The $Mo(CO)_3$ Fragment as an Organometallic Protection Group in the Synthesis of Functionalized Tripodal Phosphine Ligands

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Treatment of $Mo(CO)_6$ with *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (**L**) at elevated temperatures gives $Mo(CO)_3$(tdppcyme) (**1**) in high yield. The ester groups in complex **1** are saponed to carboxylic acid groups by lithium *n*-propyl mercaptide in DMF and reduced to alcoholic groups by lithium aluminum hydride in THF to yield the carboxylic acid complex **2** and hydroxymethyl complex **4**, respectively. Treatment of **1** with ethylenediamine and NaH results in the formation of the carboxamide **3**. The methoxymethyl complex **5** is formed from **4** in a phase transfer reaction (THF/aqueous NaOH) with dimethyl sulfate as the methylating agent. Deprotonation of compound **4** with NaH in THF results in the formation of the corresponding trisodium alcoholate which on treatment with chloromethyl methyl ether, 1-methoxy-2-[(*p*-tolylsulfonyl)oxy]ethane, and allyl bromide leads to the corresponding complexes **6**−**8**, respectively. The acid-catalyzed addition of the hydroxyl function to 5,6-dihydro-4*H*-pyran yields the acetal **9**. The modified functionalized tripodal phosphines **2a** and **5a**−**9a** can be liberated by irradiating solutions of the corresponding molybdenum carbonyl complexes in the presence of pyridine *N*-oxide or N_2O, respectively. No oxidation of the phosphines is observed; MoO_3 and CO are obtained. Single-crystal X-ray structure determinations were performed on complexes **3** and **5**.

Introduction

The complicated and expensive synthesis of many catalysts have made a facile separation of catalyst and product mandatory for industrial applications. This has led to the development of several concepts for high and selective chemical conversions and low-cost catalyst recovery. In this context, multiphase reaction systems have been investigated extensively.[1] As an example, in liquid/liquid biphasic systems the limited miscibility of two solvents, one of which contains the reagent or catalyst while the substrate and products only dissolve in the other, are taken as an advantage for separation processes.[2] Anchored catalysts which are bound to solid supports also provide an easy way to achieve the separation of the catalyst from the product.[3] In either method, the catalyst has to be modified in order to dissolve it in a particular solvent or to immobilize it on a polymer. In many examples, this is accomplished by the functionalization of the ligands to obtain the desired behavior.[2b]

The excellent ligating properties of tripodal phosphines have made them to important constituents of compounds used in the study of stoichiometric and catalytic reactions.[4] The connectivities of the backbone of tripodal phosphines have been structurally varied over a wide range; however, little work has been done on introducing functional organic groups into the backbone.[5] Huttner et al.[6] and Bianchini et al.[7] have synthesized some functionalized neopentanetriyltris(phosphine) ligands with hydroxymethyl and *p*-sulfonylbenzyl groups at the bridgehead carbon atom. These ligands have been prepared by the traditional route of introducing the phosphino groups with the aid of metalated phosphines into the preformed, functionalized backbone which contains suitable leaving groups. Further functionalization of the hydroxymethyl group in some cases required the protection of the three phosphine groups with BH_3.[6b]

In this paper, we report the modification of the sterically demanding functionalized tripodal phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme)[8] (**L**) assisted by an organometallic protection group.[9,10] The method allows the preparation of sterically crowded and potentially bistripodal phosphine ligands.

Experimental Section

General Comments. All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled under argon prior to use; xylene, diethyl ether, and THF were

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‡ X-ray structure analysis of **3**.

§ X-ray structure analysis of **5**.

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(1) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17.

(2) (a) Joó, F.; Tóth, Z. *J. Mol. Catal.* **1980**, *8*, 369. (b) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem.* **1993**, *105*, 1588; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (c) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72.

(3) (a) Bailey, D. C.; Langer, H. S. *Chem. Rev.* **1981**, *81*, 109. (b) Hartley, F. R. *Supported Metal Complexes*; Reidel: Dordrecht, 1985. (c) Campbell, I. M. *Catalysis at Surfaces*; Chapman and Hall: London, 1988. (d) Lindner, E.; Kemmler, M.; Mayer, H. A.; Wegner, P. *J. Am. Chem. Soc.* **1994**, *116*, 348.

(4) (a) Cotton, F. A.; Hong. B. *Prog. Inorg. Chem.* **1992**, *40*, 179. (b) Mayer, H. A., Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239.

(5) (a) Mayer, H. A.; Stössel, P.; Fawzi, R.; Steimann, M. *Chem. Ber.* **1995**, *128*, 719. (b) Stössel, P.; Heins, W.; Mayer, H. A.; Fawzi, R.; Steimann, M. *Organometallics* **1996**, *15*, 3393.

(6) (a) Seitz, T.; Asam, A.; Huttner, G.; Walter, O.; Zsolnai, L. *Z. Naturforsch.* **1995**, *50B*, 1287. (b) Seitz, T.; Muth, A.; Huttner, G. *Z. Naturforsch.* **1995**, *50B*, 1045.

(7) Bianchini, C.; Frediani, P.; Sernau, V. *Organometallics* **1995**, *14*, 5458.

(8) Mayer, H. A.; Stössel, P.; Fawzi, R.; Steimann, M. *J. Organomet. Chem.* **1995**, *492*, C1−C3.

(9) While this paper was being reviewed, a similar but less elegant methodology was published: Coles, S. J.; Edwards, P. G.; Fleming, J. S.; Hursthouse, M. B.; Liyanage, S. S. *J. Chem. Soc., Chem. Commun.* **1996**, 293.

(10) See also: (a) Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700. (b) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Hackney, M. L. J.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 2811.

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distilled from Na/Ph_2CO; ethylenediamine was distilled from Na; acetone was distilled from $CaCl_2$; DMF was purified by azeotropic distillation with benzene/water and then redistilled from CaO and stored on CaH_2; dichloromethane was distilled from CaH_2; *n*-pentane was distilled from $LiAlH_4$; MeOH was distilled from Mg. Propanethiol, 5,6-dihydro-4*H*-pyran (DHP), dimethyl sulfate, allyl bromide, chloromethyl methyl ether, tetra-*n*-butylammonium iodide (TBAI), and pyridine *N*-oxide were purchased commercially (Aldrich) and used without further purification. 1-Methoxy-2-[(*p*-tolylsulfonyl)oxy]ethane was prepared according to the literature.[11] Molybdenum hexacarbonyl was donated by BASF AG. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DRX250 spectrometer operating at 250.13, 62.90, and 101.26 MHz, respectively. ^{1}H chemical shifts were referenced to the residual proton peaks of the solvents versus TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplets versus TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. In addition to ^{13}C{^{1}H} NMR spectroscopy, a ^{13}C-DEPT[12] experiment was routinely performed for each compound. The assignment of the proton and carbon resonances of complex **3** was supported by a ^{1}H/^{13}C 2D HMQC[13] experiment. Infrared spectra were recorded on a Bruker IFS 48. Mass spectra (FD) were detected on a Finnigan MAT 711 A modified by AMD and a FAB Finnigan MAT TQS70. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. The single-crystal X-ray structure determinations of **3** and **5** were carried out on a CAD4 and a Siemens P4 diffractometer.

Improved Synthesis of Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]molybdenum (1).[8] A suspension of 16.2 g (20 mmol) of tdppcyme (**L**) and 5.3 g (20 mmol) of $Mo(CO)_6$ in 600 mL of xylene (mixture of isomers) was slowly heated to reflux. After completion of the CO generation (approximately 1 h), the reaction mixture was maintained at reflux for additional 2.5 h, during which a white precipitate was formed. The off-white suspension was allowed to cool to room temperature, and the precipitate was collected on a sintered-glass frit, washed once with 50 mL of xylene and four times each with 75 mL of *n*-pentane, and dried in vacuo. Yield: 19.2 g (97%). Spectroscopic data are consistent with those published in an earlier work.[8]

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(hydroxycarbonyl)cyclohexane]molybdenum (2). A 125 mg sample of lithium (18 mmol) was added to 1.8 mL (20 mmol) of 1-propanethiol in 40 mL of DMF. The mixture was stirred at 45 °C until the lithium had reacted. Then 2.0 g (2 mmol) of **1** was added to the pale yellow solution in one portion. The yellow suspension was heated at 45 °C for 15 h, during which it became a red-brown solution. The solution was poured onto 100 mL of ice-cold, degassed HCl (2 N), the resulting off-white precipitate was collected on a sintered-glass frit, washed three times each with 20 mL of degassed HCl (2 N), four times each with 20 mL of degassed water, five times each with 10 mL of diethyl ether, and three times each with 20 mL of *n*-pentane, and dried in vacuo. Yield: 1.5 g (79%). Mp: >260 °C dec. IR (KBr, cm^{-1}): 1951, 1864 ν(CO), 1723 ν(COOH). ^{31}P{^{1}H} NMR ([$^2H_5$]pyridine): $\delta = 43.4$ [s]. ^{1}H NMR ([$^2H_5$]pyridine): $\delta = 3.08-3.42$ [m, 3 H, CHH_a], 3.64−3.73 [m, 3 H, CHH_e], 7.10−8.04 [m, 30 H, C_6H_5], 12.08 [br s, 3 H, COOH]. ^{13}C{^{1}H} NMR ([$^2H_5$]pyridine): $\delta = 34.79-35.13$ [m, CH_2], 48.42 [s, CP], 127.63 [m, C_6H_5 *meta*], 129.25 [br s, C_6H_5 *para*], 136.39 [m, C_6H_5 *ortho*], 138.93−139.45 [m, C_6H_5 *ipso*], 176.20 [m, COOH]. MS (FD), *m/z*: 950.0 [M$^+$]. Anal. Calcd for $C_{48}H_{39}MoO_9P_3$ (M_r 948.69): C, 60.77; H, 4.14. Found: C, 60.31; H, 4.48.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris((aminoethyl)carbamoyl)cyclohexane]molybdenum (3). A 432 mg (18 mmol) sample of NaH was dissolved in 60 mL of warm ethylenediamine (a glass-encapsulated stirring bar is recommended). The solution was cooled to 10 °C; then 2.0 g (2 mmol) of **1** was added in one portion. The deep red reaction mixture was stirred for 16 h at 10 °C, after which 963 mg (18 mmol) of NH_4Cl was added. On 0.5 h of stirring, the color turned to yellow and an off-white precipitate was formed. After further addition of 100 mL of degassed water, the precipitate was collected on a sintered-glass frit, washed three times each with 15 mL of water and five times each with 15 mL of diethyl ether, and dried in vacuo. Complex **3** can be recrystallized from hot DMF. Yield: 1.5 g (70%). Mp: >222 °C dec. IR (KBr, cm^{-1}): 1946, 1854 ν(CO), 1653, 1512 ν(CONH). ^{31}P{^{1}H} NMR ([$^2H_7$]DMF): $\delta = 44.5$ [s]. ^{1}H NMR ([$^2H_7$]DMF): $\delta = 2.10-2.40$ [m, 6 H, NH_2], 2.47 [t, $^3J_{HH} = 6.4$ Hz, 6 H, $NHCH_2CH_2NH_2$], 2.57−2.66 [m, 6 H, CHH_e], 2.90 [m, 6 H, $NHCH_2$-CH_2NH_2], 2.88−2.96 [m, 6 H, CHH_a], 6.53 [br t, $^3J_{HH} = 6.1$ Hz, 3 H, NH], 7.11−7.55 [m, 30 H, C_6H_5]. ^{13}C{^{1}H} NMR ([$^2H_7$]DMF): $\delta = 34.43-34.74$ [m, CH_2], 41.68, 43.90 [s, $NHCH_2CH_2NH_2$], 48.75 [s, CP], 127.63 [m, C_6H_5 *meta*], 129.61 [br s, C_6H_5 *para*], 136.45−136.64 [m, C_6H_5 *ortho*], 138.65−139.17 [m, C_6H_5 *ipso*], 172.90 [br s, CONH]. MS (FD), *m/z*: 1076.2 [M$^+$]. Anal. Calcd for $C_{54}H_{57}MoN_6O_6P_3$ (M_r 1074.94): C, 60.34; H, 5.35; N, 7.82. Found: C, 59.97; H, 5.25; N, 7.95.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(hydroxymethyl)cyclohexane]molybdenum (4). A mixture of 14.9 g (15 mmol) of **1** and 2.0 g (53 mmol) of $LiAlH_4$ was suspended in 500 mL of THF. The reaction mixture was stirred at room temperature for 1 h. Then the temperature was raised to 35 °C, and the mixture was kept at this temperature for additional 1.5 h. After being cooled to 0 °C, the mixture was hydrolyzed by slow addition of 100 mL of degassed HCl (3.3 M). After separation of the phases, the organic layer was removed, and the aqueous layer was extracted three times each with 100 mL of THF. The combined organic layers were dried on 15 g of CaO (15 h). The CaO was filtered off and carefully washed twice each with 100 mL of THF. The resultant yellow solution was reduced to 50 mL in volume, during which a white microcrystalline precipitate was formed. After further addition of 200 mL of *n*-pentane, the precipitate was collected on a sintered-glass frit, washed with two 50 mL portions of *n*-pentane, and dried in vacuo. Yield: 13.0 g (96%). Mp: >284 °C dec. IR (KBr, cm^{-1}): 3578, 3406 ν(OH), 1940, 1849 ν(CO). ^{31}P{^{1}H} NMR ([$^2H_6$]DMSO): $\delta = 47.1$ [s]. ^{1}H NMR ([$^2H_6$]DMSO): $\delta = 1.56-1.61$ [m, 3 H, CHH_e], 2.54−2.74 [m, 3 H, CHH_a], 3.50 [s, 6 H, CH_2OH], 4.94 [br s, 3 H, OH], 7.11−7.34 [m, 30 H, C_6H_5]. ^{13}C{^{1}H} NMR ([$^2H_6$]DMSO): $\delta = 27.91$ [m, CH_2], 38.29 [br s, CP], 65.08 [s, CH_2OH], 127.21 [br s, C_6H_5 *meta*], 128.67 [s, C_6H_5 *para*], 135.24 [m, C_6H_5 *ortho*], 136.10−136.74 [m, C_6H_5 *ipso*]. MS (FAB), *m/z*: 908.3 [M$^+$]. Anal. Calcd for $C_{48}H_{45}MoO_6P_3$ (M_r 906.74): C, 63.58; H, 5.00. Found: C, 63.19; H, 5.12.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]molybdenum (5). A 11.5 mL portion of a degassed, aqueous solution of NaOH (19 M) was added to a vigorously stirred suspension of 1.8 g (2 mmol) of **4** and 230 mg (0.62 mmol) of TBAI in 200 mL of THF. The reaction mixture was vigorously stirred for 1 h, during which the organic layer clarified. Then 10.4 mL (110 mmol) of dimethyl sulfate was added in one portion. **(Caution dimethyl sulfate is known to be carcinogenic. This compound should only be handled in a well ventilated hood.)** After vigorous stirring for 70 h at room temperature, 6 mL of degassed, concentrated aqueous NH_3 was added to destroy excess dimethyl sulfate. After 45 min, 25 mL of degassed water was added, the aqueous layer was removed, and the organic phase was reduced to 20 mL in volume, during which a white, mushy precipitate was formed. Then 100 mL of degassed water was added to the mixture. The precipitate was collected on a sintered-glass frit, washed three times each with 25 mL of degassed water, and dried in vacuo. Yield: 1.8 g (95%). Mp: >277 °C dec. IR (KBr, cm^{-1}): 1938, 1847 ν(CO). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 46.7$ [s]. ^{1}H NMR ($CDCl_3$): $\delta = 1.87-1.98$ [m, 3 H, CHH_e], 2.52−2.84 [m, 3 H, CHH_a], 3.28 [s, 9 H, CH_2OCH_3], 3.53 [s, 6 H, CH_2OCH$_3$], 7.10−7.35 [m, 30 H, C_6H_5]. ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 29.46$ [m, CH_2], 38.68−38.83 [br m, CP], 59.79 [s, CH_2OCH_3], 77.39 [s, *C*H$_2$OCH$_3$], 127.23−127.37 [m, C_6H_5 *meta*], 128.55 [s, C_6H_5 *para*], 135.70−135.89 [m, C_6H_5 *ortho*], 137.06−137.37 [m, C_6H_5 *ipso*]. MS (FD), *m/z*: 950.1 [M$^+$]. Anal. Calcd for $C_{51}H_{51}MoO_6P_3$ (M_r 948.82): C, 64.56; H, 5.42. Found: C, 64.13; H, 5.38.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris((methoxymethoxy)methyl)cyclohexane]molybdenum (6). A mixture of 1.8 g (2 mmol) of **4** and 288 mg (12 mmol) of NaH in 250 mL of THF was heated at 85 °C for 2 h in a sealed Schlenk tube. After the mixture was cooled to room temperature, 0.9 mL (12 mmol) of chloromethyl methyl ether was added dropwise via a syringe. **(Caution**

(11) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.
(12) Benn, R.; Günther, H. *Angew. Chem., Int. Engl. Ed.* **1983**, *22*, 350.
(13) Bax, A.; Griffey, R. H.; Hawkins, B. *J. Magn. Reson.* **1983**, *55*, 301.

chloromethyl methyl ether is known to be carcinogenic. This compound should only be handled in a well-ventilated hood.) The mixture was heated at 100 °C for 60 h, after which 5 mL of a degassed, aqueous solution of K_2CO_3 (1 M) was added. After 1 h of stirring, the aqueous layer was removed, the organic layer was dried on K_2CO_3, filtered off, and reduced to 15 mL in volume under reduced pressure. On addition of 50 mL of *n*-pentane to the pale yellow solution, an off-white precipitate formed, which was collected on a sintered-glass frit, washed three times each with 20 mL of *n*-pentane, and dried in vacuo. Yield: 1.8 g (87%). Mp: >266 °C dec. IR (KBr, cm^{-1}): 1939, 1845 ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 45.9$ [s]. ^1H NMR (CD_2Cl_2): $\delta = 1.80-1.96$ [m, 3 H, CHH_e], 2.56−2.89 [m, 3 H, CHH_a], 3.24 [s, 9 H, $CH_2OCH_2OCH_3$], 3.63 [s, 6 H, $CH_2OCH_2OCH_3$], 4.50 [s, 6 H, $CH_2OCH_2OCH_3$], 7.06−7.27 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 29.46$ [m, CH_2], 38.67−38.84 [br m, CP], 55.89 [s, $CH_2OCH_2OCH_3$], 72.64 [s, $CH_2OCH_2OCH_3$], 97.03 [s, $CH_2OCH_2OCH_3$], 127.81−127.94 [m, C_6H_5 *meta*], 129.22 [s, C_6H_5 *para*], 136.05−136.11 [m, C_6H_5 *ortho*], 136.97−137.49 [m, C_6H_5 *ipso*]. MS (FAB), *m/z*: 1041.0 [M^+]. Anal. Calcd for $C_{54}H_{57}MoO_9P_3$ (M_r 1038.90): C, 62.43; H, 5.53. Found: C, 61.96; H, 5.34.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris((methoxyethoxy)methyl)cyclohexane]molybdenum (7). A mixture of 1.8 g (2 mmol) of **4** and 288 mg (12 mmol) of NaH in 250 mL of THF was heated at 85 °C for 2 h in a sealed Schlenk tube. After the mixture was cooled to room temperature, a solution of 2.8 g (12 mmol) of 1-methoxy-2-[(*p*-tolylsulfonyl)oxy]ethane in 25 mL of THF was slowly added. The mixture was heated at 85 °C for 48 h, after which a few drops of water were added. The yellow solution was reduced to 60 mL in volume under reduced pressure. A mixture of H_2O/acetone (10/2) was added dropwise to the boiling solution until it became cloudy. When the resultant mixture was allowed to stand at 0 °C, colorless plates of **7** formed. Further crops of crystals could be obtained from the mother liquor. Yield: 1.6 g (74%). Mp: >264 °C dec. IR (KBr, cm^{-1}): 1938, 1845 ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 46.1$ [s]. ^1H NMR (CD_2Cl_2): $\delta = 1.79-1.96$ [m, 3 H, CHH_e], 2.53−2.86 [m, 3 H, CHH_a], 3.29 [s, 9 H, OCH_3], 3.42−3.49 [m, 12 H, $CH_2OCH_2CH_2OCH_3$], 3.58 [br s, 6 H, $CH_2OCH_2CH_2OCH_3$], 7.10−7.30 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.97$ [m, CH_2], 38.80−38.97 [br m, CP], 59.13 [s, $CH_2OCH_2CH_2OCH_3$], 70.83, 71.99 [s, $CH_2OCH_2CH_2OCH_3$], 75.67 [s, $CH_2OCH_2CH_2OCH_3$], 127.21−127.35 [m, C_6H_5 *meta*], 128.52 [s, C_6H_5 *para*], 135.65−135.84 [m, C_6H_5 *ortho*], 136.74−137.20 [m, C_6H_5 *ipso*]. MS (FD), *m/z*: 1083.3 [M^+]. Anal. Calcd for $C_{57}H_{63}MoO_9P_3$ (M_r 1080.98): C, 63.33; H, 5.87. Found: C, 62.96; H, 5.52.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris((allyloxy)methyl)cyclohexane]molybdenum (8). A mixture of 1.8 g (2 mmol) of **4** and 288 mg (12 mmol) of NaH in 250 mL of THF was heated at 85 °C for 2 h in a sealed Schlenk tube. After the mixture was cooled to room temperature, 1 mL (12 mmol) of allyl bromide was added dropwise via a syringe. The mixture was heated at 100 °C for 16 h. Then it was reduced to 25 mL in volume under reduced pressure. On addition of 200 mL of degassed water, a pale yellow precipitate formed, which was collected on a sintered-glass frit, washed three times each with 20 mL of water, and dried in vacuo. Yield: 1.8 g (88%). Mp: >269 °C dec. IR (KBr, cm^{-1}): 1938, 1843 ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 46.0$ [s]. ^1H NMR ($CDCl_3$): $\delta = 1.81-1.96$ [m, 3 H, CHH_e], 2.75−3.09 [m, 3 H, CHH_a], 3.57 [s, 6 H, $CH_2OCH_2CHCH_2$], 3.83 [m, 6 H, $CH_2OCH_2CHCH_2$], 5.02−5.27 [m, 6 H, $CH_2OCH_2CHCH_2$], 5.71−5.86 [m, 3 H, $CH_2OCH_2CHCH_2$], 7.06−7.33 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.71-28.96$ [m, CH_2], 38.71−38.88 [m, CP], 71.63 [s, $CH_2OCH_2CHCH_2$], 74.32 [s, $CH_2OCH_2CHCH_2$], 116.10 [s, $CH_2OCH_2CHCH_2$], 127.24−127.36 [m, C_6H_5 *meta*], 128.52 [s, C_6H_5 *para*], 134.29 [s, $CH_2OCH_2CHCH_2$], 135.60−135.78 [m, C_6H_5 *ortho*], 136.68−137.14 [m, C_6H_5 *ipso*]. MS (FAB), *m/z*: 1029.0 [M^+]. Anal. Calcd for $C_{57}H_{57}MoO_6P_3$ (M_r 1026.93): C, 66.67; H, 5.59. Found: C, 66.22; H, 5.34.

Tricarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris((2-tetrahydropyranyloxy)methyl)cyclohexane]molybdenum (9). A mixture of 1.8 g (2 mmol) of **4** and 53 mg (0.3 mmol) of *p*-toluenesulfonic acid hydrate was suspended in a mixture of 60 mL of THF and 30 mL of DHP. The suspension was stirred at 50 °C for 100 h, during which a colorless solution was formed. The solution was carefully washed once with 5 mL of a degassed, aqueous solution of K_2CO_3 (1.0 M) and twice each with 10 mL of water and dried on $CaCl_2$. The solution was filtered off and reduced to 10 mL under reduced pressure. On addition of 100 mL of *n*-pentane, a white precipitate formed, which was collected on a sintered-glass frit, washed three times each with 20 mL of *n*-pentane, and dried in vacuo. Yield: 2.2 g (95%). Mp: >225 °C dec. IR (KBr, cm^{-1}): 1939, 1848 ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 45.8-47.2$ [m]. ^1H NMR ($CDCl_3$): $\delta = 1.47-1.99$ [m, 21 H, 3,4,5-CH_2-THP, CHH_e], 2.68−3.06 [m, 3 H, CHH_a], 3.25−4.15 [m, 12 H, 6-CH_2-THP, CH_2O], 4.39−4.47 [m, 3 H, 2-CH-THP], 6.83−7.54 [30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.27-19.54$, 24.30, 30.46−30.56 [m, 3,4,5-CH_2-THP], 28.10−28.62 [m, CH_2], 38.82−39.21 [m, CP], 62.30−62.62 [m, 6-CH_2-THP], 71.64 [m, CH_2O], 98.84−99.43 [m, 2-CH-THP], 126.92−127.57 [m, C_6H_5 *meta*], 128.32, 128.52, 128.66 [br s, C_6H_5 *para*], 134.70−136.45 [m, C_6H_5 *ortho*], 136.76−137.18 [m, C_6H_5 *ipso*]. MS (FD), *m/z*: 1161.5 [M^+]. Anal. Calcd for $C_{63}H_{69}MoO_9P_3$ (M_r 1159.08): C, 65.28; H, 6.00. Found: C, 64.69; H, 6.18.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris((sodiooxy)carbonyl)cyclohexane (2a).** A mixture of 949 mg (1 mmol) of **2** and 72 mg (3 mmol) of NaH was placed in a double-walled Duran Schlenk tube. The mixture suspended in 300 mL of methanol was stirred for 0.5 h and then degassed by using the freeze−pump−thaw technique. The vigorously stirred solution was cooled to 10 °C, and dinitrogen monoxide (N_2O) was added (1.0 bar). Then the reaction mixture was irradiated for 2 h with the light of a TQ 150 W (Original Hanau) high-pressure mercury lamp, which was located 5 cm from the Schlenk tube. After 2 h, the completion of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. If small amounts of the educt were still present, irradiation was continued. After complete conversion of the educt, the reaction mixture was filtered, and the filtrate was reduced to 5 mL under reduced pressure, during which an off-white microcrystalline precipitate formed. The precipitate was collected on a sintered-glass frit, washed twice each with 1 mL of methanol, and dried in vacuo. Further crops of crystals were obtained from the mother liquor. Yield: 692 mg (86%). Mp: 271 °C dec. IR (KBr, cm^{-1}): 1584, 1374 $\nu(COO^-)$. $^{31}P\{^1H\}$ NMR ([$^2H_7$]DMF): $\delta = 29.2$ [s]. ^1H NMR ([$^2H_7$]DMF): $\delta = 1.31$ [dt, $^2J_{HH} = 12.58$, $^3J_{PH} = 10.26$ Hz, 3 H, CHH_a], 3.25 [br d, $^2J_{HH} = 12.58$, $^3J_{PH} < 5.0$ Hz, CHH_e], 7.14−7.43 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ([$^2H_7$]DMF): $\delta = 44.76$ [t, $^2J_{PC} = 15.88$ Hz, CH_2], 55.19 [dt, $^1J_{PC} = 17.61$, $^3J_{PC} = 10.90$ Hz, CP], 133.22 [br s, C_6H_5 *para*], 133.62 [d, $^3J_{PC} = 6.73$ Hz, C_6H_5 *meta*], 140.18 [d, $^2J_{PC} = 21.51$ Hz, C_6H_5 *ortho*], 145.30 [d, $^1J_{PC} = 24.90$ Hz, C_6H_5 *ipso*], 188.60 [d, $^2J_{PC} = 4.09$ Hz, COO^-]. MS (FAB), *m/z*: 839.4 [M^+]. Anal. Calcd for $C_{45}H_{42}Na_3O_6P_3$ (M_r 840.71): C, 64.29; H, 5.04. Found: C, 64.42; H, 5.17.

General Procedures for the Preparation of the Phosphines 5a−9a. Method 1. To solutions of **5**−**9** in 300 mL of THF, placed in a Duran Schlenk tube, were added 1.1 g (12 mmol) of pyridine *N*-oxide and 1.1 g (12 mmol) of anhydrous $MgCl_2$. The vigorously stirred reaction mixtures were cooled to 10 °C and irradiated for 18 h with the light of a TQ 150 W (Original Hanau) high-pressure mercury lamp, which was located 5 cm from the Schlenk tube. After 18 h, the completion of the reactions was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. If small amounts of the educt were still present, a further 285 mg (3.0 mmol) of pyridine *N*-oxide was added and the irradiation was continued for 6 h. The deep red reaction mixtures were filtered, the solvent was removed in vacuo, 300 mL of CH_2Cl_2 was added to the brown residues, and the resulting suspensions were vigorously stirred for 12 h. The residual $MgCl_2$ was filtered off and carefully washed twice each with 20 mL of CH_2Cl_2. The filtrates were then washed three times each with 50 mL of degassed water and dried on $MgSO_4$. The $MgSO_4$ was filtered off and carefully washed with two 20 mL portions of CH_2Cl_2. The solvent was removed in vacuo. The phosphines were obtained as red-brown foams or tough oils.

Method 2. Solutions of **5**−**9** in 150 mL of THF, placed in a double-walled Duran Schlenk tube, were degassed by using the freeze−pump−thaw technique. Then a 5 mL portion of a degassed, aqueous solution of K_2CO_3 (2.0 M) was added to each. The vigorously stirred solutions were cooled to 10 °C, and dinitrogen monoxide (N_2O) was added (1.0 bar). The reaction mixtures were irradiated for 8 h with the light of a TQ 150 W (Original Hanau) high-pressure mercury lamp, which was

located 5 cm from the Schlenk tube. After 8 h, the completion of the reactions was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. If small amounts of the educt were still present, irradiation was continued. After complete conversion of the educts, the brown aqueous layers were removed and the organic layers were dried on 5 g of CaO (2 h). The CaO was filtered off and carefully washed twice each with 20 mL of THF. Then the THF was removed under reduced pressure, the residues were redissolved in 100 mL of CH_2Cl_2, and the resultant solutions were dried on 5 g of $MgSO_4$ (2 h). The $MgSO_4$ was filtered off and carefully washed twice each with 20 mL of CH_2Cl_2. The solvent was removed in vacuo. The phosphines were obtained as colorless to off-white foams or tough oils.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)-cyclohexane (5a).** A 949 mg (1 mmol) sample of **5** was used. Method 1: The phosphine was obtained as a red foam. Yield: 624 mg (81%). Method 2: The phosphine was obtained as an off-white foam. Yield: 692 mg (90%). Mp: 69 °C dec. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.6$ [s]. ^1H NMR ($CDCl_3$): $\delta = 1.73$ [dt, $^2J_{HH} = 14.76$, $^3J_{PH} = 9.43$ Hz, 3 H, CHH_a], 2.25 [br d, $^2J_{HH} = 14.76$, $^3J_{PH} < 5.0$ Hz, CHH_e], 2.89 [s, 9 H, CH_2OCH_3], 3.33 [d, $^3J_{PH} = 12.23$ Hz, 6 H, CH_2OCH_3], 7.12−7.36 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 33.62$ [t, $^2J_{PC} = 18.14$ Hz, CH_2], 41.69 [dt, $^1J_{PC} = 21.34$, $^3J_{PC} = 9.25$ Hz, CP], 58.31 [s, CH_2OCH_3], 76.86 [d, $^2J_{PC} = 6.40$ Hz, CH_2OCH_3], 128.07 [d, $^3J_{PC} = 7.83$ Hz, C_6H_5 *meta*], 128.49 [br s, C_6H_5 *para*], 135.23 [d, $^1J_{PC} = 20.63$ Hz, C_6H_5 *ipso*], 135.80 [d, $^2J_{PC} = 22.05$ Hz, C_6H_5 *ortho*]. MS (FAB), *m/z*: 769.1 [M^+]. Anal. Calcd for $C_{48}H_{51}O_3P_3$ (M_r 768.85): C, 74.99; H, 6.69. Found: C, 74.86; H, 6.95.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris((methoxymethoxy)-methyl)cyclohexane (6a).** A 1 g (1 mmol) quantity of **6** was used. Method 1: 138 mg (1 mmol) sample of solid K_2CO_3 was added to the reaction mixture. The CH_2Cl_2 solution was washed with an aqueous K_2CO_3 solution (50 mM). The phosphine was obtained as a red foam. Yield: 722 mg (84%). Method 2: The phosphine was obtained as an off-white foam. Yield: 756 mg (88%). Mp: 63 °C. $^{31}P\{^1H\}$ NMR (CD_3OD): $\delta = 28.3$ [s]. ^1H NMR (CD_3OD): $\delta = 1.74$ [dt, $^2J_{HH} = 14.30$, $^3J_{PH} = 9.02$ Hz, 3 H, CHH_a], 2.31 [br d, $^2J_{HH} = 14.30$, $^3J_{PH} < 5.0$ Hz, 3 H, CHH_e], 2.97 [s, 9 H, $CH_2OCH_2OCH_3$], 3.52 [d, $^3J_{PH} = 13.81$ Hz, 6 H, $CH_2OCH_2OCH_3$], 4.11 [s, 6 H, $CH_2OCH_2OCH_3$], 7.13−7.27 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 34.80$ [t, $^2J_{PC} = 17.51$ Hz, CH_2], 42.36 [dt, $^1J_{PC} = 21.56$, $^3J_{PC} = 8.76$ Hz, CP], 55.96 [s, $CH_2OCH_2OCH_3$], 73.50 [d, $^2J_{PC} = 7.41$ Hz, $CH_2OCH_2OCH_3$], 97.77 [s, $CH_2OCH_2OCH_3$], 129.40 [d, $^3J_{PC} = 8.08$ Hz, C_6H_5 *meta*], 130.08 [br s, C_6H_5 *para*], 136.27 [d, $^1J_{PC} = 20.21$ Hz, C_6H_5 *ipso*], 136.82 [d, $^2J_{PC} = 22.23$ Hz, C_6H_5 *ortho*]. MS (FD), *m/z*: 858.7 [M^+]. Anal. Calcd for $C_{51}H_{57}O_6P_3$ (M_r 858.93): C, 71.32; H, 6.69. Found: C, 71.18; H, 6.73.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris((methoxyethoxy)-methyl)cyclohexane (7a).** A 1.1 g (1 mmol) quantity of **7** was used. Method 1: The phosphine was obtained as a red foam. Yield: 739 mg (82%). Method 2: The phosphine was obtained as an off-white foam. Yield: 784 mg (87%). Mp: 57 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 29.3$ [s]. ^1H NMR ($CDCl_3$): $\delta = 1.72$ [dt, $^2J_{HH} = 14.73$, $^3J_{PH} = 9.69$ Hz, 3 H, CHH_a], 2.31 [br d, $^2J_{HH} = 14.73$, $^3J_{PH} < 5.0$ Hz, 3 H, CHH_e], 3.08−3.60 [m, 12 H, $CH_2OCH_2CH_2OCH_3$], 3.16 [s, 9 H, $CH_2OCH_2CH_2OCH_3$], 3.50 [d, $^3J_{PH} = 12.38$ Hz, 6 H, $CH_2OCH_2CH_2OCH_3$], 7.15−7.41 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 33.41$ [t, $^2J_{PC} = 17.83$ Hz, CH_2], 41.35 [dt, $^1J_{PC} = 20.73$, $^3J_{PC} = 9.33$ Hz, CP], 58.63 [s, $CH_2OCH_2CH_2OCH_3$], 69.75, 71.42 [s, $CH_2OCH_2CH_2OCH_3$], 75.00 [d, $^2J_{PC} = 5.81$ Hz, $CH_2OCH_2CH_2OCH_3$], 127.75 [d, $^3J_{PC} = 8.30$ Hz, C_6H_5 *meta*], 128.20 [br s, C_6H_5 *para*], 135.12 [d, $^1J_{PC} = 21.00$ Hz, C_6H_5 *ipso*], 135.43 [d, $^2J_{PC} = 22.39$ Hz, C_6H_5 *ortho*]. MS (FD), *m/z*: 900.5 [M^+]. Anal. Calcd for $C_{54}H_{63}O_6P_3$ (M_r 901.01): C, 71.99; H, 7.05. Found: C, 71.82; H, 7.13.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris((allyloxy)methyl)-cyclohexane (8a).** A 1 g (1 mmol) quantity of **8** was used. Method 1: The phosphine was obtained as a red-brown tough oil. Yield: 728 mg (86%). Method 2: The phosphine was obtained as a pale yellow tough oil. Yield: 737 mg (87%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 29.6$ [s]. ^1H NMR (CD_2Cl_2): $\delta = 1.88$ [dt, $^2J_{HH} = 14.36$, $^3J_{PH} = 9.49$ Hz, 3 H, CHH_a], 2.30 [br d, $^2J_{HH} = 14.36$, $^3J_{PH} < 5.0$ Hz, 3 H, CHH_e], 3.45 [d, $^3J_{PH} = 12.67$ Hz, 6 H, $CH_2OCH_2CHCH_2$], 3.56−3.61 [m, 6 H, $CH_2OCH_2CHCH_2$], 5.05−5.14 [m, 6 H, $CH_2OCH_2CHCH_2$], 5.62−5.78 [m, 3 H, $CH_2OCH_2CHCH_2$], 7.28−7.48 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 34.04$ [t, $^2J_{PC} = 18.23$ Hz, CH_2], 41.63 [dt, $^1J_{PC} = 22.30$, $^3J_{PC} = 9.23$ Hz, CP], 71.92 [s, $CH_2OCH_2CHCH_2$], 74.47 [d, $^2J_{PC} = 6.10$ Hz, $CH_2OCH_2CHCH_2$], 116.82 [s, $CH_2OCH_2CHCH_2$], 128.33 [d, $^3J_{PC} = 7.34$ Hz, C_6H_5 *meta*], 128.87 [br s, C_6H_5 *para*], 134.88 [s, $CH_2OCH_2CHCH_2$], 135.96 [d, $^2J_{PC} = 22.53$ Hz, C_6H_5 *ortho*], 136.00 [d, $^1J_{PC} = 26.66$ Hz, C_6H_5 *ipso*]. MS (FAB), *m/z*: 846.5 [M^+]. Anal. Calcd for $C_{54}H_{57}O_3P_3$ (M_r 846.96): C, 76.56; H, 6.78. Found: C, 76.48; H, 7.05.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris((2-tetrahydropy-ranyloxy)methyl)cyclohexane (9a).** A 1.2 g (1 mmol) quantity of **9** was used. Method 1: The phosphine was obtained as a red foam. Yield: 666 mg (68%). Method 2: The phosphine was obtained as an off-white foam. Yield: 715 mg (73%). Mp: 71 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 27.0−27.7$ [m]. ^1H NMR (CD_2Cl_2): $\delta = 1.32−1.94$ [m, 21 H, 3,4,5-CH_2-THP, CHH_a], 2.31−2.44 [m, 3 H, CHH_e], 3.23−4.41 [m, 15 H, 6-CH_2-THP, CH_2O, 2-CH-THP], 7.26−7.57 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.71−19.61$, 25.57−25.90, 30.09−30.41 [m, 3,4,5-CH_2-THP], 33.88−34.80 [m, CH_2], 40.86−42.14 [m, CP], 61.37−61.74 [m, 6-CH_2-THP], 72.33−72.86 [m, CH_2O], 99.11−99.21 [m, 2-CH-THP], 127.71−136.75 [m, C_6H_5]. MS (FD), *m/z*: 978.9 [M^+]. Anal. Calcd for $C_{60}H_{69}O_6P_3$ (M_r 979.12): C, 73.60; H, 7.10. Found: C, 73.34, 7.27 H.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris(hydroxymethyl)-cyclohexane *P,P′,P″*-Trioxide (4b).** A 4.1 mL portion of an aqueous solution of H_2O_2 (30%, 20 mmol) and 2 mL of aqueous HCl (32%, 20 mmol) were added to a solution of 1.8 g (2 mmol) of **4** in a mixture of 120 mL of THF and 60 mL of H_2O. The reaction mixture was stirred at 50 °C for 70 h. The yellow solution was reduced to 60 mL in volume under reduced pressure, 120 mL of H_2O was added, and the pH was adjusted to 9−10 by addition of an aqueous solution of KOH (1 N). The mixture was stirred at room temperature for 1.5 h, during which a white, fluffy solid formed. The solid was collected on a sintered-glass frit, washed once with 10 mL of aqueous KOH (1 N), six times with 20 mL portions of H_2O, and dried in vacuo. Yield: 1.4 g (90%). Mp: 256 °C dec. IR (KBr, cm^{-1}): 3247 ν(OH), 1164 ν(PO). $^{31}P-\{^1H\}$ NMR ($[^2H_6]$DMSO): $\delta = 41.4$[s]. ^1H NMR ($[^2H_6]$DMSO): $\delta = 1.57$ [br d, $^2J_{HH} = 13.81$, $^3J_{PH} < 5.0$ Hz CHH_e], 2.32 [dt, $^2J_{HH} = 13.81$, $^3J_{PH} = 14.13$ Hz, 3 H, CHH_a], 3.64 [dd, $^3J_{PH} = 22.03$ Hz, $^3J_{HH} = 3.31$ Hz, 6 H, CH_2OH], 4.96 [t, $^3J_{HH} = 3.31$ Hz, 3 H, OH], 7.45−7.80 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($[^2H_6]$DMSO): $\delta = 23.03$ [s, CH_2], 42.38 [dt, $^1J_{PC} = 64.67$, $^3J_{PC} = 11.79$ Hz, CP], 62.87 [s, CH_2-OH], 128.27 [d, $^3J_{PC} = 10.77$ Hz, C_6H_5 *meta*], 131.09 [d, $^1J_{PC} = 88.93$ Hz, C_6H_5 *ipso*], 131.53 [br s, C_6H_5 *para*], 132.06 [d, $^2J_{PC} = 8.76$ Hz, C_6H_5 *ortho*]. MS (FAB), *m/z*: 774.7 [M^+]. Anal. Calcd for $C_{45}H_{45}O_6P_3$ (M_r 774.77): C, 69.76; H, 5.87. Found: C, 69.58; H, 5.72.

***cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)-cyclohexane *P,P′,P″*-Trioxide (5b).** A 4.1 mL portion of an aqueous solution of H_2O_2 (30%, 20 mmol) and 2 mL of aqueous HCl (32%, 20 mmol) were added to a solution of 1.9 g (2 mmol) of **5** in a mixture of 200 mL of THF and 40 mL of H_2O. The reaction mixture was stirred at 50 °C for 70 h. The yellow solution was reduced to 40 mL in volume under reduced pressure, 60 mL of H_2O was added, and the pH was adjusted to 9−10 by addition of an aqueous solution of KOH (1 N). The mixture was stirred at room temperature for 1.5 h, during which a white, fluffy solid formed. The precipitate was collected on a sintered-glass frit, washed once with 10 mL of aqueous KOH (1N), six times with 20 mL portions of H_2O, and dried in vacuo. Yield: 1.5 g (92%). Mp: 153 °C dec. IR (KBr, cm^{-1}): 1169 ν(PO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 41.2$ [s]. ^1H NMR ($CDCl_3$): $\delta = 1.96$ [br d, $^2J_{HH} = 14.18$, $^3J_{PH} < 5.0$ Hz, 3 H, CHH_e], 2.27 [dt, $^2J_{HH} = 14.18$, $^3J_{PH} = 14.08$ Hz, 3 H, CHH_a], 3.05 [s, 9 H, CH_2OCH_3], 3.61 [d, $^3J_{PH} = 22.06$ Hz, 6 H, CH_2OCH_3], 7.39−7.81 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.19$ [s, CH_2], 42.72 [dt, $^1J_{PC} = 65.41$, $^3J_{PC} = 11.61$ Hz, CP], 57.93 [s, CH_2OCH_3], 73.42 [d, $^2J_{PC} = 1.58$ Hz, CH_2OCH_3], 128.12 [d, $^3J_{PC} = 11.38$ Hz, C_6H_5 *meta*], 131.25 [br s, C_6H_5 *para*], 131.12 [d, $^1J_{PC} = 91.30$ Hz, C_6H_5 *ipso*], 132.41 [d, $^2J_{PC} = 8.53$ Hz, C_6H_5 *ortho*]. MS (FAB), *m/z*: 816.8 [M^+]. Anal. Calcd for $C_{48}H_{51}O_6P_3$ (M_r 816.85): C, 70.58; H, 6.29. Found: C, 70.37, H, 6.31.

X-ray Diffraction Study. Single crystals of **3** and **5** were grown from hot DMF (**3**) and by diffusion of diethyl ether into a THF solution of **5**. The crystals were mounted on a glass fiber and transferred to a

Table 1. Selected Bond Distances (Å), Angles (deg), and Torsional Angles (deg) for **3** and **5**

	3	**5**		**3**	**5**
Mo−P(1)	2.541(2)	2.516(2)	Mo−C(1)	1.974(8)	1.962(5)
Mo−P(2)	2.534(2)	2.516(2)	Mo−C(2)	1.914(9)	1.958(5)
Mo−P(3)	2.538(2)	2.529(2)	Mo−C(3)	1.966(10)	1.971(7)

	3	**5**
P(1)−Mo−P(3)	87.68(6)	86.62(4)
P(1)−Mo−P(2)	88.31(6)	86.99(5)
P(3)−Mo−P(2)	89.36(6)	89.25(5)
P(1)−Mo−C(1)	178.6(2)	178.3(2)
P(2)−Mo−C(2)	92.1(3)	177.31(14)
P(3)−Mo−C(3)	96.3(3)	178.0(2)
P(1)−Mo−C(2)	95.9(3)	95.40(14)
P(1)−Mo−C(3)	93.9(3)	93.5(2)
P(2)−Mo−C(1)	93.0(2)	93.6(2)
P(2)−Mo−C(3)	174.0(2)	92.8(2)
P(3)−Mo−C(1)	92.0(2)	94.9(2)
P(3)−Mo−C(2)	176.2(3)	92.1(2)
C(1)−Mo−C(2)	84.4(4)	84.0(2)
C(1)−Mo−C(3)	84.8(4)	84.9(2)
C(2)−Mo−C(3)	82.1(4)	85.9(2)
C(4)−C(5)−C(6)	120.5(6)	119.8(4)
C(6)−C(7)−C(8)	120.1(6)	120.0(4)
C(4)−C(9)−C(8)	120.0(6)	119.3(4)
C(5)−C(6)−C(7)	110.3(6)	111.2(4)
C(7)−C(8)−C(9)	110.3(6)	111.4(4)
C(5)−C(4)−C(9)	109.8(6)	110.3(4)

	3	**5**
C(7)−C(6)−C(5)−C(4)	42.05(9)	41.2(5)
C(5)−C(6)−C(7)−C(8)	−40.08(9)	−39.4(7)
C(6)−C(7)−C(8)−C(9)	40.90(9)	40.1(8)
C(7)−C(8)−C(9)−C(4)	−43.09(9)	−42.4(6)
C(5)−C(4)−C(9)−C(8)	44.42(9(	43.7(9)
C(6)−C(5)−C(4)−C(9)	−43.74(9)	−43.2(8)

Table 2. Experimental Data for the X-ray Diffraction Studies of **3** and **5**

	3	**5**
formula	$C_{63}H_{78}MoN_9O_9P_3$	$C_{51}H_{51}MoO_6P_3$
fw	1294.19	948.77
space group	*I*4	$P2_1/n$
a, Å	30.558(2)	11.705(5)
b, Å	30.501(4)	16.941(9)
c, Å	13.795(3)	22.526(9)
β, deg		96.51(3)
V, Å^3	12857.6(7)	4438(3)
Z	8	4
d_{calcd}, g cm^{-3}	1.337	1.420
μ(Mo Kα), mm^{-1}		0.455
μ(Cu Kα), mm^{-1}	2.878	
temp, K	208(2)	173(2)
R1[a]	0.053	0.054
wR2[b]	0.153	0.138

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/[\sum[w(F_o^2)^2]]^{0.5}$.

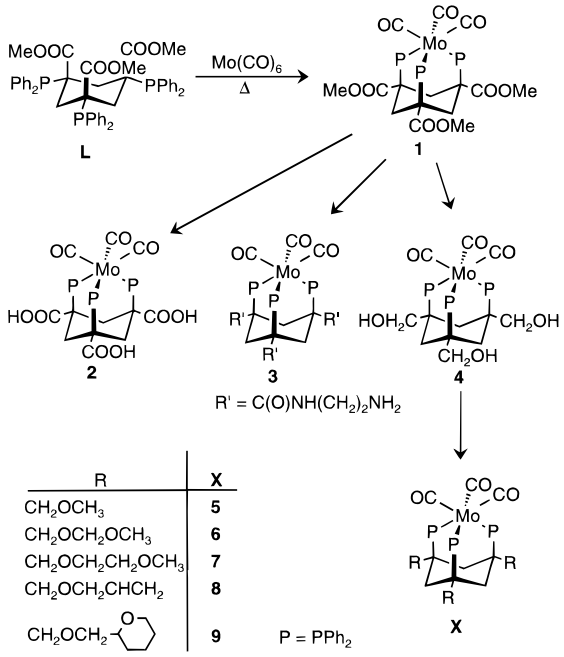
CAD4 (**3**) and a P4 Siemens diffractometer (**5**). In the case of **5**, rotation photographs were taken and a photosearch was performed to find a suitable reduced cell (graphite-monochromated Mo Kα radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods (**3**, **5**). The final cell parameters and specific data collection parameters for **3** and **5** are collected in Table 2. Intensities were collected with the *ω*-scan technique with scan speeds varying from 8 to 30° min^{-1} in *ω*. The structures of **3** and **5** were solved by direct[14] and Patterson[15] methods, respectively, and refined by least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). The hydrogen atoms bound to the nitrogen in compound **3** were determined in a difference Fourier map. Maximum and minimum peaks in the final difference synthesis were 0.943 and −0.482 e Å^{-3} (**3**) and 1.368 and −1.808 e Å^{-3} (**5**). The atoms C(604) and N(605) in complex **3** are highly disordered, due to the free rotation around the C(603)−C(604) bond. The asymmetric unit cell of compound **3** contains three molecules of DMF which were refined isotropically.

Results and Discussion

The functionalized phosphine tdppcyme (**L**) can easily be synthesized[8] on a large scale and is therefore an ideal starting material for the preparation of sterically crowded, water-soluble, and potentially bistripodal phosphine ligands and metal complexes. Structural investigations on **L** in the solid state as well as in solution showed that the ester functional groups prefer the axial positions whereas the sterically more demanding diphenylphosphine groups are oriented triequatorially at the cyclohexane backbone.[8] The sterically shielded ester groups cannot be converted to carboxylic acids or reduced to alcohols by standard organic methods. Under mild reaction conditions, no reaction is detected, whereas under more rigid conditions, two types of side reactions are observed: (i) the splitting of the phosphorus carbon bond to the cyclohexane ring; (ii) the oxidation of the phosphorus atoms to phosphine oxides. Thus the treatment of the ester tdppcyme (**L**) with an excess of aqueous acids[16] or bases,[17] as well as metal-assisted hydrolysis[18] in suitable cosolvents (THF, dioxane) at elevated temperatures and prolonged reaction times, did not lead to any reaction. The acidolysis with methanesulfonic acid in concentrated formic acid[19] at elevated temperatures resulted in oxidation of the phosphorus nuclei. A useful approach for the cleavage of sterically hindered esters involves the displacement of the carboxylate ion from the methyl group by nucleophilic reagents. Several well-established methods, lithium iodide in 2,6-luthidine, 2,4,6-collidine,[20,21] and DMF,[22] potassium *tert*-butoxide in DMSO,[23] and lithium and sodium *n*-propyl mercaptide in DMF,[24,25] were used, but either no reaction or the formation of *tert*-butoxydiphenylphosphine or (*n*-propylthio)diphenylphosphine, respectively, has been observed, as was demonstrated by $^{31}P\{^1H\}$ NMR spectroscopy. The reduction reactions performed on **L** show a similar reaction pattern. A wide variety of boron and aluminum hydrides with extremely different reactivities find application in the reduction of ester functional groups.[26] The reduction reactions performed with lithium aluminum hydride and alkoxy hydrides $Li[HAl(OMe)_3]$[27] under a variety of reaction conditions always resulted in the splitting

(14) Sheldrick, G. M. SHELX86. University of Göttingen, Germany, 1986.
(15) Sheldrick, G. M. SHELXTL 5.03 program. University of Göttingen, Germany, 1995.
(16) *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Georg-Thieme-Verlag: Stuttgart, Germany, 1952; Sauerstoffverbindungen III, Vol. 8, p 419.
(17) *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Georg-Thieme-Verlag: Stuttgart, Germany, 1952; Sauerstoffverbindungen III, Vol. 8, pp 421.
(18) Patai, S. *The Chemistry of the Carboxylic Acids*: Interscience Publishers: London, New York, Sydney, Toronto, 1969; p 538.
(19) Loev, B. *Chem. Ind. (London)* **1964** 193.
(20) Elsinger, F.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1960**, *43*, 113.
(21) Lüning, U.; Wangnick, C. *Liebigs. Ann. Chem.* **1992**, 481.
(22) Mayer, W. L.; Levinson, A. S. *J. Org. Chem.* **1963**, *28*, 2184.
(23) Chang, F.; Wood, N. F. *Tertrahedron Lett.* **1964**, 2969.
(24) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459.
(25) Feurtill, G. I.; Mirrington, R. N. *Aust. J. Chem.* **1972**, *25*, 1717, 1731.
(26) *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Georg-Thieme-Verlag: Stuttgart, New York, 1984; Alkohole III, Vol. 6/1b, pp 155.
(27) Brown, H. C.; Weissmann, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458.

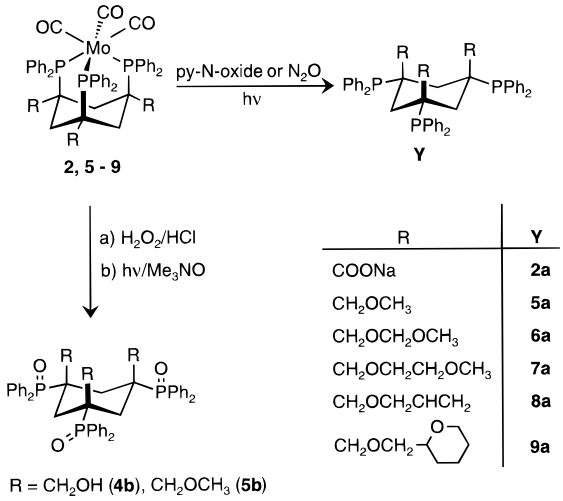
Scheme 1



of the phosphorus−carbon (cyclohexane ring) bond and the formation of lithium diphenylphosphide. In contrast, lithium and sodium boron hydrides like $LiBH_4$,[28] $NaHB(OMe)_3$,[29] and BH_3·THF[30] did not lead to any reaction, even at elevated temperatures and prolonged reaction times. This brief summary of the methods which were applied to the free ligand **L** leads to the conclusion that an even more intense search for suitable reaction conditions would not lead to a satisfying outcome.

These difficulties can be overcome by the coordination of the tdppcyme ligand (**L**) to an organometallic protection group. The $Mo(CO)_3$ fragment has turned out to be ideal for this purpose. Upon *facial* coordination of the tdppcyme ligand (**L**) to a single molybdenum center, the cyclohexane ring has to invert, which causes the ester functional groups to be located at the equatorial sites of the cyclohexane ring (Scheme 1). At these less sterically hindered positions, the ester functional groups are easily accessible to various reagents. Moreover, the strong metal−phosphorus bonds in **1** provide protection against the splitting of the phosphorus−carbon bond to the cyclohexane ring as well as the oxidation of the phosphorus nuclei. The tripodal ligand **L** reacts readily with $Mo(CO)_6$ at elevated temperatures to give the tricarbonylmolybdenum complex **1** in almost quantitative yield (Scheme 1). The colorless, heat- and air-stable $Mo(CO)_3$(tdppcyme) complex (**1**) forms an adamantane type structure as displayed in Scheme 1.[8] The ester groups in complex **1** are easily saponed to carboxylic acid groups by lithium *n*-propyl mercaptide in DMF and reduced to alcoholic groups by lithium aluminum hydride in THF to yield complexes **2** and **4**, respectively (Scheme 1). There are no side reactions, as can be seen by monitoring the reactions by $^{31}P\{^1H\}$ NMR spectroscopy. Both complexes are colorless, air stable, and slightly soluble in water. As expected for a carboxylic acid, the solubility of **2** increases in dilute aqueous bases. Treatment of **1** with ethylenediamine and NaH results in the formation of the carboxamide **3** (Scheme 1). The triol **4** smoothly reacts with alkylating agents under the conditions of the Williamson

Scheme 2



ether synthesis,[31] although elevated temperatures and prolonged reaction times are necessary for a complete conversion. Complex **5** is formed in a phase transfer reaction with dimethyl sulfate as the methylating agent during 70 h at room temperature. Deprotonation of compound **4** with NaH in THF results in the formation of the corresponding trisodium alcoholate. Consecutive treatment of the alcoholate with chloromethyl methyl ether, 1-methoxy-2-[(*p*-tolylsulfonyl)oxy]ethane,[11] and allyl bromide leads to the corresponding complexes **6**−**8**, respectively. Further, acid-catalyzed reactions can be performed without affecting the complex unit. Consequently, the acid-catalyzed addition of the hydroxyl function to 5,6-dihydro-4*H*-pyran yields the acetal **9** (Scheme 1).[32]

The examples given above demonstrate the versatility of the reaction conditions that can be applied to complexes **1** and **4** in order to alter their functional groups. To use the $Mo(CO)_3$ fragment as a convenient protection group in the synthesis of new functionalized tripodal phosphine ligands, it is compulsory to find a way of liberating the modified phosphine ligands from the $Mo(CO)_3$ fragment. Oxidizing the metal center leads to a breakdown of the adamantane-type framework and therefore exhibits a pathway for the formation of phosphine oxides (**4b**, **5b**) or the phosphine ligands (**2a**, **5a**−**9a**). When a mixture of aqueous, dilute hydrogen peroxide and hydrochloric acid[33] is added to a solution of the molybdenum complexes **4** and **5** in THF, the respective phosphine oxides **4b** and **5b** are formed in quantitative yields (Scheme 2). Under these conditions, only the phosphine oxides can be recovered irrespective of the amount of hydrogen peroxide used. If less than the stoichiometric amounts of hydrogen peroxide are added, both the molybdenum complex **4** or **5** and the phosphine oxide **4b** or **5b** are found in appropriate amounts. The phosphine oxides **4b** and **5b** cannot be deoxygenated to the corresponding phosphines with well-known and widely used reduction agents such as trichlorosilane or hexachlorodisilane.[34] The treatment of the phosphine oxides **4b** and **5b** with these silanes in refluxing

(28) Brown, H. C.; Mead, E. J.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1955**, *77*, 6209.
(29) Brown, H. C.; Mead, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 6263.
(30) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681.
(31) *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Georg-Thieme-Verlag: Stuttgart, Germany, 1965; Sauerstoffverbindungen I, Vol. 6/3; p 24.
(32) *Houben-Weyl Methoden der Organischen Chemie*; Georg-Thieme-Verlag, Stuttgart: New York, 1991; Erweiterungs- und Folgebände zur 4. Auflage, O/O- und O/S-Acetale, Vol. E 14a/1, p 330.
(33) Leipold, J. Ph.D. Thesis, University of Tübingen, 1995.
(34) (a) Fritsche, H.; Hasserodt, U.; Korte, F. *Chem. Ber.* **1965**, *98*, 171. (b) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

toluene for 14 days gave hardly any phosphines **4** and **5** but resulted in the formation of side products. The inert behavior toward reduction can be explained in terms of the steric constriction on the cyclohexane backbone and is consistent with the poor reactivity of the ester functional groups in tdppcyme (**L**) (see above).

In our search for oxidation conditions that lead directly from the molybdenum complexes to the phosphine ligands, we attempted the oxidation with trialkylamine oxides. In the case of phosphines which are coordinated to the $W(CO)_5$ fragment, the phosphines have been liberated with trimethylamine oxide thermally in the form of their oxides.[35] On treatment of **4** and **5** with trimethylamine oxide up to 160 °C, no reaction occurred. This is in agreement with the observations of Kölle et al., who clearly showed a correlation of the oxidation reaction rate with the frequency of the carbonyl vibrations.[36] In contrast, trimethylamine oxide reacts smoothly with **4** and **5** under irradiation with ultraviolet light at room or lower temperatures. Besides carbon monoxide and molybdenum trioxide, the phosphine oxides **4b** and **5b** are formed. If less than the stoichiometric amounts of trimethylamine oxide are used, both the molybdenum complex **4** or **5** and the phosphine oxide **4b** or **5b** are observed in appropriate amounts. The formation of the phosphine oxides is not unexpected, since it is a well-known fact that alkylamine oxides readily oxidize phosphines. This observation leads to the conclusion that the rate of oxidation of the phosphorus nuclei exceeds that of the breakdown of the molybdenum−phosphorus bond under these conditions. On the other hand, aromatic amine oxides like pyridine *N*-oxide are also known to react with alkyl- and arylphosphines,[37] but these oxygen transfer reactions only proceed at elevated temperatures. Therefore, activation of the oxidation of molybdenum by irradiation at room temperature and by using pyridine *N*-oxide as the oxidating agent leads to the desired functionalized tripodal phosphine ligands **2a** and **5a**−**9a** in good yields. Besides carbon monoxide and molybdenum trioxide, only the phosphines are formed, irrespective of the use of an overstoichiometric amount of pyridine *N*-oxide. The disadvantage of this procedure is the formation of deep red photo-byproducts which arise from the self-photoreaction of pyridine *N*-oxide. This necessitates work-up procedures that lead to a reduction in the overall yield.

Although the amounts of these byproducts are so small that they do not disturb the analysis of the phosphine ligands and their chemistry, it is not satisfying to obtain the phosphine ligands **2a** and **5a**−**9a** as red-brown foams or red-brown tough oils. The formation of photo-byproducts can be overcome if pyridine *N*-oxide is replaced by dinitrogen monoxide (N_2O). The irradiation of solutions of the molybdenum complexes **2** and **5**−**9** under a dinitrogen monoxide atmosphere (1 bar) at 10 °C gives the phosphine ligands as colorless to off-white foams or tough oils in high yields. Besides the phosphines **2a** and **5a**−**9a**, carbon monoxide, molybdenum trioxide, and dinitrogen are formed. Dinitrogen monoxide combines all advantages: (i) it serves as a selective oxidizing agent for the oxidation of molybdenum, (ii) it can be added in large excess, (iii) it does not absorb in the irradiation wavelength range, (iv) it can be easily separated from the reaction mixture, and (v) no photo side products besides the inert dinitrogen are formed.

Spectroscopic Characterization. The IR spectra are consistent with the facial coordination of the phosphine ligands in the molybdenum tricarbonyl complexes **2**−**9**, giving rise to two

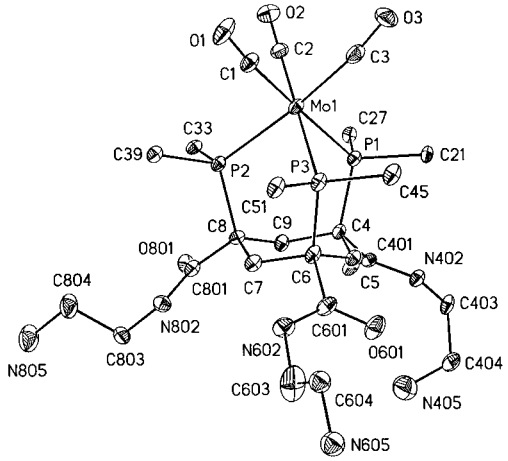


Figure 1. ORTEP drawing and atom-labeling scheme for the molybdenum complex **3**. Only the *ipso*-carbon atoms of the phenyl rings are shown for clarity.

ν(CO) absorptions in the ranges 1951−1936 and 1864−1843 cm^{-1}. Characteristic absorptions due to the vibrations of the functional groups are also observed for **2** [ν(COOH) = 1723 cm^{-1}], **3** [ν(CONH) = 1653 and 1512 cm^{-1}], and **4** [ν(OH) = 3578 and 3406 cm^{-1}], respectively.

The C_{3v} symmetry of the molybdenum complexes **2**−**8**, of the phosphine ligands **2a** and **5a**−**8a**, and of the phosphine oxides **4b** and **5b** is reflected in their ^1H, ^{13}C, and ^{31}P NMR spectroscopic data. Thus the $^{31}P\{^1H\}$ NMR spectra of all these compounds display a singlet with a chemical shift typical for coordinated and noncoordinated phosphines of this type.[5,8,38] The average coordination chemical shift is 17.1 ppm.

In the $^{13}C\{^1H\}$ NMR spectra, the ring methylene and the ring quarternary carbon atoms of the molybdenum complexes **2**−**8** display complex multiplet patterns whereas the phosphine ligands **2a** and **5a**−**8a** generate triplets and doublets of triplets caused by the interaction with the phosphorus nuclei. The exocyclic ring methylene groups of all functional groups are observed as broad singlets for **3**−**8** and as doublets for **5a**−**8a**, respectively. All other carbon nuclei of the functional groups of the complexes and ligands agree in number and multiplicity with the structures shown in Schemes 1 and 2.

Characteristic features in the ^1H NMR spectra of all compounds are the multiplets of the equatorial and axial ring methylene protons and of the protons of the functional groups (see Experimental Section). It is noteworthy that in the molybdenum complexes of **5**−**8** the chemical shifts of the axial and equatorial ring methylene protons are reversed with respect to the noncoordinated ligands **5a**−**8a**.

The chiral carbon atoms in the DHP functional groups generate four diastereomeric isomers of **9** and **9a**. In addition, in some of the diastereomers, the chiral carbon atoms cause the three phosphorus nuclei to become magnetically inequivalent. This leads to complex multiplet patterns in the NMR spectra of **9**. Further complications in the NMR spectra of **9a** originate from rotamers caused by the sterically demanding DHP groups.

X-ray Structures of 3 and 5. ORTEP drawings of the single-crystal X-ray structures of complexes **3** and **5** are shown in Figures 1 and 2, respectively. Table 1 contains selected bond distances and angles and torsional angles of both complexes. The stereochemical constraints of the tripodal phosphine ligands impose facial coordinations at the metal centers which lead to

(35) de Vaumas, R.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1992**, *114*, 261.
(36) Kölle, U. *J. Organomet. Chem.* **1977**, *133*, 53.
(37) Howard, E., Jr.; Olszewski, W. F. *J. Am. Chem. Soc*, **1959**, *81*, 1483.
(38) Mayer, H. A.; Otto, H.; Fawzi, R.; Steimann, M. *J. Organomet. Chem.* **1994**, *472*, 347.

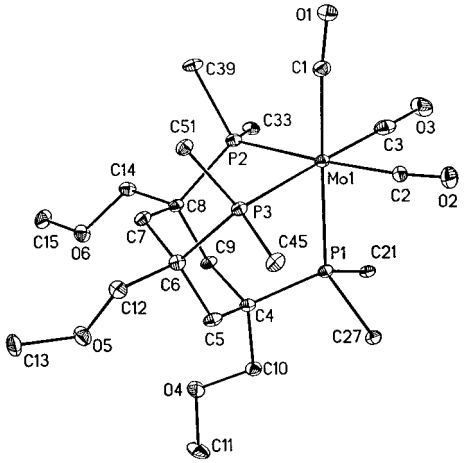


Figure 2. ORTEP drawing and atom-labeling scheme for the molybdenum complex **5**. Only the *ipso*-carbon atoms of the phenyl rings are shown for clarity.

adamantane-type structures. Three carbonyl ligands complete the octahedral environment around the molybdenum centers. The three functional groups in each complex are oriented equatorially at the *ipso* positions of the cyclohexane ring. The endocyclic bond angles at the ring methylene carbon atoms are widened to 120.2 and 119.7° (average) compared with 111.5° in cyclohexane.[39] As a consequence, the ring torsional angles are reduced to average values of ±42.4° (**3**) and of ±41.7° (**5**). This strong deviation from the ideal chair conformation of the cyclohexane ring (±55°) causes a flattening of the cyclohexane rings in **3** and **5**. In a series of comparable octahedral adamantane-type complexes {[Ir(tdppcy)Cl_3] (tdppcy = *cis*-1,3,5-tris(diphenylphosphino)cyclohexane, average ring torsional angle ±54.1°),[38] [Ir(tdppcyme)(H)(CO)Ph]$^+$ (ring torsional angles between 48.5 and 41.9°)[5b]}, the cyclohexane rings in **3** and **5** display the strongest deviations from the ideal chair conformation.

(39) (a) Wohl, R. A. *Chimia* **1964**, *18*, 219. (b) Davis, M.; Hassel, O. *Acta Chem. Scand.* **1963**, *17*, 1181.

Conclusion

In these studies it was demonstrated that the $Mo(CO)_3$ fragment can be applied as a convenient protection group for tripodal phosphines with cyclohexane as the backbone. It fulfills the requirement of protecting the phosphine from being oxidized and the P−C bond from being broken during functionalization of the ligand backbone. The modified phosphine ligands can be liberated by using oxidizing agents that are able to oxidize the metal at low temperatures and the phosphines only at elevated temperatures. In addition, UV light is required to activate the decomposition of the metal carbonyl fragment at low temperatures. The oxidation of the phosphine to phosphine oxide, which is the drawback in many other metal-assisted phosphine ligand syntheses, is thus avoided. These findings may therefore be of some importance in the synthesis of chiral phosphines.[40]

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Supporting Information Available: Listings of crystal data and structure refinement details, atomic coordinates with equivalent isotropic displacement coefficients, bond distances and angles, and anisotropic displacement parameters for **3** and **5** (29 pages). Ordering information is given on any current masthead page.

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(40) Pietrusiewicz, M. K.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.