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# Synthesis of Unsymmetrical Bidentate and Tridentate Phosphines by [4 + 2] Diels-Alder Cycloadditions and Michael Additions of (Phosphole)- and (Vinylphosphine)molybdenum Carbonyl Complexes

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The reaction of divinylphenylphosphine with (1-phenyl-3,4-dimethylphosphole)pentacarbonylmolybdenum(0) (**1**) yields two diastereomers of *syn-exo*-[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (**2a,b**) by an intramolecular [4 + 2] Diels-Alder cycloaddition. These two diastereomers were separated by a combination of column chromatography on silica gel and fractional crystallization. The major diastereomer (**2a**) undergoes Michael additions with $Ph_2PH$ and $Ph_2AsH$ to produce $Mo(CO)_4$ complexes of the new unsymmetrical asymmetric ligands 2-((2-(diphenylphosphino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene (**3**) and 2-((2-(diphenylarsino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene (**4**), respectively. In **3** and **4** the ligands are bidentate with dangling phosphino and arsino donor arms. Heating **3** and **4** liberates CO and converts them into their *fac*-$LMo(CO)_3$ counterparts (**5** and **6**). Similar Diels-Alder cycloadditions occur with **1** and vinyldiphenylphosphine and vinyldiethylphosphine and with the (vinylphosphine)molybdenum pentacarbonyl complexes and 1-phenyl-3,4-dimethylphosphole. New complexes have been characterized by elemental analyses, physical properties, $^1H$, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^1H/^{13}C$ HETCOR, COSY, and 2-DJ nuclear magnetic resonance spectroscopy and infrared spectroscopy. Compounds **2b** and **5** have been characterized by X-ray crystallography. Crystal data for **2b**: monoclinic, $C2/c$, $a = 18.277$ (5) Å, $b = 10.006$ (3) Å, $c = 27.650$ (8) Å, $\beta = 91.99$ (2)°, $V = 5053.6$ Å$^3$, $Z = 8$, $R = 0.033$ for 2596 independent observed ($I > 3\sigma(I)$) reflections. The donor abilities of the two phosphorus donors are quite different; Mo-P = 2.449 (1) and 2.513 (2) Å, and the C-P-C angle for the bridging phosphorus is small (80.1 (2)°). The chelate ring is rigid, and the molecule contains five asymmetric centers. Crystal data for **5**: monoclinic, $P2_1/c$, $a = 18.286$ (5) Å, $b = 11.379$ (3) Å, $c = 16.109$ (4) Å, $\beta = 91.99$ (2)°, $V = 3329.1$ Å$^3$, $Z = 4$, $R = 0.030$ for 3061 independent observed ($I > 3\sigma(I)$) reflections. The donor abilities of the three phosphorus donors are slightly different; Mo-P = 2.486 (1), 2.470 (1), and 2.481 (1) Å, and the C-P-C angle for the bridging phosphorus is small (79.7 (2)°). The molecule contains two fused five-membered chelate rings and five asymmetric centers.

## Introduction

We have recently reported that palladium,[2,3] platinum,[2,3] ruthenium,[4,5] and nickel[6] phosphole complexes undergo facile intramolecular [4 + 2] Diels-Alder cycloadditions with vinyl donor ligands. The nature of the vinyl donor that will participate is highly metal dependent. In each case these reactions were very diastereoselective, and for each of these metals the same diastereomers predominate. In order to gain a better understanding of those factors that influence the diastereoselectivity and to explore further the scope and limitations of these reactions, we have studied reactions of (1-phenyl-3,4-dimethylphosphole)pentacarbonylmolybdenum(0) with vinyl donors. We have also probed the utility of Michael additions to one of the products for the synthesis of unsymmetrical asymmetric triphosphines and arsino diphosphines and report the results herein. Our overall goal in this research is to develop a general process for the synthesis of novel chiral bidentate and tridentate ligands with a defined stereochemistry that will be useful in asymmetric synthesis and catalysis.

## Experimental Section

**A. Reagents and Physical Measurements.** Diphenylvinylphosphine, phenyldivinylphosphine, and diethylvinylphosphine (all from Organometallics, Inc.), diphenylphosphine and diphenylarsine (Pressure Chemical Co.), and 2,2′-azo bis(isobutyronitrile) (AIBN, Aldrich) were used as received. DMPP (1-phenyl-3,4-dimethylphosphole) was prepared as previously described.[7] Trimethylamine *N*-oxide dihydrate (Aldrich) was dried by mixing it with dry benzene and then removing the solvent on a rotary evaporator with heat. $CoCl_2 \cdot 2H_2O$ was obtained by heating $CoCl_2 \cdot 6H_2O$ (Baker Chemicals) under vacuum (0.1 mmHg) at 50 °C for approximately 5 h. Silica gel used for column chromatography (grade 12, 28-200 mesh) was obtained from Aldrich. All preparations were carried out under a dry dinitrogen atmosphere. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Infrared spectra were obtained on a Perkin-Elmer 599 spectrometer as $CH_2Cl_2$ or hexane solutions in sealed NaCl cells. $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer in the FT mode. $^1H$, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 300, 300, and 75 MHz, respectively, on a GE GN-300 spectrometer. Heteronuclear chemical shift correlated (HETCOR), homonuclear chemical shift correlated (COSY), and 2-DJ spectra were obtained as previously described[8] on a GN-300 spectrometer. Proton and carbon chemical shifts are relative to internal $Me_4Si$, while phosphorus chemical shifts are relative to external 85% $H_3PO_4$ with a positive value being downfield of the respective reference.

**B. Synthesis. (1-Phenyl-3,4-dimethylphosphole)pentacarbonylmolydbenum(0) (1).** A mixture containing 2.00 g (7.57 mmol) of molybdenum hexacarbonyl and 0.08 g of $CoCl_2 \cdot 2H_2O$[9] (0.48 mmol) in 10 mL of toluene and 10 mL of *n*-butyl ether was refluxed for 15 min. To the hot light blue solution was added 1.5 mL (7.97 mmol) of DMPP via syringe, and refluxing was continued for an additional 40 min. The green solution was cooled to room temperature, and 10 g of silica gel was added to adsorb the catalyst ($CoCl_2 \cdot 2H_2O$). The silica gel was extracted with five 10-mL portions of toluene; the extracts were combined, filtered, and evaporated to dryness. The oily greenish product contained a mixture of pentacarbonyl and tetracarbonylmolybdenum(0) complexes. Separation and purification was carried out by column chromatography on silica gel (hexane eluent). Evaporation of the hexane yielded colorless needles: yield 2.63 g, 82%; mp 92-93 °C (lit.[10] mp 91.5-92 °C). IR (hexane): $\nu_{CO}$ 2072 ($A_1{}^1$), 1991 ($B_1$), 1954 ($A_1{}^2$, E) cm$^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 2.0 (s, $CH_3$, 6 H), 6.2 (d, $^2J_{PH} = 35.5$ Hz, =CH, 2 H), 7.3-7.5 (m, Ar H, 5 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 16.83 (d, $^3J_{PC} = 10.25$ Hz, $CH_3$), 128.34 (d, $^3J_{PC} = 10.26$ Hz, $C_m$), 129.68 (d, $^2J_{PC} = 39.56$ Hz, $C_\alpha$), 129.71 (s, $C_p$), 130.76 (d, $^2J_{PC} = 14.62$ Hz, $C_o$), 149.25 (d, $^2J_{PC} = 8.8$ Hz, $C_\beta$), 204.80 (d, $^2J_{PC} = 8.8$ Hz, $CO_{cis}$), 209.24 (d, $^2J_{PC} = 19.05$ Hz, $CO_{trans}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 27.2. Anal. Calcd for $C_{17}H_{13}MoO_5P$: C, 48.13; H, 3.09. Found: C, 48.18; H, 2.92. Elution of the column with $CH_2Cl_2$ produced 0.4 g of *cis*-$(DMPP)_2Mo(CO)_4$[10] (mp 98-99 °C (lit.[10] mp 98-99 °C)) as bright yellow crystals. IR

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(hexane): $\nu_{CO}$ 2013, 1920, 1877 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.97 (s, CH$_3$, 12 H), 6.2 (d, $^2J_{PH}$ = 35.5 Hz, =CH, 4 H), 7.3–7.5 (m, Ar H, 10 H). $^{13}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 29.3. Anal. Calcd for $C_{28}H_{26}MoO_4P_2$: C, 57.54; H, 4.48. Found: C, 57.29; H, 4.27.

**(Phenyldivinylphosphine)pentacarbonylmolybdenum(0) (9).** To 2.67 g (10 mmol) of Mo(CO)$_6$ in 100 mL of methylcyclohexane was added 1.46 g (9 mmol) of PhVy$_2$P via syringe, and the mixture was refluxed for 2.5 h under N$_2$. The very pale yellow solution was filtered hot to remove unreacted Mo(CO)$_6$. Removal of the solvent via a rotary evaporator, extraction of the residue with hexane, and chromatography on silica gel with hexane gave a pale yellow oil;[11] yield 1.31 g, 33%. IR (hexane): $\nu_{CO}$ 2070 (A$_1{}^1$), 1992 (B$_1$), 1954 (A$_1{}^2$, E) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.78 (ddd, $^2J_{bc}$ = 1.46 Hz, $^3J_{ac}$ = 17.58 Hz, $^3J_{PH}$ = 17.60 Hz, H$_c$, 2 H), 6.15 (ddd, $^2J_{bc}$ = 1.46 Hz, $^3J_{ab}$ = 11.72 Hz, $^3J_{PH}$ = 36.13 Hz, H$_b$, 2 H), 6.55 (ddd, $^3J_{ab}$ = 11.72 Hz, $^3J_{ac}$ = 17.58 Hz, $^2J_{PH}$ = 20.76 Hz, H$_a$, 2 H), 7.4–7.6 (m, Ar H, 5 H). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 128.40 (d, $^3J_{PC}$ = 8.79 Hz, C$_m$), 129.71 (s, C$_p$, C$_\beta$), 131.00 (d, $^2J_{PC}$ = 11.72 Hz, C$_0$), 133.51 (d, $^1J_{PC}$ = 34.18 Hz, C$_\alpha$), 205.01 (d, $^2J_{PC}$ = 8.79 Hz, CO$_{cis}$), 209.52 (d, $^2J_{PC}$ = 22.0 Hz, CO$_{trans}$). $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 20.3.

**[2-(Phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (2). Method A.** A mixture containing 1.13 g (2.78 mmol) of (DMPP)Mo(CO)$_5$ (**1**) and 0.5 mL (3.08 mmol) of phenyldivinylphosphine in 25 mL of toluene was refluxed for 24 h. The green solution was cooled, decolorized with activated carbon, and filtered. The resulting yellow solution was evaporated to dryness and purified by column chromatography on silica gel (CH$_2$Cl$_2$/hexane (30:70) eluent). This effected separation of the two diastereomers of **2** from a mixture of facial and meridional tricarbonyl complexes. Both **2a** and **2b** elute from the column in advance of the other products. The two diastereomers, however, could not be separated from one another by column chromatography on silica gel. Fractional crystallization of the diastereomeric mixture from CH$_2$Cl$_2$/hexane afforded a separation. Diastereomer **2a** crystallized first as pale yellow crystals in yields of about 40%, with mp 181–183 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2027 (m), 1923 (sh), 1905 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.56 (s, CH$_3$, 6 H), 1.82 (m, $^3J_{PH}$ = 24.0 Hz, $^3J_{PH}$ = 19.2 Hz, $^2J_{HH}$ = 13.02 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 0.9 Hz, H$_4$, 1 H), 2.39 (ddt, $^3J_{P'H}$ = 22.4 Hz, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 2.1 Hz, $^3J_{PH}$ = 2.1 Hz, H$_3$, 1 H), 2.69 (dt, $^2J_{PH}$ = 4.8 Hz, $^3J_{PH}$ = 2.1 Hz, $^4J_{HH}$ = 2.1 Hz, H$_1$, 1 H), 2.86 (dtt, $^3J_{PH}$ = 34.9 Hz, $^2J_{P'H}$ = 9.2 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 2.1 Hz, $^2J_{HH}$ = 2.1 Hz, H$_2$, 1 H), 2.90 (dt, $^4J_{P'H}$ = 4.5 Hz, $^2J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 2.1 Hz, H$_5$, 1 H), 6.03 (ddd, $^3J_{P'H}$ = 42.4 Hz, $^3J_{HH}$ = 11.4 Hz, $^2J_{HH}$ = 1.5 Hz, H$_b$, 1 H), 6.03 (ddd, $^3J_{P'H}$ = 20.3 Hz, $^3J_{HH}$ = 17.9 Hz, $^2J_{HH}$ = 1.5 Hz, H$_c$, 1 H), 6.44 (ddd, $^3J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 11.4 Hz, $^2J_{P'H}$ = 10.5 Hz, H$_a$, 1 H), 7.20–7.76 (m, Ar H, 10 H). Anal. Calcd for $C_{26}H_{24}MoO_4P_2$: C, 55.93; H, 4.43. Found: C, 55.95; H, 4.35. Diastereomer **2b** was isolated from the filtrate as pale yellow crystals in yields of about 35%, with mp 151–155 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2026 (m), 1923 (sh), 1905 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.52 (s, CH$_3$, 3 H), 1.60 (m, $^3J_{PH}$ = 39.1 Hz, $^3J_{P'H}$ = 18.3 Hz, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 0.9 Hz, H$_4$, 1 H), 1.62 (s, CH$_3$, 3 H), 2.03 (m, $^3J_{P'H}$ = 22.8 Hz, $^2J_{HH}$ = 13.4 Hz, $^3J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 0.6 Hz, H$_3$, 1 H), 2.76 (m, $^3J_{PH}$ = 34.9 Hz, $^2J_{P'H}$ = 9.0 Hz, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 2.2 Hz, H$_2$, 1 H), 2.79 (m, $^2J_{PH}$ = 3.0 Hz, $^3J_{P'H}$ = 3.0 Hz, $^4J_{HH}$ = 1.2 Hz, H$_1$, 1 H), 2.84 (m, $^4J_{P'H}$ = 3.5 Hz, $^2J_{PH}$ = 1.8 Hz, $^4J_{HH}$ = 1.2 Hz, H$_5$, 1 H), 5.72 (ddd, $^3J_{P'H}$ = 18.3 Hz, $^3J_{HH}$ = 18.2 Hz, $^2J_{HH}$ = 0.9 Hz, H$_c$, 1 H), 5.92 (ddd, $^3J_{P'H}$ = 36.2 Hz, $^3J_{HH}$ = 11.8 Hz, $^2J_{HH}$ = 0.9 Hz, H$_b$, 1 H), 6.52 (ddd, $^3J_{HH}$ = 18.2 Hz, $^2J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 11.8 Hz, H$_a$, 1 H), 7.20–7.80 (m, Ar H, 10 H). Anal. Calcd for $C_{26}H_{24}MoO_4P_2$: C, 55.93; H, 4.33. Found: C, 55.91; H, 4.32.

**Method B.** A mixture containing 1.19 g (3 mmol) of (PhVy$_2$P)Mo(CO)$_5$ (**9**) and 0.56 mL (3.0 mmol) of DMPP in 35 mL of toluene was refluxed for 12 h. The resulting brown solution was evaporated to dryness and purified by column chromatography and fractional crystallization as in method A. There was obtained a 40% yield of diastereomer **2a** and a 35% yield of diastereomer **2b**.

**[2-(Diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (7).** A mixture containing 2.00 g (4.9 mmol) of (DMPP)Mo(CO)$_5$ (**1**) and 1.2 mL (5.09 mmol) of Ph$_2$VyP in 25 mL of toluene was refluxed for 24 h. The resulting green solution was cooled to room temperature, decolorized with activated carbon, and filtered. The resulting yellow solution was evaporated to dryness and purified by column chromatography on silica gel (CH$_2$Cl$_2$/hexane (30:70) eluent), followed by recrystallization from CH$_2$Cl$_2$/95% ethanol to yield 0.890 g (30%) of light yellow, slightly light-sensitive crystals, mp 230–232 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2027 (m), 1920 (sh), 1905 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.56 (s, CH$_3$, 3 H), 1.60 (m, $^3J_{PH}$ = 24.7 Hz, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{PH}$ = 7.8 Hz, H$_4$, 1 H), 1.65 (s, CH$_3$, 3 H), 2.18 (m, $^3J_{P'H}$ = 22.9 Hz, $^2J_{HH}$ = 13.7 Hz, $^3J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 1.0 Hz, H$_3$, 1 H), 2.87 (s, H$_1$, 1 H), 2.88 (d, $^4J_{HH}$ = 1.4 Hz, H$_5$, 1 H), 3.23 (m, $^3J_{PH}$ = 34.6 Hz, $^2J_{P'H}$ = 9.0 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 1.0 Hz, H$_2$, 1 H), 7.1–7.9 (m, Ar H, 15 H). Anal. Calcd for $C_{30}H_{26}MoO_4P_2$: C, 59.22; H, 4.31. Found: C, 58.93; H, 4.41.

**[2-(Diethylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (8).** In a similar manner as for **7**, from 3.66 g (8.63 mmol) of (DMPP)Mo(CO)$_5$ (**1**) and 1.0 mL (8.61 mmol) of Et$_2$VyP were obtained 2.40 g (55%) of colorless crystals, mp 153–154 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2022 (m), 1918 (sh), 1905 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.14 (td, $^3J_{P'H}$ = 4.2 Hz, $^3J_{HH}$ = 7.8 Hz, CH$_2$C*H*$_3$, 3 H), 1.18 (td, $^3J_{P'H}$ = 5.1 Hz, $^3J_{HH}$ = 7.5 Hz, CH$_2$C*H*$_3$, 3 H), 1.54 (s, CH$_3$, 3 H), 1.56 (s, CH$_3$, 3 H), 1.76 (m, $^3J_{PH}$ = 22.5 Hz, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{P'H}$ = 2.1 Hz, H$_4$, 1 H), 1.82–2.04 (m, CH$_2$, 4 H), 2.21 (m, $^3J_{PH}$ = 35.5 Hz, $^2J_{P'H}$ = 8.1 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 1.6 Hz, H$_2$, 1 H), 2.27 (m, $^3J_{P'H}$ = 20.1 Hz, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 2.4 Hz, H$_3$, 1 H), 2.68 (dd, $^2J_{PH}$ = 3.0 Hz, $^3J_{P'H}$ = 1.2 Hz, H$_1$, 1 H), 2.84 (m, $^2J_{PH}$ = 3.0 Hz, $^4J_{P'H}$ = 3.0 Hz, $^4J_{HH}$ = 1.6 Hz, H$_5$, 1 H), 7.2–7.4 (m, Ar H, 5 H). Anal. Calcd for $C_{22}H_{26}MoO_4P_2$: C, 51.58; H, 5.11. Found: C, 51.84; H, 5.12.

**[Dimeric (1-phenyl-3,4-dimethylphosphole)]tetracarbonylmolybdenum(0) (10).** A mixture containing 1.08 g (2.66 mmol) of (DMPP)Mo(CO)$_5$ (**1**) and 0.5 mL (1.89 mmol) of DMPP in 25 mL of toluene was refluxed in the dark for 24 h. The resulting green solution was cooled to room temperature, decolorized with activated carbon, and filtered. The resulting yellow solution was evaporated to dryness. A $^{31}$P{$^1$H} NMR spectrum of the crude product showed it to be a mixture of *cis*-(DMPP)$_2$Mo(CO)$_4$[10] ($\delta$($^{31}$P) = 29.3) and the Diels–Alder dimer[10] ($\delta$($^{31}$P) = 52.62, 159.35; $^2J_{PP}$ = 9.8 Hz). Separation and purification of the Diels–Alder dimer was carried out by column chromatography on silica gel (CH$_2$Cl$_2$/hexane (30:70) eluent) followed by recrystallization from CH$_2$Cl$_2$/95% ethanol to yield 0.56 g (36%) of yellow crystals, mp 230–235 °C (lit.[10] mp 170 °C). IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2007 (m), 1915 (s), 1875 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.20 (s, CH$_3$, 3 H), 1.51 (d, $^4J_{HH}$ = 1.2 Hz, CH$_3$, 3 H), 1.56 (s, CH$_3$, 3 H), 2.00 (d, $^4J_{PH}$ = 1.2 Hz, CH$_3$, 3 H), 2.65 (ddd, $^3J_{PH}$ = 40.9 Hz, $^2J_{P'H}$ = 6.3 Hz, $^3J_{HH}$ = 3.3 Hz, H$_2$, 1 H), 2.69 (dd, $^2J_{PH}$ = 6.0 Hz, $^4J_{HH}$ = 1.8 Hz, H$_5$, 1 H), 3.01 (ddd, $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.8 Hz, $^2J_{PH}$ = 1.5 Hz, H$_1$, 1 H), 6.23 (dq, $^2J_{PH}$ = 34.3 Hz, $^4J_{HH}$ = 1.2 Hz, =CH, 1 H), 7.3–7.6 (m, Ar H, 10 H). Anal. Calcd for $C_{28}H_{26}MoO_4P_2$: C, 57.54; H, 4.48. Found: C, 57.39; H, 4.42.

**[2-((2-(Diphenylphosphino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (3).** A mixture containing 0.29 g (0.51 mmol) of **2a**, 0.2 mL (1.15 mmol) of Ph$_2$PH, and 0.10 g (0.61 mmol) of AIBN was heated without solvent (in an oil bath) at 75 °C for 17 h. Excess Ph$_2$PH was then removed at 80 °C under vacuum for 2 h. The creamish colored oily product was crystallized from CH$_2$Cl$_2$/CH$_3$OH at 0 °C to yield 0.285 g (75%) of colorless crystals, mp 260–267 °C dec. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2025 (m), 1924 (sh), 1900 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.48 (s, CH$_3$, 3 H), 1.55 (s, CH$_3$, 3 H), 1.6 (m, H$_4$, 1 H), 1.9 (m, $^3J_{P'H}$ = 21.9 Hz, $^2J_{HH}$ = 14.0 Hz, $^3J_{PH}$ = 0.9 Hz, H$_3$, 1 H), 1.95–2.1 (m, CH$_2$, 2 H), 2.15–2.4 (m, CH$_2$, 2 H), 2.58 (m, $^3J_{PH}$ = 34.9 Hz, $^2J_{P'H}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 1.8 Hz, H$_2$, 1 H), 2.72 (s, H$_1$, 1 H), 2.73 (m, H$_5$, 1 H), 7.0–7.81 m (Ar H, 20 H). Anal. Calcd for $C_{38}H_{35}MoO_4P_3$: C, 61.30; H, 4.74. Found: C, 61.52; H, 4.83.

***fac*-[2-((2-(Diphenylphosphino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tricarbonylmolybdenum(0) (5).** A solution containing 0.10 g (0.13 mmol) of **3** in 15 mL 2-methoxyethyl ether was refluxed for 4 h. The solvent was removed under vacuum at 50 °C, and the resulting oily product was recrystallized from CH$_2$Cl$_2$/CH$_3$OH to yield 0.250 g (27%) of colorless crystals, mp 265–271 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 1943 (s), 1855 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.24 (d, $^4J_{PH}$ = 1.5 Hz, CH$_3$, 3 H), 1.41 (m, $^3J_{PH}$ = 21.0 Hz, $^3J_{P'H}$ = 21.0 Hz, $^2J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 8.4 Hz, H$_4$, 1 H), 1.56 (d, $^4J_{PH}$ = 0.9 Hz, CH$_3$, 3 H), 2.15–2.50 (m, CH$_2$, 4 H), 2.19 (m, H$_1$, 1 H), 2.32 (m, H$_3$, 1 H), 2.62 (m, $^3J_{PH}$ = 35.5 Hz, $^3J_{HH}$ = 8.4 Hz, $^2J_{P'H}$ = 7.5 Hz, $^3J_{HH}$ = 0.9 Hz, H$_2$, 1 H), 2.73 (s, H$_5$, 1 H), 7.0–8.0 (m, Ar H, 20 H). Anal. Calcd for $C_{37}H_{35}MoO_3P_3$: C, 62.02; H, 4.92. Found: C, 61.97; H, 4.92.

**[2-((2-(Diphenylarsino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (4).** To a solution containing 0.50 g (0.85 mmol) of **2a** in 20 mL of dry tetrahydrofuran (THF) was added 0.06 g (0.53 mmol) of potassium *tert*-butoxide and 0.2 mL (0.87 mmol) of Ph$_2$AsH in 15 mL of dry THF. The reaction mixture was refluxed for 15 h, after which the solvent was removed on a rotary evaporator at 50 °C. The resulting pasty residue was chromatographed on silica gel (CH$_2$Cl$_2$/hexane (50:50) eluent) and the product recrystallized from CH$_2$Cl$_2$/CH$_3$OH to yield 0.67 g (82%) of colorless crystals, mp 248–254 °C dec. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 2025 (m),

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(11) Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288.

**Table I.** Crystal and Refinement Data for Compounds **2b** and **5**

| | **2b** | **5** |
|---|---|---|
| formula | $C_{26}H_{24}MoO_4P_2$ | $C_{37}H_{35}MoO_3P_3$ |
| fw | 558.37 | 716.55 |
| *a*, Å | 18.277 (5) | 18.286 (5) |
| *b*, Å | 10.006 (3) | 11.379 (3) |
| *c*, Å | 27.650 (8) | 16.109 (4) |
| *β*, deg | 91.99 (2) | 96.67 (2) |
| space group | *C*2/*c* | *P*2$_1$/*c* |
| *Z* | 8 | 4 |
| *d*(calcd), g cm$^{-3}$ | 1.468 | 1.430 |
| *μ*, cm$^{-1}$ | 57.837 | 49.442 |
| abs factor range | 0.79–1.22 | 0.78–1.29 |
| temp, °C | -100 | -100 |
| final *R*(*F*)[a] | 0.033 | 0.030 |
| final $R_w(F)$ | 0.061 | 0.050 |

[a] Minimizing $\sum w(|F_o| - |F_c|)^2$ with $\sigma^2(F^2) = \sigma^2(\text{counts}) + (pI)^2$.

**Table II.** Atom Coordinates for $C_{26}H_{24}MoO_4P_2$ (**2b**)[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Mo | 0.63715 (2) | 0.24126 (3) | 0.66554 (1) | 2.522 (9) |
| P1 | 0.76353 (6) | 0.2240 (1) | 0.63950 (4) | 2.51 (2) |
| P2 | 0.65604 (6) | −0.0059 (1) | 0.65582 (4) | 2.56 (2) |
| C1 | 0.7801 (2) | 0.0641 (5) | 0.6073 (1) | 2.73 (9) |
| C2 | 0.8632 (2) | 0.0604 (5) | 0.6045 (2) | 3.2 (1) |
| C3 | 0.8943 (2) | 0.1121 (4) | 0.6447 (2) | 2.96 (9) |
| C4 | 0.8367 (2) | 0.1524 (4) | 0.6796 (2) | 2.64 (9) |
| C5 | 0.8981 (3) | −0.0049 (5) | 0.5623 (2) | 4.5 (1) |
| C6 | 0.9750 (3) | 0.1192 (5) | 0.6591 (2) | 4.5 (1) |
| C7 | 0.7994 (2) | 0.0201 (4) | 0.6941 (2) | 2.88 (9) |
| C8 | 0.7564 (2) | −0.0299 (4) | 0.6491 (2) | 2.83 (9) |
| C9 | 0.8015 (2) | 0.3625 (4) | 0.6057 (2) | 2.67 (9) |
| C10 | 0.8236 (3) | 0.4745 (5) | 0.6302 (2) | 3.3 (1) |
| C11 | 0.8463 (3) | 0.5865 (5) | 0.6061 (2) | 4.4 (1) |
| C12 | 0.8465 (3) | 0.5858 (5) | 0.5564 (2) | 4.9 (1) |
| C13 | 0.8255 (3) | 0.4749 (6) | 0.5308 (2) | 5.2 (1) |
| C14 | 0.8030 (3) | 0.3589 (5) | 0.5556 (2) | 4.1 (1) |
| C15 | 0.6153 (2) | −0.1039 (4) | 0.6058 (2) | 2.84 (9) |
| C16 | 0.6452 (3) | −0.2263 (5) | 0.5925 (2) | 3.7 (1) |
| C17 | 0.6094 (3) | −0.3036 (6) | 0.5572 (2) | 4.2 (1) |
| C18 | 0.5464 (3) | −0.2602 (5) | 0.5349 (2) | 4.4 (1) |
| C19 | 0.5170 (3) | −0.1395 (6) | 0.5479 (2) | 4.6 (1) |
| C20 | 0.5508 (2) | −0.0616 (5) | 0.5829 (2) | 3.8 (1) |
| C21 | 0.6341 (2) | −0.1128 (4) | 0.7060 (2) | 3.2 (1) |
| C22 | 0.5899 (2) | −0.0723 (5) | 0.7403 (2) | 3.6 (1) |
| C23 | 0.6447 (2) | 0.4368 (5) | 0.6756 (2) | 3.09 (9) |
| O1 | 0.6522 (2) | 0.5492 (3) | 0.6827 (1) | 4.68 (8) |
| C24 | 0.6085 (3) | 0.2740 (5) | 0.5956 (2) | 3.5 (1) |
| O2 | 0.5930 (2) | 0.3003 (5) | 0.5563 (1) | 6.4 (1) |
| C25 | 0.5307 (3) | 0.2374 (4) | 0.6822 (2) | 3.4 (1) |
| O3 | 0.4706 (2) | 0.2390 (4) | 0.6916 (2) | 5.5 (1) |
| C26 | 0.6699 (2) | 0.2196 (5) | 0.7358 (2) | 2.99 (9) |
| O4 | 0.3096 (2) | 0.2081 (3) | 0.7242 (1) | 3.85 (7) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table III.** Atom Coordinates for $C_{37}H_{35}MoO_3P_3$ (**5**)[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Mo | 0.74993 (2) | 0.05862 (3) | 0.12027 (2) | 1.926 (8) |
| P1 | 0.84116 (6) | 0.2064 (1) | 0.08380 (7) | 2.14 (2) |
| C1 | 0.8300 (2) | 0.2456 (4) | −0.0291 (3) | 2.21 (9) |
| C2 | 0.9026 (2) | 0.3043 (4) | −0.0411 (3) | 2.46 (9) |
| C3 | 0.9575 (2) | 0.2538 (4) | 0.0067 (3) | 2.34 (9) |
| C4 | 0.9298 (2) | 0.1493 (4) | 0.0527 (3) | 2.6 (1) |
| C5 | 0.9053 (3) | 0.4047 (5) | −0.1010 (3) | 3.5 (1) |
| C6 | 1.0387 (3) | 0.2820 (5) | 0.0145 (3) | 4.0 (1) |
| C7 | 0.9013 (2) | 0.0603 (4) | −0.0171 (3) | 2.6 (1) |
| C8 | 0.8310 (2) | 0.1168 (4) | −0.0640 (3) | 2.31 (9) |
| C9 | 0.8690 (2) | 0.3394 (4) | 0.1397 (3) | 2.39 (9) |
| C10 | 0.8439 (3) | 0.4499 (4) | 0.1129 (3) | 3.4 (1) |
| C11 | 0.8667 (3) | 0.5502 (5) | 0.1535 (3) | 4.6 (1) |
| C12 | 0.9163 (3) | 0.5441 (5) | 0.2236 (3) | 4.5 (1) |
| C13 | 0.9434 (3) | 0.4370 (5) | 0.2532 (3) | 4.5 (1) |
| C14 | 0.9190 (3) | 0.3341 (5) | 0.2121 (3) | 3.6 (1) |
| P2 | 0.75185 (6) | 0.0342 (1) | −0.03182 (7) | 2.13 (2) |
| C15 | 0.7617 (2) | −0.1088 (4) | −0.0808 (3) | 2.08 (9) |
| C16 | 0.7645 (2) | −0.2106 (4) | −0.0342 (3) | 2.29 (9) |
| C17 | 0.7705 (3) | −0.3184 (4) | −0.0717 (3) | 3.1 (1) |
| C18 | 0.7734 (3) | −0.3269 (4) | −0.1568 (3) | 3.2 (1) |
| C19 | 0.7719 (3) | −0.2254 (4) | −0.2040 (3) | 3.2 (1) |
| C20 | 0.7661 (2) | −0.1177 (4) | −0.1667 (3) | 2.8 (1) |
| C21 | 0.6694 (2) | 0.0996 (4) | −0.0923 (3) | 2.7 (1) |
| C22 | 0.6052 (2) | 0.1040 (4) | −0.0390 (3) | 2.6 (1) |
| P3 | 0.63604 (6) | 0.1649 (1) | 0.06524 (7) | 2.25 (2) |
| C23 | 0.5542 (2) | 0.1538 (4) | 0.1216 (3) | 2.57 (9) |
| C24 | 0.4893 (3) | 0.2103 (5) | 0.0905 (3) | 3.6 (1) |
| C25 | 0.4298 (3) | 0.2108 (5) | 0.1356 (4) | 4.2 (1) |
| C26 | 0.4338 (3) | 0.1546 (2) | 0.2115 (3) | 4.6 (1) |
| C27 | 0.4967 (3) | 0.0954 (6) | 0.2418 (3) | 5.1 (1) |
| C28 | 0.5562 (3) | 0.0950 (5) | 0.1955 (3) | 3.8 (1) |
| C29 | 0.6361 (2) | 0.3235 (4) | 0.0493 (3) | 2.33 (9) |
| C30 | 0.6127 (3) | 0.3790 (5) | −0.0251 (3) | 4.5 (1) |
| C31 | 0.6098 (4) | 0.5007 (5) | −0.0300 (4) | 5.4 (1) |
| C32 | 0.6303 (3) | 0.5680 (4) | 0.0384 (4) | 3.9 (1) |
| C33 | 0.6558 (3) | 0.5156 (5) | 0.1123 (3) | 4.0 (1) |
| C34 | 0.6585 (3) | 0.3929 (5) | 0.1176 (3) | 3.6 (1) |
| C35 | 0.8337 (2) | −0.0488 (4) | 0.1537 (3) | 2.5 (1) |
| O1 | 0.8793 (2) | −0.1166 (3) | 0.1720 (2) | 4.23 (8) |
| C36 | 0.6847 (3) | −0.0774 (4) | 0.1316 (3) | 3.0 (1) |
| O2 | 0.6484 (2) | −0.1603 (3) | 0.1370 (2) | 4.44 (8) |
| C37 | 0.7435 (2) | 0.1200 (4) | 0.2340 (3) | 2.7 (1) |
| O3 | 0.7370 (2) | 0.1607 (4) | 0.2983 (2) | 5.16 (9) |

[a] See footnote *a* of Table II.

1922 (sh), 1900 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.48 (d, $^4J_{PH}$ = 1.5 Hz, CH$_3$, 3 H), 1.55 (s, CH$_3$, 3 H), 1.6 (m, H$_4$, 1 H), 1.89 (dd, $^3J_{P'H}$ = 22.0 Hz, $^2J_{HH}$ = 13.4 Hz, H$_3$, 1 H), 2.06 (m, CH$_2$, 4 H), 2.58 (m, $^3J_{PH}$ = 35.1 Hz, $^2J_{P'H}$ = 8.6 Hz, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 1.7 Hz, H$_2$, 1 H), 2.71 (d, $^3J_{PH}$ = 1.7 Hz, H$_1$, 1 H), 2.73 (d, $^3J_{PH}$ = 1.8 Hz, H$_5$), 7.0–7.8 (m, Ar H, 20 H). Anal. Calcd for $C_{38}H_{35}AsMoO_4P_2 \cdot C_6H_5CH_3$: C, 59.73; H, 4.71. Found: C, 59.54; H, 5.09. The presence of toluene was confirmed by $^1$H NMR spectroscopy.

***fac*-[2-((2-(Diphenylarsino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tricarbonylmolybdenum(0) (6).** A solution containing 0.26 g (0.33 mmol) of **4** in 30 mL of 2-methoxyethyl ether was refluxed for 6 h. The solvent was removed under vacuum at 60 °C and the residue recrystallized from CH$_2$Cl$_2$/CH$_3$OH to yield 0.17 g (67%) of colorless crystals, mp 246–249 °C. IR (CH$_2$Cl$_2$): $\nu_{CO}$ 1942 (m), 1852 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 1.26 (d, $^4J_{PH}$ = 0.9 Hz, CH$_3$, 3 H), 1.42 (m, $^3J_{PH}$ = 21.0 Hz, $^3J_{P'H}$ = 21.0 Hz, $^2J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 8.0 Hz, H$_4$, 1 H), 1.53 (s, CH$_3$, 3 H), 1.92 (m, $^3J_{P'H}$ = 14.4 Hz, $^2J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 7.6 Hz, H$_3$, 1 H), 2.17 (d, $^2J_{PH}$ = 1.5 Hz, H$_1$, 1 H), 2.26–2.44 (m, CH$_2$, 2 H), 2.44–2.60 (m, CH$_2$, 2 H), 2.64 (m, $^3J_{P'H}$ = 35.5 Hz, $^2J_{PH}$ = 8.7 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 1.0 Hz, H$_2$, 1 H), 2.74 (s, H$_5$, 1 H), 6.8–8.0 (m, Ar H, 20 H). Anal. Calcd for $C_{37}H_{35}AsMoO_3P_2$: C, 58.44; H, 4.64. Found: C, 58.79; H, 4.81.

**C. X-ray Data Collection and Processing.** Yellow plates of **2b** and **5** were isolated from CH$_2$Cl$_2$/CH$_3$OH solutions at room temperature. Crystal data and details of data collection are given in Table I. Data were obtained at −100 °C, achieved by using a locally built gas-flow device. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[12] was used with the exception of a local data reduction program. The raw step-scan data were converted to intensities by using the Lehmann–Larsen methods[13] and then corrected for Lorentz and polarization factors.

The structures were solved by using the heavy-atom method. After refinement of the heavy atoms, difference-Fourier maps revealed maximas of residual electronic densities close to the positions expected for the hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B(\text{H}) = 1.3[B_{eqv}(\text{C})]$ Å$^2$ but not refined. For **2b** the C22 hydrogen atoms were not introduced. At this stage empirical absorption corrections were applied by using the method of Walker and Stuart[14] since face indexation was not possible under the cold gas stream. Final difference maps revealed no significant maxima. The scattering

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(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1983**, *A39*, 158.

Table IV. Selected Bond Distances (Å) for Compounds **2b** and **5**

| **2b** | | **5** | |
|---|---|---|---|
| Mo-P1 | 2.499 (1) | Mo-P1 | 2.486 (1) |
| Mo-P2 | 2.513 (2) | Mo-P2 | 2.470 (1) |
| Mo-C23 | 1.980 (4) | Mo-P3 | 2.481 (1) |
| Mo-C24 | 2.014 (6) | Mo-C35 | 1.986 (5) |
| Mo-C25 | 2.017 (5) | Mo-C36 | 1.976 (5) |
| Mo-C26 | 2.024 (5) | Mo-C37 | 1.976 (5) |
| P1-C1 | 1.861 (4) | P1-C1 | 1.861 (5) |
| P1-C4 | 1.851 (4) | P1-C4 | 1.867 (4) |
| C2-C3 | 1.337 (6) | C2-C3 | 1.323 (6) |
| C23-O1 | 1.150 (5) | C35-O1 | 1.149 (5) |
| C24-O2 | 1.143 (6) | C36-O2 | 1.161 (6) |
| C25-O3 | 1.136 (6) | C37-O3 | 1.154 (5) |
| C26-O4 | 1.162 (5) | | |

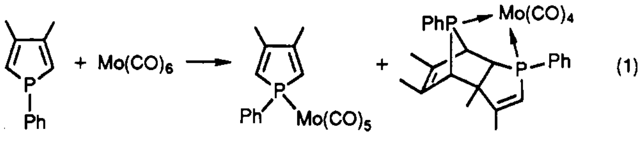
Table V. Selected Bond Angles (deg) for Compounds **2b** and **5**

| **2b** | | **5** | |
|---|---|---|---|
| P1-Mo-P2 | 76.38 (3) | P1-Mo-P2 | 75.78 (4) |
| P1-Mo-C23 | 92.9 (2) | P1-Mo-P3 | 98.30 (4) |
| P1-Mo-C24 | 86.9 (1) | P1-Mo-C35 | 87.8 (1) |
| P1-Mo-C25 | 173.5 (1) | P1-Mo-C36 | 168.6 (1) |
| P1-Mo-C26 | 91.4 (1) | P1-Mo-C37 | 95.4 (1) |
| P2-Mo-C23 | 168.0 (2) | P2-Mo-P3 | 78.97 (4) |
| P2-Mo-C24 | 95.1 (1) | P2-Mo-C35 | 95.7 (1) |
| P2-Mo-C25 | 98.2 (1) | P2-Mo-C36 | 94.7 (1) |
| P2-Mo-C26 | 87.8 (1) | P2-Mo-C37 | 165.6 (1) |
| C23-Mo-C24 | 89.3 (2) | P3-Mo-C35 | 170.6 (1) |
| C23-Mo-C25 | 92.9 (2) | P3-Mo-C36 | 85.7 (1) |
| C23-Mo-C26 | 87.4 (2) | P3-Mo-C37 | 91.2 (1) |
| C24-Mo-C25 | 90.1 (2) | C35-Mo-C36 | 87.0 (2) |
| C24-Mo-C26 | 176.2 (2) | C35-Mo-C37 | 95.4 (2) |
| C25-Mo-C26 | 92.0 (2) | C36-Mo-C37 | 95.2 (2) |
| C1-P1-C4 | 80.1 (2) | C1-P1-C4 | 79.7 (2) |

factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 15. Final atom coordinates for **2b** and **5** are given in Tables II and III and selected bond lengths and angles in Tables IV and V, respectively.

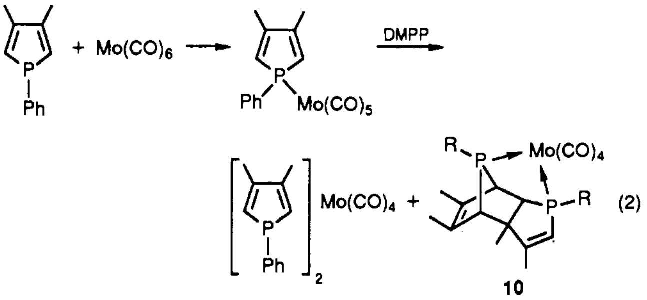
## Results and Discussion

**I. General Reactions of Molybdenum Carbonyl Complexes. A. Reaction of DMPP with Molybdenum Hexacarbonyl.** Mathey and co-workers[10] discovered that, in a photochemical reaction between DMPP and $Mo(CO)_6$, the Diels-Alder *exo*-phosphole dimer **10** was formed along with the classical $(DMPP)Mo(CO)_5$ (reaction 1). Since the free phosphole does not dimerize, they concluded that dimerization takes place within the coordination sphere of the metal. In view of the Woodward-Hoffmann rules, they postulated that the initial [2 + 2] photodimer underwent thermal rearrangement to the [4 + 2] dimer. In the present work, the reaction of $Mo(CO)_6$ with a 1:2 molar ratio of DMPP in refluxing methylcyclohexane led only to the formation of *cis*-$(DMPP)_2Mo(CO)_4$. In contrast, a stepwise reaction (reaction 2) led to the formation of both *cis*-$(DMPP)_2Mo(CO)_4$ and **10** (10:1 ratio). $(DMPP)Mo(CO)_5$ was first prepared and isolated with use of the $CoCl_2{\cdot}2H_2O$ catalyst developed by Albers[9] et al. This procedure is rapid and proceeds cleanly in high yield. A solution of $(DMPP)Mo(CO)_5$ and DMPP in toluene was then refluxed in the dark. The resultant *cis*-$(DMPP)_2Mo(CO)_4$ and **10** were separated by a combination of column chromatography and fractional crystallization. The complex **10** was easily identified by its characteristic $^{31}P\{^1H\}$ NMR spectrum, which contains a low-field resonance ($\delta$ = 159.36 ppm) typical of 7-phosphanorbornenes.[2-6,10] Since $(DMPP)_2Mo(CO)_4$ does not react to form **10**, it is possible that the key intermediate in the formation of **10** by reaction 2 is the seven-coordinate $(DMPP)_2Mo(CO)_5$. We thank a reviewer for this suggestion.



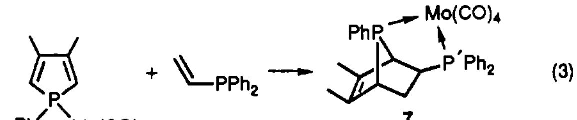
DMPP

**10**



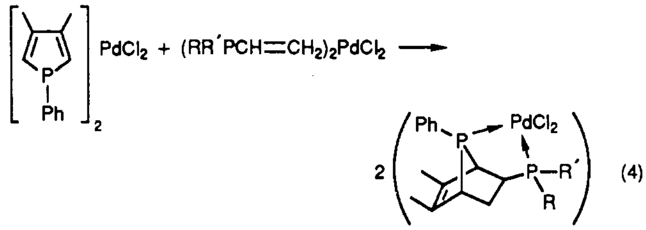
**10**

**B. Reactions of $(DMPP)Mo(CO)_5$ with Vinylphosphines.** The results of reaction 2 suggested that $(DMPP)Mo(CO)_5$ would undergo [4 + 2] Diels-Alder cycloadditions, as we have found to occur for palladium,[2,3] platinum,[2,3] ruthenium,[4,5] and nickel[6] complexes of DMPP. A racemic mixture of a single diastereomer (**7**) was obtained by reacting $(DMPP)Mo(CO)_5$ with $Ph_2VyP$ (reaction 3). In addition to **7**, traces of a tricarbonyl complex were also obtained. The tricarbonyl complex was found to be a mixture of the facial and meridional isomers formed from the reaction of **7** with an additional molecule of $Ph_2VyP$ and was not further characterized.

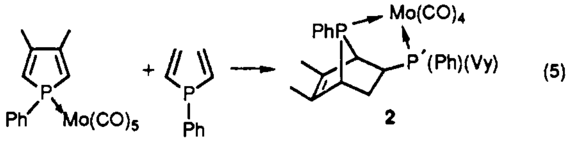


**7**

In the [4 + 2] cycloaddition reactions on palladium[2,3] (reaction 4) only a racemic mixture of a single diastereomer (>90% isolated yield) was formed when R = phenyl and R′ = vinyl, even though the presence of a small amount of the other diastereomer was observed in the reaction mixture.[2,3] In the analogous reaction of $(DMPP)Mo(CO)_5$ with $PhVy_2P$ (reaction 5) $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixture showed the presence of two diastereomers (approximately 2:1 **2a**:**2b** ratio) and a trace of a tricarbonyl complex. Column chromatography on silica gel only led to separation of the diastereomeric mixture from the other species. The two diastereomers were then separated by fractional crystallization.



**11**: R = R′ = phenyl
**12**: R = phenyl, R′ = vinyl



**2**

Reaction 5 was repeated with use of several different solvent systems and with varying reaction conditions. In all cases both diastereomers were obtained. Using higher boiling solvents such as 2-methoxyethyl ether or *n*-butyl ether led to a shorter reaction time period. This also led to an increase in the relative amounts of diastereomer **2b** to give a ratio of about 1:1 **2a**:**2b**. This suggests that formation of diastereomer **2b** is slightly favored by more vigorous reaction conditions. Use of the catalyst[16] trimethylamine

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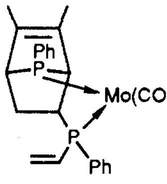
(15) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Table 2.2b. (b) *Ibid.*, Table 2.3.1.

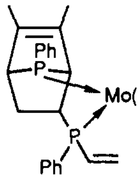
*N*-oxide with lower boiling solvents also led to formation of both diastereomers in a ratio of about 3:2 **2a**:**2b**.

Thus, the distereoselectivity of reaction 5 appears to be kinetically controlled, as **2a** and **2b** are not interconvertible. To confirm this, the cycloaddition reaction was performed in the reverse direction; i.e., (PhVy$_2$P)Mo(CO)$_5$ was reacted with DMPP. This reaction also produced both diastereomers (3:2 **2a**:**2b**).

The two diastereomers are schematically represented by

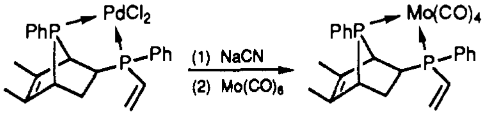


i



ii

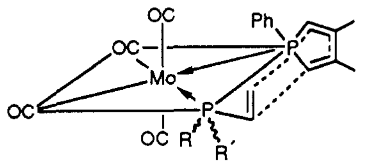
The crystal structure[2,3] of dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) shows it to be the diastereomer analogous to i. It is of especial interest to determine if the major diastereomer formed in reaction 5 (**2a**) has the same stereochemistry. A cyanide displacement[2,3] of the ligand from the palladium complex followed by reaction of the ligand with Mo(CO)$_6$ (reaction 6) gave a



(6)

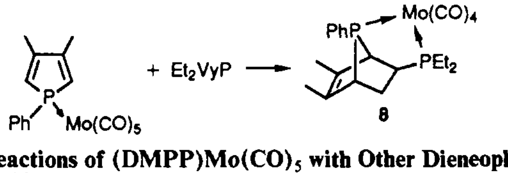
product whose $^{31}$P{$^1$H} NMR spectrum was identical with that of the minor diastereomer (**2b**). Since both steps of reaction 6 should proceed with retention of the stereochemistry, **2a** is diastereomer ii and **2b** is diastereomer i. This is unambiguously confirmed by X-ray crystallography (vide infra).

The different stereoselectivity of the cycloaddition reaction for the molybdenum complex can most easily be explained on the basis of steric factors. It was previously suggested[2,3] that the reaction mechanism probably involves a polar stepwise intramolecular [4 + 2] Diels–Alder cycloaddition between phosphine and phosphole in mutually cis positions. The metal provides both electronic activation and molecular direction[2-6,10] for the transition state schematically represented by



When R ≠ R′, the larger of the two groups will normally occupy the less congested region to reduce steric hindrance. In contrast to the square-planar palladium(II) and platinum(II) complexes, where the steric hindrance from the two cis halides causes a much preferred orientation of the R groups on the vinylphosphine, there is a less organized transition state in the six-coordinate molybdenum(0) system. The four carbonyls on the molybdenum complex impose almost equal steric constraints for any orientation of the vinylphosphine, leading to much lower diastereoselectivity for Mo(0) than for Pd(II) or Pt(II).

(DMPP)Mo(CO)$_5$ also reacts cleanly with Et$_2$VyP (reaction 7) to yield a single diastereomer of **8**.



(7)

## C. Reactions of (DMPP)Mo(CO)$_5$ with Other Dieneophiles.

Since we[4,5] have recently shown that ruthenium(II) complexes of DMPP react with other vinyl donors to form a new class of conformationally rigid asymmetric hemilabile[17] ligands, we wished to determine if similar reactions would also occur with (DMPP)Mo(CO)$_5$. Reactions of (DMPP)Mo(CO)$_5$ with phenyl vinyl sulfoxide, phenyl vinyl sulfide, and *N*,*N*-dimethylacrylamide generally led to extensive decomposition or, under less vigorous conditions, to no reaction at all. However, after 2 days at reflux in toluene (DMPP)Mo(CO)$_5$ reacted with phenyl vinyl sulfoxide to produce modest yields of the phosphole self-dimer **10**, suggesting a disproportionation or ligand redistribution reaction.

Table VI. 40.26-MHz $^{31}$P{$^1$H} NMR Data[a] for LMo(CO)$_n$ Complexes

| compd | $\delta(^{31}P)$, ppm ($J_{PP}$, Hz) |
|---|---|
| **2a** | 49.0, 143.4 (17.1) |
| **2b** | 47.2, 142.5 (17.1) |
| **3** | −13.3, 53.0, 142.4 (PP′, 17.1; P′P″, 36.6) |
| **4** | 53.0, 142.3 (17.1) |
| **5** | 60.9, 82.7, 146.4 (PP′, 17.1; P′P″, 22.0) |
| **6** | 86.6, 146.4 (17.1) |
| **7** | 50.5, 142.1 (17.1) |
| **8** | 44.8, 141.7 (22.0) |
| **10** | 52.62, 159.36 (9.8) |

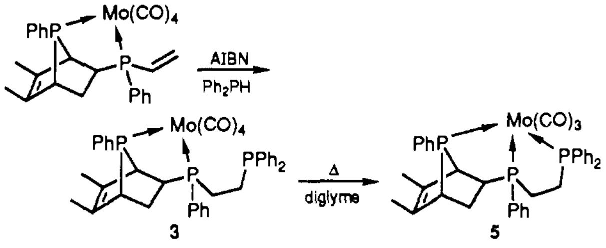
[a] In CDCl$_3$ at 300 K.

## D. Michael Additions of Ph$_2$PH and Ph$_2$AsH to 2b.

Michael type additions have extensive use as a basis for the synthesis of polytertiary phosphines:

$$R_2P{-}H + CH_2{=}CHPR_2 \rightarrow R_2PCH_2CH_2PR_2$$

King[18] has shown that addition of secondary phosphines to vinylphosphines is base catalyzed, and Meek and co-workers[19] have shown that these reactions are also free radical catalyzed. Keiter and co-workers[20] have studied the same addition reactions and found that they are just as effective when the vinylphosphine is coordinated to a transition-metal carbonyl. More recently, Shaw and co-workers[21-23] have shown that when activated by coordination to a metal, the vinylidene diphosphine (Ph$_2$P)$_2$C=CH$_2$ (Vdpp) undergoes Michael additions with a variety of nucleophiles. On the basis of these precedents, it was anticipated that the 2-vinyl group of complex **2b** should also be quite reactive toward Michael additions. Reaction 8 was found to occur readily in good yield (75%) to produce **3**. As expected, the addition occurred only on the 2-vinyl group with no reaction at the hindered 5-ene. It is also of interest to note that addition of Ph$_2$PH did not directly result in the formation of the tridentate ligand. The triphosphine is present as a bidentate ligand with the added phosphorus behaving as a "dangling arm". This complex can be converted into the *fac*-tridentate tricarbonyl **5** by refluxing in a high-boiling solvent for a few hours.



(8)

A similar addition reaction with Ph$_2$AsH under free-radical conditions (AIBN catalyst) was not successful; only the starting

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(16) Shi, Y.; Gao, Y.; Shi, Q.; Kershner, D. L.; Basolo, F. *Organometallics* **1987**, *6*, 1528 and references therein.

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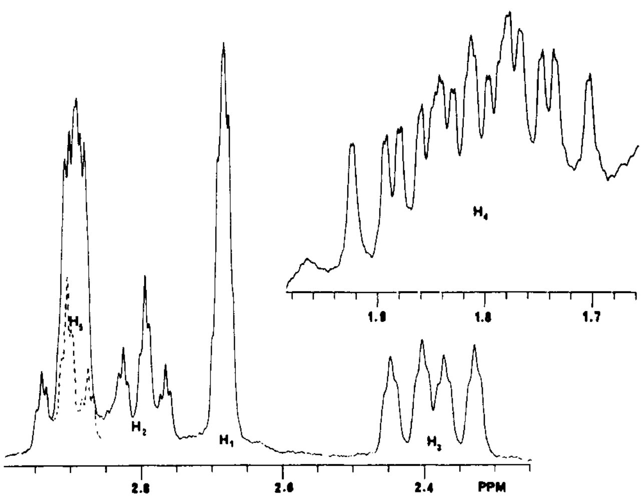

**Figure 1.** 300-MHz $^1$H NMR spectra of the norbornene ring protons of **2b** in $CDCl_3$ at 300 K.

material **2b** was recovered. The base-catalyzed approach with KOBu$^t$ gave the analogous **4**, which was converted to **6**, both in good yield.

**II. Characterization of the Diels–Alder Adducts. A. Phosphorus NMR and Infrared Spectroscopy.** These new compounds show $\nu_{CO}$ vibrations that are characteristic of tetracarbonyl and tricarbonyl systems.[24] The $\nu_{CO}$ vibrations of **2a** and **2b** are almost identical and cannot be used to distinguish the two diastereomers. Both **5** and **6** exhibit $\nu_{CO}$ bands characteristic[24] of facial isomers, with none of the meridional isomers being formed.

The $^{31}P\{^1H\}$ NMR data (Table VI) show that each complex possesses a low-field resonance ($\delta > 141$ ppm) that is diagnostic of the conversion of a phosphole into a 7-phosphanorbornene.[2–6,10] The other resonances occur in the region (40–60 ppm) that is typical of a phosphorus in a five-membered chelate ring.[25] Each of the diastereomers of **2** showed distinct chemical shifts, allowing for easy diastereomer recognition.[26,27]

For complex **3** there are three different resonances corresponding to the three different phosphorus atoms. The doublet at $\delta = -13.3$ ppm is assigned to the phosphorus on the dangling arm since this is close to the chemical shift of $EtPh_2P$ (−13 ppm).[28]

The values of $^2J_{PP}$ (9.8–22 Hz) are somewhat larger than what is normally observed[29] for five-membered chelate rings on molybdenum(0). Grim et al.[30] have suggested that the observed $J_{PP}$ coupling in a chelated diphosphine complex is a sum of contributions transmitted through the ligand backbone ($J_{PP}(B)$) and through the metal center ($J_{PP}(M)$); i.e., $J_{PP} = J_{PP}(B) + J_{PP}(M)$. Since $^3J_{PP}$ for the 2-phosphino-7-phosphanorbornene disulfides is nil,[2,3] it is assumed that $^3J_{PP}$ will also be zero in the chelate complexes. Thus, the PP couplings observed in compounds **2**, **7**, **8**, and **10** are probably transmitted solely through the metal center[31] and are probably negative in sign.[29] For complexes **3** and **5** there is additional coupling to the third phosphorus. In **3** the dangling-arm phosphorus (P″) is coupled only to the 2-phosphino phosphorus (P′) by a large through-backbone coupling (36.6 Hz). This coupling seemingly disappears upon coordination of P″ to form **5**. This can be justified on the basis of Grim's explanations as discussed above. Garrou[25] has stated that, in a five-membered chelate ring, the metal $J_{PP}(M)$ and backbone $J_{PP}(B)$ contributions to $J_{PP}$ are almost equal but are of opposite signs, thus leading to a small value of $J_{PP}$ (e.g. in $(dppe)Mo(CO)_4$, $J_{PP} = -4.0$ Hz[29]).

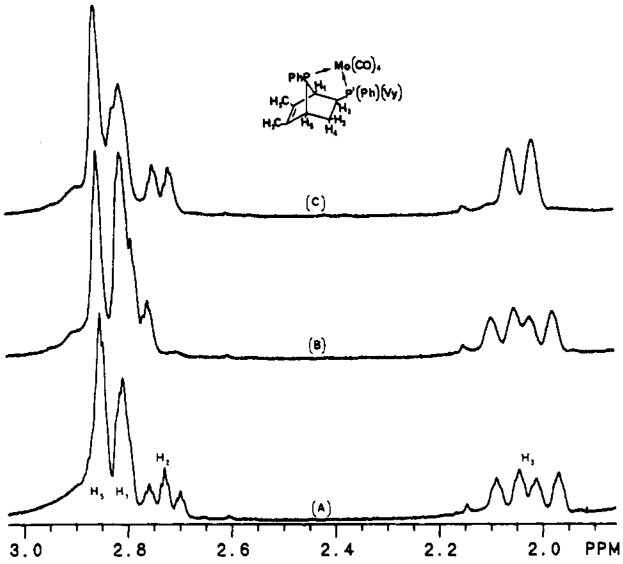

**Figure 2.** 300-MHz $^1H\{^{31}P\}$ NMR spectra in the norbornene ring proton region of **2a** in $CDCl_3$ at 300 K: (A) normal $^1$H spectrum; (B) decoupling of the 7-phospha phosphorus; (C) decoupling of the 2-phosphino phosphorus.

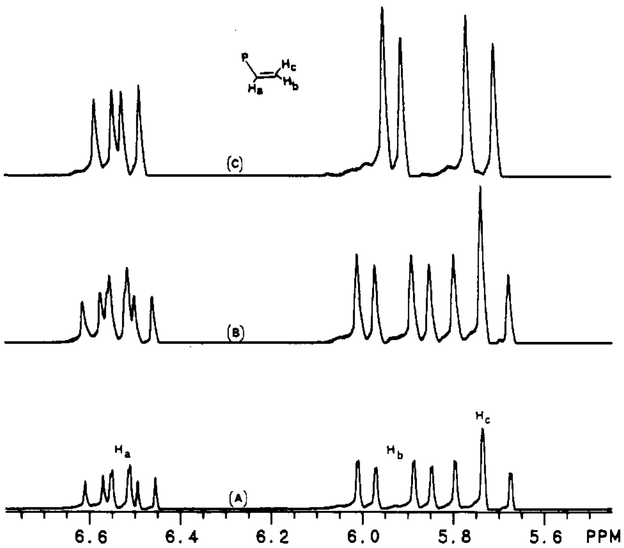

**Figure 3.** 300-MHz $^1H\{^{31}P\}$ NMR spectra in the vinyl proton region of **2a** in $CDCl_3$ at 300 K: (A) normal $^1$H spectrum; (B) decoupling of the 7-phospha phosphorus; (C) decoupling of the 2-phosphino phosphorus.

**B. Proton and Carbon NMR Spectroscopy.** Assignments of the $^1$H and $^{13}$C chemical shifts were made by comparison with the data reported for similar palladium,[2,3] platinum,[2,3] ruthenium,[4,5] and nickel[6] complexes. COSY, HETCOR, and $^1H\{^{31}P\}$ decoupling experiments confirmed the assignments for most complexes.

Each proton in the norbornene ring has a line shape that is characteristic of its type (Figure 1). The $H_1$ and $H_5$ resonances usually appear as broad singlets, with $H_5$ being the most downfield of the ring protons. Sometimes both of these protons show additional small coupling to each other and to phosphorus, as is evident in Figure 1 but not in Figure 2. The $H_2$ resonance appears as a doublet of triple triplets, with the largest coupling being to the 7-phospha phosphorus and nearly equal-magnitude couplings occurring to the 2-phosphino phosphorus and $H_4$. The $H_3$ resonance is a doublet of double triplets, with the largest couplings being to the 2-phosphino phosphorus and to $H_4$. The $H_4$ resonance is very complex (Figure 1) and is often obscured by the methyl resonances. For $H_4$ the largest coupling is to the 7-phospha phosphorus.

The large values of $^3J_{PH}$ for $H_2$ and $H_4$ and the smaller $^3J_{PH}$ value for $H_3$ are in keeping with expectations from previous

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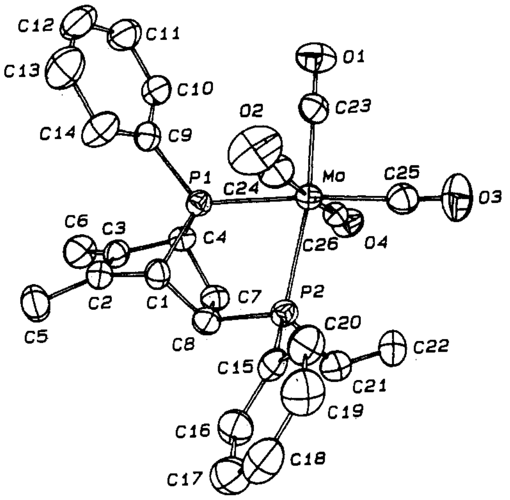

**Figure 4.** ORTEP plot of the structure of [2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tetracarbonylmolybdenum(0) (**2b**) showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

studies.[32] The $^3J_{PH}$ values are also in agreement with Karplus type relationships found for phosphonates.[33]

The vinyl protons in **2a** and **2b** (Figure 3) display the same general splitting as observed for vinylphosphine complexes of palladium and platinum.[3,11,34]

The relative $H_3$ chemical shifts readily distinguish the diastereomers **2a** and **2b**. $H_3$ lies in the deshielding region of a neighboring magnetically anisotropic phenyl ring for **2a**, and as a result its chemical shift lies downfield (2.39 ppm) of that of $H_3$ in **2b** (2.03 ppm).

The $^{13}C$ assignments were accomplished via HETCOR experiments. All complexes except for **5** and **6** display distinct sets of carbonyl $^{13}C$ resonances for the carbonyl groups respectively cis to both phosphorus atoms and trans to one phosphorus atom. The chemical shifts for the trans carbonyls are downfield of those for the cis carbonyls.[35] The cis carbonyl resonances appear as triplets and the trans carbonyl resonances as doublets of doublets with the larger $^2J_{PC}$ value being to the trans phosphorus. Both **5** and **6** show carbonyl resonances characteristic of facial $L_3$-$Mo(CO)_3$ complexes. For **5** these are each doublets of triplets with the larger $^2J_{PC}$ value to the trans phosphorus. For **6** these are each doublets of doublets, again with the larger $^2J_{PC}$ value to the trans phosphorus.

Each of the ring carbon resonances appears in a region that is typical of its type. The $C_3$ resonance, a doublet of doublets, is the most upfield except for **10**, where it is the most downfield ring resonance. The $C_2$ and $C_1$ resonances are also doublets of doublets, while the $C_4$ resonance is generally a doublet with coupling only to the 7-phospha phosphorus. The larger coupling is to the 7-phospha phosphorus for $C_1$, $C_3$, and $C_4$ and to the 2-phosphino phosphorus for $C_2$.[2-6]

There are distinct sets of phenyl resonances for each carbon type in the complexes that have more than one phenyl group. For example, **3** displays four distinct $C_m$ doublets, the most upfield phenyl resonances. Since **8** has only one phenyl group (the phenyl on the 7-phospha phosphorus), the assignment of its set of phenyl resonances could be used to distinguish these phenyl carbons from the others, assuming that the chemical shifts do not change very much. Similarly, the phenyl carbon resonances for the phenyl groups attached to arsenic in **4** and **6** were readily identified, as they are singlets. In general, however, the phenyl resonances could not be assigned to a particular phenyl group.

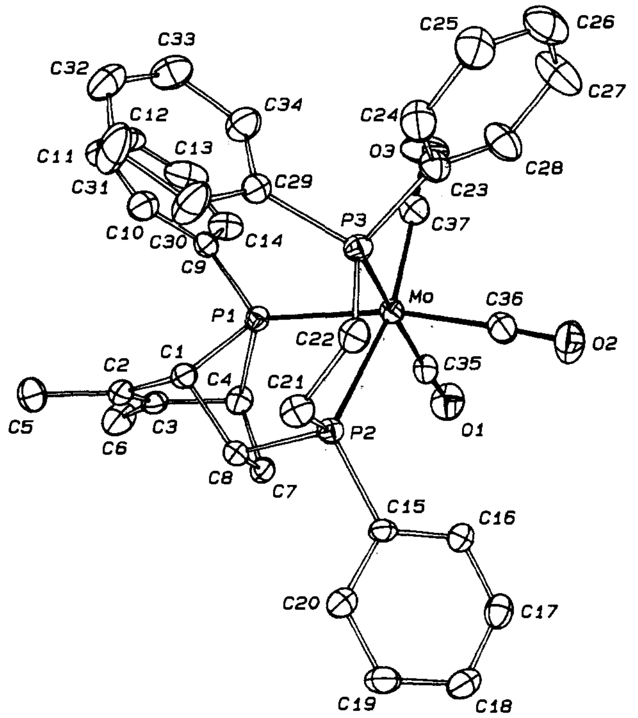

**Figure 5.** ORTEP plot of the structure of *fac*-[2-((2-(diphenylphosphino)ethyl)phenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]tricarbonylmolybdenum(0) (**5**) showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

For complexes **2a** and **2b** there are two vinyl carbon ($C_\alpha$ and $C_\beta$) resonances. $C_\alpha$ is always upfield of $C_\beta$. It is noteworthy that in **2a** $C_\alpha$ has a very large coupling to the 2-phosphino phosphorus (~51 Hz) while in **2b** the same coupling is only about 13 Hz. $C_\beta$ has a larger coupling (25–27 Hz) than expected.[34]

The near-constancy of the proton and carbon NMR data suggests that the general structures are the same for all complexes.

**C. Crystal Structure Analysis.** In order to gain conclusive support for the structural assignments of diastereomers **2a** and **2b** and to characterize the new ligand systems, X-ray crystal structures of **2b** and **5** were obtained. The structures of these two molecules are shown in Figures 4 and 5, respectively. Both complexes exist as discrete molecules with no abnormal intermolecular contacts. Neither complex contains any element of symmetry. As a result, both complexes are chiral. As can be seen in Figures 4 and 5, the chelate rings are rigid, **2b** is the diastereomer i, and **5** is the facial isomer. The phosphanorbornene rings in these molecules have strains similar to those observed in **10** and in a Cr(0) complex.[36] This strain can best be examined by considering the angles made by the bridgehead carbons and the 7-phospha phosphorus, which are 80.1 (2) and 79.7 (2)° for **2a** and **5**, respectively, compared to 79.4 (2)° for **10** and 79.0 (1)° for the Cr(0) complex.[36] This angle strain in the [4 + 2] adducts is in part responsible for the downfield position of the 7-phospha phosphorus $^{31}P$ NMR chemical shift.

The coordination geometries of both **2b** and **5** show considerable distortion from regular octahedra. In **2b** the P1–Mo–P2 angle is small (76.38 (2)°), and in **5** the P1–Mo–P2 (75.78 (4)°) and P2–Mo–P3 (78.97 (4)°) angles are small while the P1–Mo–P3 angle (98.30 (4)°) is large.

The Mo–P bond lengths in **2b** are significantly different (2.449 (1), 2.513 (2) Å) and are respectively shorter and longer than those observed[10] for **10** (2.480 (1), 2.470 (1) Å). For both **2b** and **10** the short Mo–P bonds are to the 7-phospha phosphorus, suggesting that it is the better donor. The Mo–CO bond lengths are in the

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(32) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley-Interscience: New York, 1981.

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**Table VII.** 75-MHz $^{13}C\{^1H\}$ NMR Data for $LMo(CO)_n$ Complexes[a]

| position | $\delta(^{13}C)$ ($J_{PC}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **2a** | **2b** | **3** | **4** | **5** | **6** | **7** | **8** | **10** |
| $C_1$ | 56.88 (26.0, 14.9) | 56.46 (25.9, 15.0) | 56.17 (25.8, 14.2) | 56.09 (25.9, 14.4) | 53.33 (21.8, 12.1) | 54.45 (22.1, 12.4) | 56.79 (24.9, 14.6) | 56.88 (25.7, 14.7) | 59.22 (27.5, 17.4) |
| $C_2$ | 35.01 (23.7, 35.0) | 33.47 (24.2, 34.7) | 35.15 (20.3, 35.0) | 34.92 (19.7, 35.4) | 36.51 (19.9, 37.8) | 36.94 (19.2, 37.9) | 33.85 (22.0, 35.2) | 32.73 (21.6, 35.1) | 52.10 (22.4, 30.1) |
| $C_3$ | 31.58 (18.2, 8.4) | 30.86 (18.4, 7.9) | 32.13 (18.1, 7.3) | 32.10 (18.2, 7.3) | 31.34 (22.2, 19.5) | 33.67 (12.5, 10.5) | 31.57 (19.0, 8.8) | 30.48 (18.7, 9.3) | 62.48 (15.3, 5.2) |
| $C_4$ | 50.51 (19.0) | 50.63 (19.4, 4.9) | 50.22 (19.2) | 50.17 (19.2) | 52.79 (21.6, 3.5) | 52.15 (21.5) | 50.53 (19.0) | 50.64 (9.7) | 55.55 (5.2, 3.1) |
| $C_{5,6}$ | 136.65 | 136.50 | 136.70 | 136.68 | 137.26 | 137.12 | 136.59 | 136.43 | 137.40 |
| 5,6-$CH_3$ | 13.74, 14.66 | 13.81, 14.64 | 13.36, 14.91 | 13.72 (1.5), 14.72 | 13.37, 14.93 | 13.37, 14.92 | 13.76, 14.69 | 13.66, 14.62 | 14.98, 17.25 |
| $CH_2$ | | | 21.99 (15.3) | 20.78 | 33.72 (11.6, 11.6) | 28.75 (35.8) | | 20.37 (16.9) | |
| | | | 28.52 (17.5, 14.9) | 29.01 (13.6) | 28.69 (17.4, 17.4) | 28.76 | | 19.13 (16.8) | |
| $C_i$ | 133.19 (32.2) | 134.60 (20.0, 5.1) | 132.57 (27.9) | 132.56 (29.4, 1.7) | 134.33 (17.5, 5.1) | 134.54 (19.5, 6.2) | 134.50 (25.5, 5.2) | 135.12 (23.7, 5.4) | 132.46 (14.1) |
| | 134.66 (25.8, 10.2) | 134.85 (29.8) | 134.61 (25.6, 5.2) | 134.60 (25.5, 5.4) | 135.16 (28.3) | 135.04 (29.2, 2.5) | 135.13 (30.0) | | 133.86 (19.8, 4.4) |
| | | | 137.62 (43.5) | 130.10 | 137.97 (25.0) | 138.32 (2.0) | 136.80 (31.6) | | |
| | | | 137.79 (43.3) | 130.28 | 139.55 (33.5) | 140.30 (3.9) | | | |
| $C_o$ | 130.78 (10.4) | 130.71 (10.6) | 130.76 (10.4) | 130.75 (10.4) | 131.19 (11.9) | 131.06 | 130.75 (10.3) | 130.82 (10.4) | 129.69 (10.1) |
| | 133.44 (13.8) | 131.75 (11.7) | 132.19 (17.9) | 132.49 | 131.96 (11.9) | 131.51 (10.7) | 131.23 (12.5) | | 132.88 (15.1) |
| | | | 132.82 (19.0) | 132.96 | 131.96 (11.9) | 132.10 | 133.05 (13.5) | | |
| | | | 133.37 (12.7) | 133.38 (12.9) | 133.42 (13.7) | 133.43 (13.7) | | | |
| $C_m$ | 128.22 (8.5) | 128.16 (7.9) | 128.21 (8.4) | 128.21 (9.7) | 127.50 (7.9) | 127.57 (8.0) | 128.12 (8.5) | 128.13 (8.3) | 128.22 (7.9) |
| | 128.77 (9.7) | 128.84 (8.5) | 128.51 (5.7) | 128.63 | 128.08 (9.0) | 128.38 (11.9) | 128.58 (8.5) | | 128.77 (9.9) |
| | | | 128.54 (6.6) | 128.66 | 128.50 (8.9) | 128.81 | 128.69 (8.3) | | |
| | | | 128.77 (10.0) | 128.72 (10.3) | 128.70 (10.0) | 128.87 | | | |
| $C_p$ | 129.27 | 129.22 | 128.55 | 128.47 | 128.37 | 128.66 | 129.21 | 129.13 | 128.65 |
| | 130.47 | 130.17 | 128.84 | 128.63 | 128.76 | 128.46 | 129.69 | | 130.90 (1.8) |
| | | | 129.27 | 129.25 | 128.95 | 129.02 | 130.02 (1.4) | | |
| | | | 130.60 (1.4) | 130.54 (1.3) | 130.39 | 130.45 | | | |
| $C_\alpha$ | 130.20 (51.2) | 132.83 (13.2) | | | | | | | 129.37 (39.5) |
| $C_\beta$ | 136.24 (24.7) | 134.95 (27.6) | | | | | | | 150.70 (3.6) |
| $CO_{cis}$[c] | 209.76 t (9.0) | 209.27 t (9.0) | 209.42 t (9.1) | 209.52 t (9.0) | 221.27 dt (23.2, 10.7) | 221.20 dd (24.2, 9.1) | 208.91 t (8.3) | 208.91 t (9.1) | 207.86 dd (8.8, 7.0) |
| | 210.66 t (9.1) | 211.08 t (9.3) | 210.30 t (9.4) | 210.30 t (9.5) | 222.06 dt (26.4, 11.8) | 222.76 dd (7.5, 3.4) | 210.93 t (9.0) | 210.92 t (9.1) | 210.27 t (9.0) |
| | | | | | 223.10 dt (30.0, 9.9) | 223.01 dd (20.6, 9.0) | | | |
| $CO_{trans}$ | 215.73 dd | 215.73 dd | 215.35 dd | 215.46 dd | | | 215.76 dd | 215.62 dd | 217.00 dd |
| | (24.6, 7.4) | (25.2, 7.9) | (16.8, 7.8) | (24.6, 7.8) | | | (23.9, 10.0) | (25.5, 7.8) | (24.3, 7.8) |
| | 217.65 dd | 217.72 dd | 218.16 dd | 218.17 dd | | | 218.18 dd | 218.07 dd | 218.24 dd |
| | (23.4, 9.1) | (23.3, 9.6) | (23.6, 9.2) | (23:4, 8.2) | | | (24.9, 7.6) | (23.3, 9.6) | (24.0, 9.9) |

[a] In $CDCl_3$ at 300 K; $\delta$ in ppm , $J$ in Hz. [b] The largest $J_{PC}$ values for $C_1$, $C_3$, and $C_4$ correspond to coupling to the 7-phospha phosphorus; for $C_2$ the largest $J_{PC}$ values correspond to coupling to the 2-phosphino phosphorus. [c] Multiplicities: d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets.

normal range. The structural results show that the bonding of these new rigid chiral ligands to Mo(0) is typical of bidentate and tridentate phosphines in five-membered chelate rings.

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**Registry No.** **1**, 74363-92-1; **2a**, 123642-42-2; **2b**, 123749-01-9; **3**, 123642-43-3; **4**, 123642-44-4; **5**, 123642-45-5; **6**, 123642-46-6; **7**, 123642-47-7; **8**, 123642-48-8; **9**, 72868-88-3; **10**, 74364-03-7; DMPP, 30540-36-4; $Et_2VyP$, 13652-21-6; $Ph_2P(CH{=}CH_2)$, 2155-96-6; $PhP(CH{=}CH_2)_2$, 26681-88-9; $Ph_2PH$, 829-85-6; $Ph_2AsH$, 829-83-4; molybdenum hexacarbonyl, 13939-06-5; [2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene (isomer a), 123642-41-1.

**Supplementary Material Available:** For the two structure studies, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*) (12 pages); listings of observed and calculated structure factors (×10) (24 pages). Ordering information is given on any current masthead page.

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# Synthetic and Mechanistic Investigations of the Reactions of Organic Nitriles with Thiazyl Chloride and the Thermolysis of 1,3-Dichloro-1,3,2,4,6-dithiatriazines

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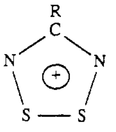
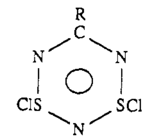
The reaction of organic nitriles with $(NSCl)_3$ at 23 °C produces good yields of the six-membered rings $RCN_3S_2Cl_2$ (**2**, R = ${}^tBu$, $CCl_3$, Ph) in the absence of a solvent or **2** (R = $Me_2N$, $Et_2N$, ${}^iPr_2N$) in chloroform. The reaction is complete in a few days for R = $R'_2N$, but it requires several weeks for the other derivatives. For R = Ph and ${}^tBu$ the formation of **2** is accompanied by smaller amounts of the five-membered ring $RCN_2S_2{}^+Cl^-$ (**1**). The reaction rate is accelerated by UV irradiation, although the yields of **2** are lower. A red intermediate in the reaction of $Me_2NCN$ with 2 mol of NSCl is tentatively identified as $Me_2NCNS(Cl)N$ on the basis of ${}^1H$, ${}^{13}C$, and ${}^{14}N$ NMR spectroscopy. The thermolysis of **2** (R = ${}^tBu$, $CCl_3$, Ph, $Me_2N$, $Et_2N$, ${}^iPr_2N$) generates **1** in excellent yields. This ring contraction is shown by ${}^{14}N$ NMR spectroscopy to occur at temperatures ranging from 40 °C (R = ${}^tBu$) to 110 °C (R = $Me_2N$) and by ${}^1H$ NMR spectroscopy to be second-order. A mechanism for the conversion of **2** into **1** is proposed. The reaction of $Me_2NCN$ with NSCl in a 1:1 molar ratio at 23 °C in $CCl_4$ produces the eight-membered ring 1,3-$(Me_2NC)_2N_4S_2Cl_2$ (**8**, R = $NMe_2$), in 80% yield, whereas a mixture of **8** and $Me_2NCN_4S_3Cl$ is obtained in nitromethane.

## Introduction

The first investigations of the reactions of organic nitriles RCN (R = ${}^tBu$, $CCl_3$, Ph) with $(NSCl)_3$ were carried out at ≥60 °C and led to the isolation of the corresponding 1,2,3,5-dithiadiazolium chloride (**1**) in ≤50% yields.[1] Subsequently, the reaction of $CF_3CN$ with $(NSCl)_3$ at 50 °C in an autoclave was reported to give **1** (R = $CF_3$) as the major product (45%) with the 1,3-dichloro-1,3,2,4,6-dithiatriazine (**2**, R = $CF_3$), as a minor product (21%).[2] By contrast, we found that **2** (R = $Me_2N$, $Et_2N$, ${}^iPr_2N$) is obtained in >80% yields by the cycloaddition reaction of the corresponding dialkylcyanamide, $R_2NCN$, with two NSCl units generated from dilute solutions of $(NSCl)_3$ in $CCl_4$ at 60 °C.[3] It is not clear from these results whether the difference in the identity of the products from the RCN–$(NSCl)_3$ reaction is determined by variations in the reaction conditions or by the nature of the R group (or both).


cation of **1**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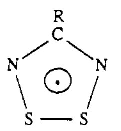
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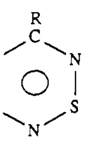
**4**

The synthesis, structures, and properties of the seven-π-electron 1,2,3,5-dithiadiazolyl radicals (**3**)[4-7] and the eight-π-electron 1,3,2,4,6-dithiatriazines (**4**)[2,8-12] are of current interest, and these ring systems are usually prepared by the reduction of **1** and **2**, respectively.[13] Consequently, we have examined several RCN–$(NSCl)_3$ systems in detail in order to (a) determine the effect of the R group on the outcome of the reaction, (b) establish the appropriate reaction conditions for the synthesis of **1** and **2**, (c) elucidate the mechanism of the RCN–$(NSCl)_x$ cycloaddition reaction, and (d) identify any other products that may be formed

**Table I.** ${}^{14}N$ NMR Chemical Shifts for $RCN_3S_2Cl_2$ (**2**)$^a$

| R | $\delta(N)^b$ | $\delta(N)^c$ | $\delta(R_2N)$ |
|---|---|---|---|
| $Me_2N$ | -211 | -263 | -211 |
| $Et_2N$ | -213 | -240 | -213 |
| ${}^iPr_2N$ | -205 | -241 | -220 |
| $Cl_3C$ | -181 | -248 | |
| ${}^tBu$ | -191 | -242 | |
| Ph | -196 | -237 | |

$^a$ In $CH_2Cl_2$. Chemical shifts are relative to $MeNO_2$(l). $^b$ The two equivalent ring nitrogen atoms. $^c$ The unique ring nitrogen atom.

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(13) The synthesis of **4** by the direct insertion of plasma-generated nitrogen atoms into the S–S bond of **3** has been reported, but this reaction appears to be limited to aryl derivatives.[10]

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