{1}H NMR ($CDCl_3$): δ_H = 1.35 (br. m, 12 H, $PCH_2CH_2CH_2P$, $PCH_2CH_2CH_2OCH_3$), 1.58 (q, J = 8 Hz, 6 H, $PCH_2CH_2CH_2OCH_3$), 1.69 (m, 12 H, $PCH_2CH_2CH_2P$), 3.26 (s, OCH_3), 3.34 (t, J = 7 Hz, 6 H, $PCH_2CH_2CH_2OCH_3$). – ^{13}C NMR ($CDCl_3$): δ_C = 19.2 (br, $PCH_2CH_2CH_2P$), 23.2 (d, J = 7 Hz, $PCH_2CH_2CH_2O$), 27.1 (dd, J = 14 and 9 Hz, $PCH_2CH_2CH_2P$), 29.5 (d, J = 14 Hz, $PCH_2CH_2CH_2O$), 58.4 (s, OCH_3), 73.4 (d, J = 13 Hz, $PCH_2CH_2CH_2O$). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = –39.7 (s). – Positive-ion EI-MS: m/z = 438 [M^+], 365 [$M - EtOC_2H_4]^+$.

Crystal Data for Complex 2: $C_{21}H_{34}MoO_6P_3$, M = 571.33, T = 150(2) K, monoclinic, space group $P2_1/c$, a = 12.5069(9), b = 14.561(3), c = 15.4095(14) Å, β = 111.990(8)°, (by least-squares refinement of the setting angles for 250 reflections within θ = 1.76–24.74°), V = 2602.1(6) Å^3, Z = 4, D = 1.458 g cm^{-3}, μ(Mo-K_α) = 0.971cm^{-1}, F(000) = 1180, crystal size = 0.3 × 0.2 × 0.2 mm. All crystallographic measurements were made on an Enraf Nonius FAST area detector diffractometer. The structure was solved by direct methods[12] and refined on F_o^2 by full-matrix least-squares[13] using all unique data after correction for Lorentz and polarisation factors. All non-hydrogen atoms were refined with anisotropic thermal parameters. O6 was disordered between two half-occupied positions. Atoms C8, C13 and C14 were refined with the restraint ISOR = 0.0075. The hydrogen atoms were inserted in idealised positions with U_{iso} set at 1.5 times the U_{eq} of the parent. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0739P)^2]$, where $P = [\mathrm{Max}(F_o)^2 + 2(F_c)^2]/3$; this gave satisfactory agreement analyses. Final R_1 (on F) and wR_2 (on F_o^2) values were 0.0789 and 0.1441 for all 3656 data and 291 parameters. The corresponding R values were 0.0543 and 0.1361 for 2467 data with $I > 2\sigma(I)$. Sources of scattering factors as given in ref.[13]

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159939. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data for Complex 3a: $C_{15}H_{27}MoO_4P_3$, M = 460.22, T = 150(2) K, monoclinic, space group $P2_1/c$, a = 10.453(19), b = 12.300(3), c = 15.777(8) Å, β = 108.41(5)°, (by least-squares refinement of the setting angles for 250 reflections within θ = 2.05–24.8°), V = 1924.7(36) Å^3, Z = 4, D = 1.588 g cm^{-3}, μ(Mo-K_α) = 0.971cm^{-1}, F(000) = 944, crystal size = 0.25 × 0.22 × 0.18 mm. All crystallographic measurements were made on an Enraf Nonius FAST area detector diffractometer. The structure was solved by direct methods[12] and refined on F_o^2 by full-matrix least-squares[13] using all unique data after correction for Lorentz and polarisation factors. All non-hydrogen atoms were anisotropic. The hydrogen atoms were inserted in idealised positions with U_{iso} set at 1.5 times the U_{eq} of the parent. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0566P)^2]$, where $P = [\mathrm{Max}(F_o)^2 + 2(F_c)^2]/3$; this gave satisfactory agreement analyses. Final R_1 (on F) and wR_2 (on F_o^2) values were 0.0365 and 0.0834 for all 2943 data and 217 parameters. The corresponding R values were 0.0315 and 0.0790 for 2615 data with $I > 2\sigma(I)$. Sources of scattering factors as in ref.[13] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159940. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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