FULL PAPER

Dalton
www.rsc.org/dalton

Tridentate phosphine ligands with novel linker-units

Ralf A. Findeis and Lutz H. Gade*

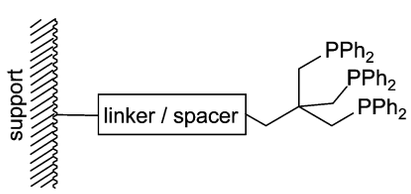
Laboratoire de Chimie Organométallique et de Catalyse, CNRS UMR 7513, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg, France

Received 30th September 2002, Accepted 14th November 2002
First published as an Advance Article on the web 12th December 2002

The synthesis of two novel types of tripodal phosphine ligands containing vinyl and alkynyl linker functions in their ligand backbones are reported. Using pentaerythritol (**1**) as the starting material the functionalized phosphines $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**), $Me_3SiC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) and $HC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**11**) were obtained in good yield in 4–5-step syntheses. $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**) and the silyl protected alkinyl derivative $(CH_3)_3Si{-}C{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) were reacted with one molar equivalent of $[Mo(CO)_3(MeCN)_3]$ to yield the yellow-brown, air stable triphosphine–molybdenum complexes $[\{H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**12**) and $[\{(CH_3)_3Si{-}C{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**13**) the latter of which was characterized by X-ray diffraction.

Introduction

The leaching of metal is a major practical problem in the application of immobilized molecular catalysts which are thought to combine the virtues of homogeneous catalysis (high activity and selectivity, directed catalyst design) with those of heterogeneous catalysts (*e.g.* facile catalyst separation and recycling).[1,2] The loss of catalyst may be suppressed to various degrees by using polydentate ligands which form thermally and kinetically stable complexes with the catalyst metal. Among the large number of ligand systems, which have been employed in this context, polydentate phosphines such as the "triphos" ligand, $MeC(CH_2PPh_2)_3$, are good examples for this capacity.[3] However, their use as ligands in heterogenized metal catalysts requires the functionalization of their backbone structure, preferentially in the apical position. Such modified tripodal phoshines have been employed for the physisorption of Ru and Rh complexes on oxidic supports[4] and the covalent fixation of such catalyst precursors to polystyrene.[5] These catalytic phases have been studied in catalytic hydrogenation and hydroformylation as well as the isomerization of allylic alcohols.[6] Additionally, backbone-functionalized triphos-complexes were employed in two-phase catalysis.[7]



Many previously published syntheses of tripodal phosphines partially suffer from the non-tolerance of certain functional groups (*e.g.* C–C multiple bonds)[8] or the fact that the phosphino groups are introduced at a very early stage of the reaction sequence, making subsequent work up more difficult.[9–13] In particular, if expensive (chiral) phosphino functions are to be introduced in an early reaction step of the synthetic pathway,[14] the loss in phosphine during the overall sequence may be considerable. We recently developed a strategy, in which the phosphine is introduced in the final step of the ligand-linker synthesis which was applied to the synthesis of a tripodal phosphine containing an ether–alcohol function in the ligand backbone.[15] In this paper we generalize this strategy and report the efficient synthesis of triphos-derivatives containing C=C double or C≡C triple bonds in the linker unit which is attached to the ligand framework.

Results and discussion

Synthesis of the tripodal phosphine ligand $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (6)

The synthesis of the functionalized phosphine tripods is based in part on the previous reports by Huttner and co-workers in this field.[9–13] The starting material is pentaerythritol (**1**) which is a cheap basic chemical which possesses a functionalized neopentane structure and thus appears to be well suited for the synthetic objective. The four hydroxyl functions in **1** are chemically equivalent, and in order to attach a linker group to only one of these, it had to be differentiated with respect to the others. This is readily achieved by reaction of **1** with triethyl orthoacetate in toluene to give the known methyl trioxabicyclooctane derivative **2** (Scheme 1).[16] The unreacted "apical" OH-function was then coupled with allyl bromide as a linker unit to give $H_2C{=}CH{-}CH_2OCH_2C(CH_2O)_3CCH_3$ (**3**) which in turn was hydrolyzed yielding the triol $H_2C{=}CH{-}CH_2OCH_2C(CH_2OH)_3$ (**4**). Functional group interconversion with $SOCl_2$ in dry pyridine gave the trichloride **5** which was reacted with $LiPPh_2$ in DME to yield the target phosphine $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**) in good yield.

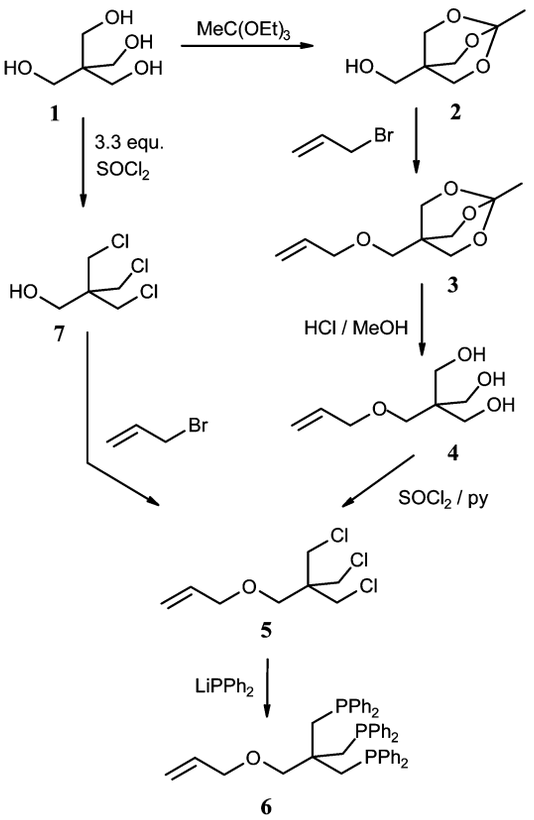
The differentiation of the OH-groups by orthoester protection requires the multistep sequence in the synthesis of **6** as discussed above. This leads to moderate overall yields of the triphos derivative in spite of the relatively high yields in each individual reaction step. It was therefore desirable to devise a shorter route to compound **6**. This was possible *via* the 3-chloro-2,2-bis(chloromethyl)propan-1-ol (**7**) which is directly prepared from pentaerythritol (Scheme 1).[17] Reaction of **7** with allyl bromide directly gave the key intermediate **5** which was thus accessible in large quantities.

Synthesis of the tripodal phosphine ligands $Me_3SiC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (10) and $HC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (11)

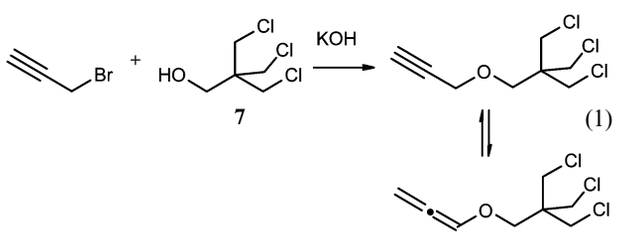
The direct application of the synthetic strategy outlined above to the preparation of alkynyl-functionalized tripodal phosphines simply by reaction of chloro-2,2-bis(chloromethyl)-propan-1-ol (**7**) with propargyl bromide proved to be unsuccessful. This was due to a partial isomerization of the reaction product to the corresponding allene derivative (eqn. (1)) under the reaction conditions.

This undesired rearrangement could be suppressed by use of the Me_3Si-protected propargyl chloride which reacted with **7** cleanly to give the trichloride **8**. Under the reaction conditions, which involved the use of KOH as base, the alkynyl group was

DOI: 10.1039/b209589k



Scheme 1 The two alternative synthetic strategies for the preparation of $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**).



desilylated. The direct reaction of **8** with $LiPPh_2$ to give the triphosphine ligand gave a product mixture containing the phosphine which could, however, not be isolated in pure form. This problem was circumvented by renewed trimethylsilylation of **8**, yielding **9** which in turn gave the triphosphine $Me_3SiC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) selectively in the subsequent functional group interconversion. Desilylation with KF/[18]crown-6 yielded the target molecule $HC{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**11**) (Scheme 2).

Synthesis and structural characterization of the complexes $[\{L\}Mo(CO)_3]$

In order to establish the structural details and the ligand properties of the new triphosphines $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**) and the silyl protected alkynyl derivative $(CH_3)_3Si{-}C{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) were reacted with one molar equivalent of $[Mo(CO)_3(MeCN)_3]$ to yield the yellow-brown, air stable triphosphine–molybdenum complexes $[\{H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**12**) and $[\{(CH_3)_3Si{-}C{\equiv}C{-}CH_2OCH_2C(CH_2PPh_2)_3\}Mo(CO)_3]$ (**13**) (Scheme 3).

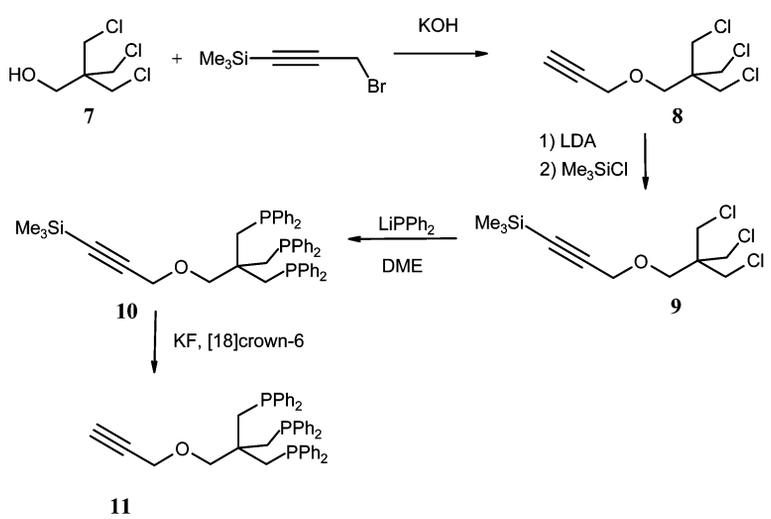
The ^{31}P NMR resonance of the coordinated phosphine ligand is observed at δ 15.6 for complex **12** (**6**: δ −26.5) and at δ 17.7 for complex **13** (**10**: δ −26.8). The IR ν(CO) band patterns are consistent with facial tricoordination of the triphosphine and the molecular ion peaks at m/z = 862.1 (**12**) and at m/z = 930.9 (**13**) confirm their formulation.

Single crystals of complex **13**, which were suitable for an X-ray diffraction study, were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of the compound. The molecular structure of **13** is displayed in Fig. 1 along with its principal bond lengths and angles.

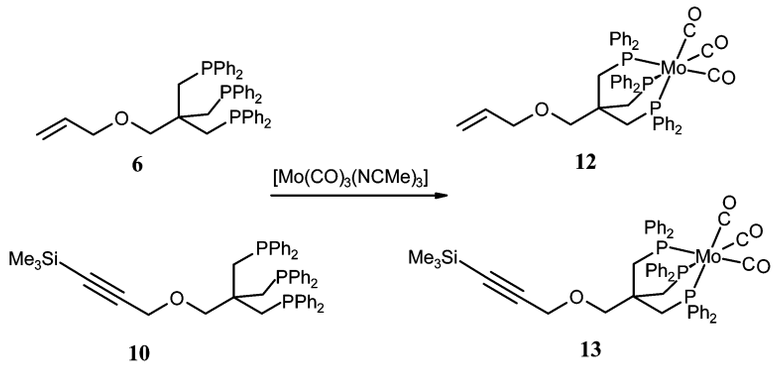
The phosphine ligand adopts the expected facial coordination mode for a molybdenum complex having a slightly distorted octahedral coordination geometry. The Mo–P distances of 2.534(1)–2.552(1) Å and the M–CO bond lengths of 1.947(4)–1.973(4) Å are within the expected range.[18] Both the P–Mo–P and the C–Mo–C angles, which lie in the ranges of 79.73(3)–85.99(3)° and 83.1(2)–86.7(2)°, respectively, are below 90° defining a slightly enlongated trigonal antiprismatic first coordination sphere.

Conclusion

The introduction of the phosphine functions in the final step of the synthesis of backbone-functionalized tripodal phosphine ligands provides an efficient access to such ligands while minimising the loss in phosphine. This will be the prerequisite to the extension of this work to C_3 chiral derivatives using *inter alia* Burk's 1,4-dialkylphospholane units.[14] This and the fixation of the ligands to support materials is currently under way in our laboratory.



Scheme 2 Synthesis of the alkynyl-functionalized phosphines **10** and **11**.



Scheme 3 Synthesis of the complexes [{L}Mo(CO)$_3$], **12** and **13**.

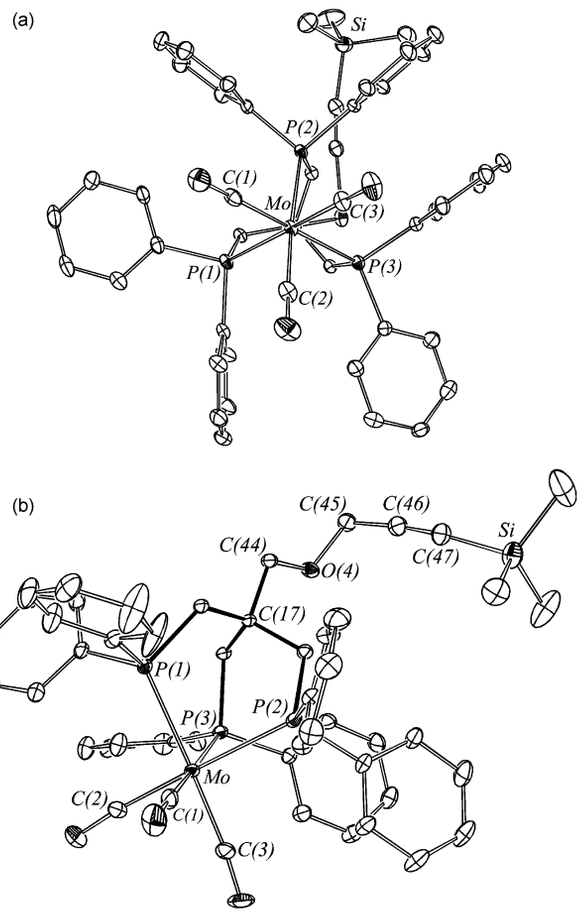


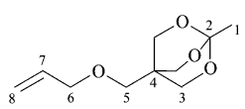
Fig. 1 Two views of the molecular structure of [{(CH$_3$)$_3$Si–C≡C–CH$_2$OCH$_2$C–(CH$_2$PPh$_2$)$_3$}Mo(CO)$_3$] (**13**). Principal bond lengths (Å) and interbond angles (°): Mo–P(1) 2.540(1), Mo–C(1) 1.973(4), C(45)–C(46) 1.476(7), Mo–P(2) 2.552(1), Mo–C(2) 1.963(5), C(46)–C(47) 1.205(6), Mo–P(3) 2.534(1), Mo–C(3) 1.947(4), C(47)–Si 1.830(5); P(1)–Mo–P(2) 85.99(3), C(1)–Mo–C(2) 85.8(2), C(44)–O(4)–C(45) 112.0(3), P(1)–Mo–P(3) 85.63(3), C(1)–Mo–C(3) 86.7(2), C(45)–C(46)–C(47) 174.2(5), P(2)–Mo–P(3) 79.73(3), C(2)–Mo–C(3) 83.1(2), C(46)–C(47)–Si 172.0(4)

Experimental

All manipulations were performed under nitrogen (desiccant P_4O_{10}, Granusic®, J. T. Baker) on a high vacuum line using standard Schlenk techniques, or in a glovebox. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and stored over 4-Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT-NMR spectrometers. ^{1}H and ^{13}C NMR data are listed in parts per million [ppm] relative to tetramethylsilane and were referenced using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C). ^{29}Si and ^{31}P NMR data are listed in ppm relative to, respectively, tetramethylsilane and 85% H_3PO_4 as external standards. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. HOCH$_2$-C(CH$_2$O)$_3$CCH$_3$ (**3**),[16] diphenylphosphine,[19] and [(MeCN)$_3$-Mo(CO)$_3$][20] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of H$_2$C=CH–CH$_2$OCH$_2$C(CH$_2$O)$_3$CCH$_3$ (3)

Allyl bromide (22.7 g = 187 mmol) was added dropwise to a stirred suspension of 33.1 g (591 mmol) of finely powdered KOH and 19.9 g (124.2 mmol) of 4-(hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane in 150 ml of dmso. The reaction mixture was stirred at 60 °C for 2 h and then cooled to room temperature. 500 ml of water were added, the organic layer separated and the aqueous phase extracted twice with 200 ml of Et$_2$O. The combined organic phases were treated with 100 ml of a saturated aqueous solution of NaCl-Lösung, then washed with 100 ml of water and finally dried over Na_2SO_2. After filtration and removal of the solvent by distillation the oily residue was fractionated at reduced pressure to give H$_2$C=CH–CH$_2$OCH$_2$C(CH$_2$O)$_3$CCH$_3$ (**6**) as a colourless liquid.

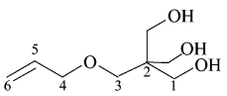


Yield: 21.6 g (107.9 mmol, 87%); bp: 88–89 °C/0.50 Torr. ^{1}H-NMR (400.1 MHz, CDCl$_3$, 295 K): δ = 1.37 (s, 3 H, H-1), 3.11 (s, 2 H, H-5), 3.83 (dt, 2 H, $^3J_{HH}$ = 5.60 Hz, $^4J_{HH}$ = 1.40 Hz, H-6), 3.93 (s, 6 H, H-3), 5.09–5.18 (m, 2 H, H-8), 5.70–5.80 (m, 1 H, H-7). {^{1}H}^{13}C-NMR (100.6 MHz, CDCl$_3$, 295 K): δ = 23.6 (CH$_3$, C-1), 35.1 (C, C-4), 68.6 (CH$_2$, C-6), 69.7 (CH$_3$, C-3), 72.6 (CH$_2$, C-5), 108.7 (C, C-2), 117.5 (CH$_2$, C-8), 134.2 (CH, C-7). IR (film): ν = 3008 (w), 2949 (m), 2878 (m), 1738 (w), 1647 (w), 1476 (m), 1447(m), 1401 (s), 1352 (m), 1297 (s), 1263 (m), 1209 (m), 1155 (m), 1128 (s), 1055 (s), 990 (m), 929 (m), 884 (m), 864 (s), 751 (w), 714 (w) cm^{-1}. $C_{10}H_{16}O_4$ (200.23 g mol^{-1}): calcd.: C 59.98, H 8.05; found: C 60.22, H 7.91%.

Preparation of H$_2$C=CH–CH$_2$OCH$_2$C(CH$_2$OH)$_3$ (4)

A solution of 15.1 g (75.2 mmol) of H$_2$C=CH–CH$_2$OCH$_2$-C(CH$_2$O)$_3$CCH$_3$ (**3**) in 40 ml of methanol and 50 ml of 2 M HCl was stirred at ambient temperature for 6 h. Solid Na_2CO_3

(12.1 g = 87.5 mmol) was carefully added in small portions to the reaction mixture which was then stirred at room temp. for another 18 h. The solvent was removed by distillation and the residue extracted with methanol. After removal of the solvent *in vacuo* the analytically pure compound $H_2C{=}CH{-}CH_2{-}OCH_2C(CH_2OH)_3$ (**4**) was obtained as a soft colourless solid.

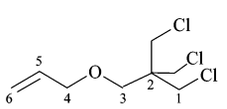


Yield: 10.3 g (58.6 mmol, 78%). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.42 (s, 2 H, H-3), 3.66 (s, 6 H, H-1), 3.94 (dt, 2 H, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.5 Hz, H-4), 5.14–5.26 (m, 2 H, H-6), 5.78–5.85 (m, 1 H, H-5). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 44.8 (C, C-2), 64.5 (CH_2, C-4), 72.4 (CH_2, C-3), 72.6 (CH_2, C-1), 117.4 (CH_2, C-6), 133.9 (CH, C-5). IR (film): ν = 3411 (b), 2949 (m), 2883 (m), 1647 (m), 1570 (m), 1411 (s), 1131 (m), 1083 (m), 1040 (s), 923 (m), 654 (m) cm^{-1}. $C_8H_{16}O_4$ (176.21 g mol^{-1}): calcd.: C 54.33, H 9.15; found: C 54.68, H 9.37%.

Preparation of $H_2C{=}CH{-}CH_2OCH_2C(CH_2Cl)_3$ (5)

Method A. To a mixture of 8.92 g (50.6 mmol) of $H_2C{=}CH{-}CH_2OCH_2C(CH_2OH)_3$ (**4**) and 13.2 g (167 mmol) of dry pyridine, which was stirred at 0 °C, were added dropwise 19.9 g (167 mmol) of $SOCl_2$. After completed addition, the reaction mixture was first stirred at 0 °C for 30 min, then for another 30 min at room temperature and finally for 2.5 h at 110–120 °C. After cooling to 0 °C, 150 ml of iced water was addded to the stirred solution. The aqueous phase was extracted twice with 50 ml of CH_2Cl_2 and the combined organic layers were washed with 100 ml 2 M HCl, 2 × 100 ml of water and then dried over Na_2SO_4. After filtration, the solvent was removed by distillation and the residue then fractionated under reduced pressure. The reaction product $H_2C{=}CH{-}CH_2OCH_2C(CH_2Cl)_3$ (**7**) was obtained as a colourless liquid. Yield: 8.08 g (34.9 mmol, 69%).

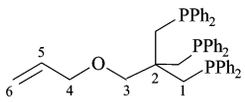
Method B. Finely powdered KOH (7.83 g = 139 mmol) was rapidly added to a vigorously stirred solution of 6.71 g (35.0 mmol) of 3-chloro-(2,2-chloromethyl)propan-1-ol (**7**) and 12.7 g (105 mmol) of allyl bromide in 35 ml of dmso. The exothermic reaction, which immediately set in, was controlled with the aid of an ice bath, thus keeping the reaction temperture below 60 °C. After the reaction had subsided the stirred solution was heated at 60 °C for another 2 h. After cooling to room temperature, 150 ml of water were added and the aqueous phase extracted with 3 × 50 ml of CH_2Cl_2. Work up as described above. Yield: 6.65 g (28.7 mmol, 82%).



bp: 78–80° C/0.50 Torr. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.45 (s, 2 H, H-3), 3.63 (s, 6 H, H-1), 3.99 (dt, 2 H, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.5 Hz, H-4), 5.15–5.29 (m, 2 H, H-6), 5.79–5.92 (m, 1 H, H-5). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 44.3 (CH_2, C-1), 46.1 (C, C-2), 67.3 (CH_2, C-4), 72.3 (CH_2, C-3), 117.1 (CH_2, C-6), 134.2 (CH, C-5). IR (film): ν = 3081 (w), 2965 (m), 2857 (m), 1647 (m), 1474 (m), 1439 (s), 1307 (m), 1268 (m), 1136 (s), 1109 (s), 986 (m), 930 (s), 870 (m), 760 (m), 743 (m), 703 (m) cm^{-1}. $C_8H_{13}Cl_3O$ (231.55 g mol^{-1}): calcd.: C 41.50, H 5.66; found: C 41.18, H 5.81%.

Preparation of $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (6)

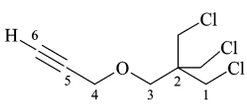
To a stirred solution of 6.63 g (35.6 mmol) of $HPPh_2$ in 25 ml of DME, which was cooled at −10 °C, were added dropwise 14.2 ml (35.6 mmol) of a 2.5 molar solution of *n*-BuLi in *n*-hexane. The resulting deep red solution was warmed to room temperature and then stirred for another 30 min. A solution of 2.62 g (11.3 mmol) of $H_2C{=}CH{-}CH_2OCH_2C(CH_2Cl)_3$ (**5**) in 8 ml of DME was then added dropwise to the lithium phosphide solution which was subsequently stirred for 24 h. All volatiles were removed *in vacuo*, the residue was extracted with 20 ml of toluene and the extract washed with 3 × 10 ml of degassed water. The organic phase was dried over Na_2SO_4 and after filtration all remaining volatile components were removed *in vacuo*. The crude product was taken up in methanol from which the pure reaction product $H_2C{=}CH{-}CH_2OCH_2C(CH_2PPh_2)_3$ (**6**) was obtained as a colourless, highly viscous oil.



Yield: 5.15 g (7.57 mmol, 67%). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 2.80 (s, 6 H, H-1), 3.40 (s, 2 H, H-3), 3.54 (d, 2 H, $^3J_{HH}$ = 5.7 Hz, H-4), 5.08–5.21 (m, 2 H, H-6), 5.53–5.65 (m, 1 H, H-5), 7.32–7.61 (m, 30 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 38.04 (m, CH_2, C-1), 42.6 (q, C, $^1J_{PC}$ = 12.2 Hz, C-2), 71.1 (s, CH_2, C-4), 76.3 (q, CH_2, $^4J_{PC}$ = 8.6 Hz, C-3), 116.0 (s, CH_2, C-6), 128.0–128.2 (m, aromat. C), 132.5–133.1 (m, aromat. C), 134.7 (s, CH, C-5), 139.4–139.5 (m, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, $CDCl_3$, 295 K): δ = −26.5 (s). IR (film): ν = 3069 (m), 3050 (m), 2923 (m), 2851 (m), 1644 (m), 1584 (m), 1480 (s), 1433 (s), 1372 (m), 1305 (m), 1184 (m), 1093 (s), 1026 (m), 999 (m), 924 (m), 826 (m), 739 (m), 695 (m) cm^{-1}. $C_{44}H_{43}OP_3$ (680.75 g mol^{-1}): calcd.: C 77.63, H 6.37; found: C 77.28, H 6.59%.

Preparation of $HC{\equiv}C{-}CH_2OCH_2C(CH_2Cl)_3$ (8)

Finely powdered KOH (6.73 g = 120 mmol) was added to a vigorously stirred solution of 10.0 g (52.3 mmol) of 3-bromo-(1-trimethylsilyl)-1-propyne and 5.10 g (26.6 mmol) of 3-chloro-(2,2-chloromethyl)propan-1-ol (**7**) in 20 ml of dmso. The strongly exothermic reaction was controlled with an ice bath. After the evolution of heat had subsided, the reaction mixture was stirred at 70 °C for another 30 min and then cooled to room temperature. After addition of 150 ml of water, the phases were separated and the aqueous phase extracted with 2 × 50 ml of CH_2Cl_2. The combined organic phases were washed with 2 × 100 ml of water and then dried over Na_2SO_4. After removal of the solvent by distillation, the crude product was fractionated at reduced pressure. The desired product $HC{\equiv}C{-}CH_2OCH_2C(CH_2Cl)_3$ (**8**) was obtained as a colourless liquid.

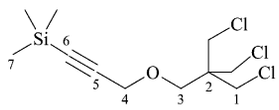


Yield: 3.78 g (16.5 mmol, 62%); bp: 72° C/0.45 Torr. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 2.45 (t, 1 H, $^4J_{HH}$ = 2.4 Hz, H-6), 3.58 (s, 2 H, H-3), 3.65 (s, 6 H, H-1), 4.17 (d, 2 H, $^4J_{HH}$ = 2.4 Hz, H-4). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 44.2 (CH_2, C-1), 45.9 (C, C-2), 58.7 (CH_2, C-4), 67.4 (CH_2, C-3), 75.0 (CH, C-6), 78.9 (C, C-5). IR (film): ν = 3295 (s), 2964 (m), 2878 (m), 1470 (m), 1439 (s), 1359 (m), 1308 (m), 1270 (m), 1103 (s), 1023 (m), 956 (m), 913 (m), 871 (m), 846 (m), 809 (m), 761 (m), 743 (m), 702 (m), 641 (m) cm^{-1}. $C_8H_{11}Cl_3O$ (229.53 g mol^{-1}): calcd.: C 41.86, H 4.83; found: C 41.62, H 4.91%.

Preparation of $(CH_3)_3Si{-}C{\equiv}C{-}CH_2OCH_2C(CH_2Cl)_3$ (9)

A solution of 4.40 ml (2.5 molar, 11.0 mmol) of LDA in thf/ethylbenzene/*n*-hexane was added with a syringe to a stirred

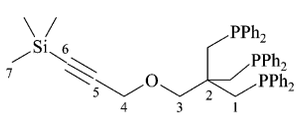
solution of 2.03 g (8.84 mmol) of HC≡C–$CH_2OCH_2C(CH_2Cl)_3$ (**8**) in 20 ml of thf which was cooled at −78 °C. After stirring for 30 min at −78 °C, 2.20 ml (17.6 mmol) of trimethylchlorosilane were added and the reaction mixture was subsequently stirred at room temperature for 16 h. The volatiles were then removed *in vacuo* and the crude product taken up in 50 ml of Et_2O. The solution was washed with 2 × 25 ml of water, the combined aqueous phases twice extracted with 20 ml of Et_2O and the combined organic phases dried over Na_2SO_4. After removal of the solvent *in vacuo*, the crude product was fractionated at reduced pressure. The product, $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2Cl)_3$ (**9**) was obtained as a colourless liquid.



Yield: 2.38 g (7.87 mmol, 89%). bp: 87 °C/0.50 Torr. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.16 (s, 9 H, H-7), 3.56 (s, 2 H, H-3), 3.63 (s, 6 H, H-1), 4.13 (s, 2 H, H-4). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = −0.3 (CH_3, C-7), 44.3 (CH_2, C-1), 46.0 (C, C-2), 59.4 (CH_2, C-4), 67.0 (CH_2, C-3), 92.2 (C, C-6), 100.7 (C, C-5). {^{1}H} ^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ = −17.8 (s). IR (Film): ν = 2961 (s), 2898 (m), 2176 (m), 1596 (w), 1470 (m), 1439 (m), 1353 (m), 1307 (m), 1250 (s), 1101 (s), 1025 (s), 995 (m), 943 (m), 844 (s), 761 (m), 703 (m), 655 (w), 620 (w) cm^{-1}. $C_{11}H_{19}Cl_3OSi$ (301.80 g mol^{-1}): calcd.: C 43.78, H 6.35; found: C 43.63, H 6.29%.

Preparation of $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (10)

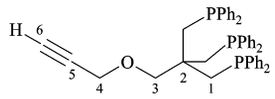
To a stirred solution of 2.28 g (12.3 mmol) of $HPPh_2$ in 20 ml of DME, which was cooled at −30 °C, were added 7.6 ml of a solution of *n*-BuLi in hexanes (1.6 M, 12.3 mmol). After stirring the resulting deep red solution for another 30 min at room temperature, a solution of 1.17 g (3.89 mmol) of $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2Cl)_3$ (**9**) in 6 ml of DME was added drop wise and the reaction mixture was stirrred at ambient temperature for another 24 h. All volatiles were removed *in vacuo* and the residue was taken up in 20 ml of toluene, washed with 2 × 10 ml of degassed water and dried over Na_2SO_4. After evaporation of the solvent, the residue was redissolved in methanol and stored at −30 °C to give $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) as a colourless solid.



Yield: 2.28 g (2.88 mmol, 74%); mp: 102 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.20 (s, 9 H, H-7), 2.59 (d, 6 H, H-1), 3.26 (s, 2 H, H-3), 3.37 (s, 2 H, H-4), 7.27−7.42 (m, 30 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = − 0.1 (s, CH_3, C-7), 38.1 (m, CH_2, C-1), 42.5 (q, C, C-2), 58.1 (s, CH_2, C-4), 76.0 (q, CH_2, C-3), 90.6 (s, C, C-6), 101.8 (s, C, C-5), 127.2−139.6 (m, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, $CDCl_3$, 295 K): δ = −26.8 (s). {^{1}H} ^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ = −18.6 (s). IR (film): ν = 3051 (w), 2953 (w), 2895 (w), 2170 (w), 1584 (w), 1480 (m), 1432 (s), 1407 (m), 1349 (w), 1305 (w), 1249 (m), 1181 (w), 1084 (s), 1017 (m), 991 (m), 944 (w), 841(s), 738 (s), 695 (s) cm^{-1}. $C_{47}H_{49}OP_3Si$ (750.91 g mol^{-1}): calcd.: C 75.18, H 6.58; found: C 74.87, H 6.41%.

Preparation of HC≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (11)

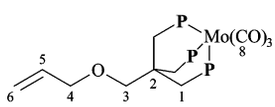
Solid KF (502 mg = 8.64 mmol) and 473 mg (1.79 mmol) of [18]crown-6 were added to a stirred solution of 1.34 g (1.69 mmol) of $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) in 5 ml of methanol/thf (1 : 1). The reaction mixture was stirred at room temperature for 7 d. All volatiles were removed subsequently, the residue was taken up in 10 ml of toluene, washed with 3 × 10 ml degassed water and the organic phase was dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product reprecipitated at −30 °C from methanol giving HC≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (**11**) as a soft colourless solid.



Yield: 713 mg (1.05 mmol, 62%). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.29 (t, 1 H, $^4J_{HH}$ = 2.4 Hz, H-6), 2.53 (m, 6 H, H-1), 3.19 (s, 2 H, H-3), 3.29 (d, 2 H, $^4J_{HH}$ = 2.4 Hz, H-4), 7.25–7.48 (m, 30 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 38.5 (m, CH_2, C-1), 42.0 (q, C, $^2J_{PC}$ = 13.2 Hz C-2), 57.8 (s, CH_2, C-4), 74.3 (s, CH, C-6), 76.7 (q, CH_2, $^3J_{PC}$ = 7.3 Hz C-3), 80.1 (s, C, C-5), 127.3–128.8 (m, CH, aromat. C), 133.3–133.6 (m, CH, aromat. C), 140.1–140.3 (m, C, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = −27.4 (s). IR (KBr): ν = 3287 (w), 3048 (w), 2922 (m), 2847 (m), 1479 (m), 1432 (s), 1262 (w), 1182 (w), 1094 (s), 1024 (m), 998 (m), 826 (w), 738 (s), 694 (s) cm^{-1}. $C_{44}H_{41}OP_3$ (678.73 g mol^{-1}): calcd.: C 77.86, H 6.09; found: C 77.61, H 6.02%.

Preparation of [{H_2C=CH–$CH_2OCH_2C(CH_2PPh_2)_3$}$Mo(CO)_3$] (12)

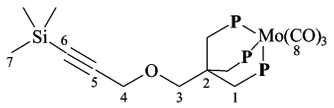
A solution of 287 mg (946 μmol) of [$(MeCN)_3Mo(CO)_3$] in 30 ml of CH_2Cl_2 was added to a solution of 644 mg (946 μmol) of H_2C=CH–$CH_2OCH_2C(CH_2PPh_2)_3$ (**6**) in 10 ml of CH_2Cl_2. After stirring at room temperature for 18 h, the reaction mixture was filtered through Celite, the volume decreased to 10 ml and the product was precipitated by addition of Et_2O. The reaction product was washed with 3 × 15 ml of Et_2O and dried *in vacuo*, yielding H_2C=CH–$CH_2OCH_2C(CH_2PPh_2)_3$-$Mo(CO)_3$ (**12**) as a yellow-brown microcrystalline solid.



Yield: 675 mg (787 μmol, 83%); mp: 247 °C (decomp.). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.38 (bs, 6 H, H-1), 3.38 (s, 2 H, H-3), 4.13 (d, 2 H, $^3J_{HH}$ = 5.2 Hz, H-4), 5.25–5.39 (m, 2 H, H-6), 5.96–6.09 (m, 1 H, H-5), 7.08–7.39 (m, 30 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 31.3 (m, CH_2, C-1), 41.6, (q, C, $^2J_{PC}$ = 7.2 Hz, C-2), 72.6 (s, CH_2, C-4), 83.7 (t, CH_2, $^3J_{PC}$ = 8.5 Hz, C-3), 116.8 (s, CH_2, C- 6), 128.4–129.3 (m, aromat. C), 132.1–132.3 (m, aromat. C), 135.1 (s, CH, C-5), 138.9–139.4 (m, aromat. C), 221.2–221.6 (m, CO, C-8). {^{1}H}^{31}P-NMR (161.9 MHz, CD_2Cl_2, 295 K): δ = 15.6 (s). IR (Film): ν = 3051 (w), 2901 (w), 2844 (w), 1928 (vs), 1835 (vs), 1482 (m), 1433 (m), 1260 (w), 1180 (w), 1092 (w), 1019 (m), 996 (w), 831 (w), 738 (m), 696 (s), 622 (m) cm^{-1}. MS (FAB): *m*/*z* = 862.1 [M + H]$^+$. $C_{47}H_{43}MoO_4P_3$ (860.72 g mol^{-1}): calcd.: C 65.59 H 5.04; found: C 65.48, H 4.93%.

Preparation of [{$(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3$}-$Mo(CO)_3$] (13)

Same procedure as for **12**, using 85.2 mg (113 μmol) of $(CH_3)_3$-Si–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3$ (**10**) and 34.3 mg (113 μmol) of [$(MeCN)_3Mo(CO)_3$]. The reaction product $(CH_3)_3Si$–C≡C–$CH_2OCH_2C(CH_2PPh_2)_3Mo(CO)_3$ (**13**) was obtained as a yellow-brown microcrystalline solid.



Yield: 92.6 mg (99.0 μmol, 88%); mp: 218 °C (decomp.). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 0.19 (s, 9 H, H-7), 2.36 (d, 6 H, H-1), 3.46 (s, 2 H, H-3), 4.29 (s, 2 H, H-4), 7.08–7.40 (m, 30 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 0.0 (s, CH_3, C-7), 31.3 (m, CH_2, C-1), 41.4 (q, C, $^2J_{PC}$ = 7.0 Hz C-2), 59.7 (s, CH_2, C-4), 82.8 (q, CH_2, $^3J_{PC}$ = 9.7 Hz C-3), 92.3 (s, C, C-6), 101.8 (s, CH, C-5), 128.4–129.3 (m, aromat. C), 132.0–133.2 (m, aromat. C), 138.9–139.4 (m, aromat. C), 221.3 (m, CO, C-8). {^{1}H}^{31}P-NMR (121.51 MHz, CD_2Cl_2, 295 K): δ = 17.7 (s). {^{1}H} ^{29}Si-NMR (79.49 MHz, CD_2Cl_2, 295 K): δ = 19.6 (s). IR (film): ν = 3279 (w), 3055 (w), 2919 (w), 2839 (w), 1929 (vs), 1841 (vs), 1482 (m), 1433 (s), 1087 (m), 1025 (w), 997 (w), 841 (s), 647 (s) cm^{-1}. MS (FAB): m/z = 930.9 [M]$^+$. $C_{50}H_{49}MoO_4P_3Si$ (930.88 g mol^{-1}): calcd.: C 64.51; H 5.31; found: C 64.27, H 5.22%.

X-Ray crystallographic study of 13

Suitable crystals of complex **13** were obtained by layering concentrated solutions of the compounds in dichloromethane or chloroform with hexanes and allowing slow diffusion at room temperature. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transfered to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[21] The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors (B(H) = 1.3B_{eq}(C) Å^2) but not refined. The hydrogen atoms of the solvents were not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from ref. 22. Crystal data and experimental details for the crystals of **13** are given in Table 1.

Table 1 X-Ray experimental data of compound **13**

Formula	$C_{50}H_{49}MoO_4P_3Si$
Molecular weight	930.88
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.9160(2)
b/Å	22.8277(4)
c/Å	17.9896(4)
β/°	97.864(5)
V/Å^3	4440.6(1)
Z	4
D_{calc}/ g cm^{-3}	1.39
F000	1928
μ/mm^{-1}	0.475
T/K	294
λ/Å	0.71073
Number of data measured	10365
Number of data with $I > 3\sigma(I)$	6776
Number of variables	532
R	0.044
Rw	0.056
GOF	1.035
Largest peak in final difference/e Å^{-3}	0.479

CCDC reference number 197230.

See http://www.rsc.org/suppdata/dt/b2/b209589k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the CNRS, and the Institut Universitaire de France for funding and Dr André DeCian and Natalie Gruber for carrying out the X-ray diffraction study.

References

1 (*a*) B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1982; (*b*) C. Lecuyer, F. Quignard, A. Choplin, D. Olivier and J.-M. Basset, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1660; (*c*) T. A. Budzichowski, S. T. Chacon, M. H. Chisholm, F. J. Feher and W. Streib, *J. Am. Chem. Soc.*, 1991, **113**, 689.
2 (*a*) F. R. Hartley, *Supported Metal Complexes – A New Generation of Catalysts*, D. Reidel Publishing Company, Dortrecht, 1989; (*b*) Yu. I. Yermakov, B. N. Kuznetsov, V. A. Zakharov, *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981; (*c*) W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524.
3 (*a*) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Coord. Chem Rev.*, 1992, **120**, 193; (*b*) H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239.
4 (*a*) C. Bianchini, D. G. Burnaby, J. Evans, P. Frediani, A. Meli, W. Oberhauser, R. Psaro, L. Sordelli and F. Vizza, *J. Am. Chem. Soc.*, 1999, **121**, 5961; (*b*) C. Bianchini, V. Dal Santo, A. Meli, W. Oberhauser, R. Psaro and F. Vizza, *Organometallics*, 2000, **19**, 2433.
5 (*a*) P. Schober, G. Huttner, L. Zsolnai and A. Jacobi, *J.Organomet. Chem.*, 1998, **571**, 279; (*b*) C. Bianchini, M. Frediani and F. Vizza, *Chem. Commun.*, 2001, 479; (*c*) C. Bianchini, M. Frediani, G. Mantovani and F. Vizza, *Organometallics*, 2001, **20**, 2660.
6 C. Bianchini, A. Meli and W. Oberhauser, *New J. Chem.*, 2001, **25**, 11.
7 (*a*) C. Bianchini, A. Meli, V. Patinec, V. Sernau and F. Vizza, *J Am. Chem. Soc.*, 1997, **119**, 4945; (*b*) I. Rojas, F. L. Linares, N. Valencia and C. Bianchini, *J. Mol. Catal. A*, 1999, **144**, 1.
8 B. C. Janssen, V. Sernau, G. Huttner, A. Asam, O. Walter, M. Büchner and L. Zsolnai, *Chem. Ber.*, 1995, **128**, 63.
9 A. Muth, A. Asam, G. Huttner, A. Barth and L. Zsolnai, *Chem. Ber.*, 1994, **127**, 305.
10 T. Seitz, A. Muth, G. Huttner, T. Klein, O. Walter, M. Fritz and L Zsolnai, *J. Organomet. Chem.*, 1994, **469**, 155.
11 T. Seitz, G. Huttner and M. Büchner, *Z. Naturforsch., Teil B*, 1994, **49**, 1813.
12 G. Huttner, O. Walter and L. Zsolnai, *Z. Naturforsch., Teil B*, 1995, **50**, 1287.
13 P. Schober, R. Soltek, G. Huttner, L. Zsolnai and K. Heinze, *Eur. J. Inorg. Chem.*, 1998, 1407–1415.
14 (*a*) M. J. Burk and R. L. Harlow, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1462; (*b*) M. J. Burk, J. E. Feaster and R. L. Harlow, *Tetrahedron: Asymmetry*, 1991, **2**, 569.
15 R. A. Findeis, L. H. Gade, *Eur. J. Inorg. Chem.*, 2003, in press.
16 T. J. Dunn, W. L. Neumann, M. M. Rogic and S. R. Woulfe, *J. Org. Chem.*, 1990, **55**, 636.
17 (*a*) M. Y. Etienne and R. Soulas, *Bull. Soc. Chim. Fr.*, 1957, 978; (*b*) K. M. Lynch and W. P. Dailey, *J. Org. Chem.*, 1995, **60**, 4666.
18 Cambridge Structural Data Base, Cambridge, April 2002.
19 W. Gee, R. A. Shaw and B. C. Smith, *Inorg. Synth.*, 1967, **9**, 19.
20 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.
21 OpenMoleN, Interactive Structure Solution, Nonius, Delft, 1997.
22 D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, 1974.