lowship. P.D.H. is indebted to Mrs. R. Zamojska for the chemical analyses for Pd, Cl, and Br, and to Mr. Y. Huang (McGill University) for some of the Raman studies.

Supplementary Material Available: A complete table of crystal data for I, II, and III and tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $Pd_2(dmb)_2Cl_4{\cdot}H_2O$, $Pd_2(tmb)_2Cl_4{\cdot}2CH_3CN$, and $Pd_2(dmb)_2Br_2Cl_2$ (14 pages); tables of observed and calculated structure factors for $Pd_2(dmb)_2Cl_4{\cdot}H_2O$, $Pd_2(tmb)_2Cl_4{\cdot}2CH_3CN$, and $Pd_2(dmb)_2Br_2Cl_2$ (30 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of a New Tetratertiary Phosphine Ligand

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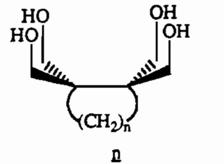
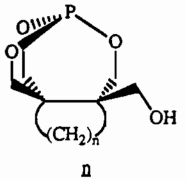
The synthesis and characterization of the new tetratertiary phosphine 2,3-bis[(diphenylphosphino)methyl]-1,4-bis(diphenylphosphino)butane (**5**) is reported. Oxidation of **5** with *t*-BuOOH or S_8 yields the tetraphosphoryl and tetrathiophosphoryl derivatives **6** and **7**, respectively. The molecular structure of **6** was confirmed by X-ray crystallography. Crystals of **6** are triclinic, space group $P\bar{1}$, with unit cell dimensions a = 11.70 (3) Å, b = 21.80 (3) Å, c = 9.28 (6) Å, α = 94.0 (3)°, β = 102.7 (3)°, and γ = 88.4 (2)°. The complexes $[CH(CH_2PPh_2)_2ML_n]_2$ have been prepared for ML_n = $PdCl_2$, $PdBr_2$, PdI_2, $NiCl_2$, $PtCl_2$, $Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$, and $Fe(CO)_3$, in which **5** coordinates in a bis(bidentate) manner to two metals with the formation of two six-membered chelate rings. This coordination mode was confirmed by single-crystal X-ray diffraction studies on the complexes $[CH(CH_2PPh_2)_2ML_n]_2$ for ML_n = $PdCl_2$ and $NiCl_2$. Crystals of $[CH(CH_2PPh_2)_2PdCl_2]_2$ are monoclinic, space group $P2_1/n$, with unit cell dimensions a = 21.798 (8) Å, b = 13.927 (5) Å, c = 22.802 (9) Å, and β = 115.81 (4)°. Crystals of $[CH(CH_2PPh_2)_2NiCl_2]_2$ are triclinic, space group $P\bar{1}$, with unit cell dimensions a = 14.320 (5) Å, b = 14.601 (2) Å, c = 19.448 (15) Å, α = 92.39 (2)°, β = 99.83 (4)°, γ = 99.00 (1)°, and Z = 4. The monometallic complex $(Ph_2P(O)CH_2)_2CHCH(CH_2PPh_2)_2PdCl_2$ was also synthesized. Crystals of this complex are orthorhombic, space group *Pna*2, No. 33, with unit cell dimensions a = 33.375 (5) Å, b = 11.125 (2) Å, c = 14.886 (3) Å, and Z = 4. The monometallic complexes (**5**-*P*,*P*′,*P*″)$Mo(CO)_3$ were prepared in which **5** exhibits a tridentate (*P*,*P*′,*P*″) coordination mode and where the fourth P of **5** can have a lone pair or be bonded to *O* or S in addition to two phenyl groups. The monometallic complex (**5**)RhCl was also prepared, but ^{31}P NMR spectroscopy indicated a complicated solution behavior for this complex. Similarly, attempted syntheses of monometallic complexes of Ni(II) and Pd(II) yielded mixtures which also exhibit complex behavior in solution as shown by ^{31}P NMR spectroscopy.

Introduction

Recently our group has been investigating the coordination chemistry of the main-group elements P, As, Si, and Ge with the tetrol frameworks **1a**–**1d**. These investigations have focused on the synthesis and reactivity of the orthoesters of these elements, such as phosphorus in **2a**–**2d**,[1] as well as the attempted synthesis of novel rectangular pyramidal five-coordinate species. Whereas five-coordinate phosphorus, arsenic, silicon, and germanium compounds typically favor a TBP geometry, the structural requirements of **1a**–**1d** are such that five-coordinate tetraalkoxide species of these elements must exhibit a SP geometry. As a step toward this goal we have recently reported the results of deprotonation studies of the pendant alcohol group of **2a**–**2d**[1,2] and the structures of the two novel silicon isomers **3a** and **3b**.[3]



	n
1a	0
1b	1
1c	2
1d	3



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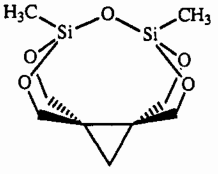
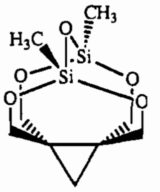
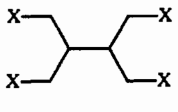


3a

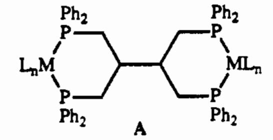


3b

We have now undertaken an elaboration of this project to include the chemistry of the transition-metal elements with donor atoms other than oxygen in **1a**–**1d**. Of present interest is the introduction of phosphine groups into the tetradentate framework. A tetradentate phosphine of this kind may exhibit any one of four possible coordination modes, A–D. One interesting possibility

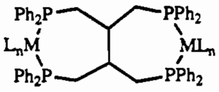


4 X = Cl
5 X = PPh_2
6 X = $P(O)Ph_2$
7 X = $P(S)Ph_2$

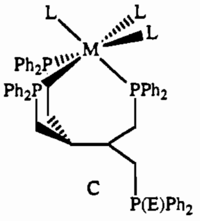


A

ML_n		ML_n	
8	$PdCl_2$	**14**	$Mo(CO)_4$
9	$PdBr_2$	**15**	$W(CO)_4$
10	PdI_2	**16**	$Fe(CO)_3$
11	$NiCl_2$		
12	$PtCl_2$		
13	$Cr(CO)_4$		



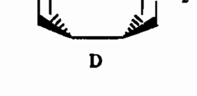
B



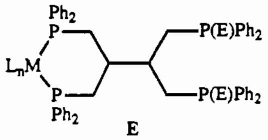
C

ML_3 = $Mo(CO)_3$

17 E = lone pair
18 E = O
19 E = S



D



E

ML_n = $PdCl_2$

20 E = lone pair
21 E = O

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for such a ligand is that it can potentially act as a bis(bidentate) chelating ligand to two metal centers to form homo- or heterobimetallic complexes. Bimetallic complexes may be formed with either of the two isomeric structures A and B since such a ligand could coordinate with the formation of two six- or two seven-membered rings. On the basis of models, a tridentate coordination mode C of fac geometry is also obtainable. A tetraphosphine based on frameworks **1a–1d** may also form mononuclear transition-metal complexes of type D where the metal must possess a square-planar or square-pyramidal geometry. Although the steric bulk and structural limitations of this framework may not be ideal for the formation of complexes of type D, the possibility of forcing square-planar geometries on tetrahedral metals such as Ag^+, Ni^0, Pd^0, and Pt^0 is an intriguing one.

Here we report the synthesis and characterization of the new tetradentate phosphine 2,3-bis[(diphenylphosphino)methyl]-1,4-bis(diphenylphosphino)butane (**5**) and its phosphoryl and thiophosphoryl derivatives **6** and **7**. Some of the scope of the transition-metal coordination chemistry of **5** is reported here for Cr, Mo, W, Fe, Rh, Ni, Pd, and Pt, through the characterization of the new homobimetallic complexes **8–16** of structural type A, the monometallic complexes **17–19** of structural type C, and the unexpected monometallic complexes **20** and **21** of type E. The structures of **6**, **8**, **10**, and **11** and of the partially oxidized product **21** have been confirmed by X-ray crystallography. Attempts to synthesize mononuclear square-planar complexes of type D for Rh(I), Ni(II), and Pd(II) are also presented herein.

Experimental Section

General Procedures. All reactions were performed under an inert atmosphere of argon or nitrogen using standard inert atmosphere techniques. Toluene, pentane, tetrahydrofuran, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Methylene chloride, acetonitrile, and dimethyl sulfoxide were distilled from calcium hydride. Ph_2PH,[4] (η^6-cycloheptatriene)$Mo(CO)_3$,[5] (NBD)$Cr(CO)_4$,[6] $(pip)_2Mo(CO)_4$,[7] (COD)$W(CO)_4$,[8] (benzylideneacetone)$Fe(CO)_3$,[9] $(PhCN)_2PdCl_2$,[10] (NBD)$PdBr_2$,[11] $NiCl_2$ (anhydrous),[12] $Rh_2Cl_2(COD)_2$,[13] $[Ni(DMSO)_6][(BF_4)]_2$,[14] (COD)$PtCl_2$,[15] and 2,3-bis(hydroxymethyl)-1,4-butanediol[16] were prepared as previously described. $Pd(BF_4)_2 \cdot 4CH_3CN$ and $AgBF_4$ were purchased from Strem and Aldrich, respectively, and used without further purification. Solution NMR spectra were recorded on Nicolet NT300 (^1H, ^{13}C), Bruker WM200 (^{13}C, ^{31}P), Bruker WM300 (^{13}C, ^{31}P), Varian Unity 500 (^1H, ^{13}C, $^1H\{^{31}P\}$), or Varian VXR300 (^1H, ^{13}C, ^{31}P) spectrometers using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were recorded on Kratos MS-50 (EI, HRMS) or Finnigan 4000 (EI, CI) spectrometers. IR spectra were recorded using an IBM 98 FT-IR spectrometer. Conductance measurements were made with a Markson ElectroMark Analyzer. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of 2,3-Bis(chloromethyl)-1,4-dichlorobutane (4). The title tetrachloride was prepared as previously reported:[16] mp 53–54 °C. lit. mp 52–53 °C; ^1H NMR ($CDCl_3$) δ 3.90 (dd, $^2J_{HH} = 11.5$ Hz, $^3J_{HH} = 2.8$ Hz, 4 H, CH_2), 3.73 (dd, $^2J_{HH} = 11.5$ Hz, $^3J_{HH} = 6.0$ Hz, 4 H, CH_2), 2.29 (m, 2 H, CH).

Preparation of 2,3-Bis[(diphenylphosphino)methyl]-1,4-bis(diphenylphosphino)butane (5). A red-orange solution of Ph_2PNa was generated in situ by stirring Ph_2PH (10.0 g, 54.0 mmol) and sodium metal (1.28 g, 55.6 mmol) in 150 mL of THF overnight. Excess sodium was removed by filtration. The phosphide solution was cooled to 0 °C and was treated dropwise with a solution of **4** (3.00 g, 13.4 mmol) in 50 mL of THF. The reaction mixture was allowed to warm to room temperature with stirring for 3 h and was then refluxed for 30 min. Excess phosphide was quenched by the slow addition of water until the red color of the phosphide faded. The volume of the solvent was reduced in vacuo to approximately 50 mL, and diethyl ether and water were added. The ether layer was separated, and the aqueous layer was extracted twice more with 75 mL of diethyl ether. The organic extracts were combined and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to yield a thick residue which partially solidified on standing. Recrystallization of this residue from 3:1 MeOH/benzene or from THF/EtOH yielded white needles. The product was isolated by filtration, rinsed with EtOH, and dried in vacuo; yield 8.0 g (73%). An additional crop of product was isolated upon cooling the filtrate; yield 1.20 g (10%). Further purification may be achieved by flash chromatographic separation on Kieselgel 60 silica, eluting with benzene: mp 91–93 °C; HRMS (EI) *m/z* for $C_{54}H_{50}P_4$ (M^+), calcd 821.769, found 821.817; ^{31}P NMR (CD_2Cl_2) δ −22.0; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.8 (m, Ph-ipso), 133.0 (d, $^2J_{PC} = 20.4$ Hz, Ph-ortho), 132.9 (d, $^2J_{PC} = 19.9$ Hz, Ph-ortho), 128.2 (m, Ph-meta), 35.1 (tt, CH), 32.0 (m, CH_2); ^1H NMR ($CDCl_3$; 500 MHz) δ 7.35–7.10 (m, Ph), 2.26 (dd, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.0$ Hz, 4 H, CH_2), 2.12 (m, CH, 2 H), 2.03 (dd, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 7.0$ Hz, 4 H, CH_2). Anal. Calcd for $C_{54}H_{50}P_4 \cdot {}^1/_2C_6H_6$: C, 79.62; H, 6.68; P, 13.69. Found: C, 79.56; H, 6.31; P, 13.58.

Preparation of 2,3-bis[(diphenylphosphoryl)methyl]-1,4-bis(diphenylphosphoryl)butane (6). Method A. Strong heating (100–130 °C) for 24 h or sonication for 16 h of **5** (0.321 g, 0.391 mmol) in DMSO in the presence of a catalytic amount of water quantitatively yields **6**. Sonication was carried out by immersion of the reaction flask into a Branson 50–60-Hz ultrasonic cleaning bath. The solvent was removed in vacuo, and the product was recrystallized from CH_3CN to yield 0.331 g of **6** (96%).

Method B. A solution of **5** (0.50 g, 0.61 mmol) in 15 mL of toluene was cooled to 0 °C and was treated with a solution of *t*-BuOOH in toluene (0.8 mL, 3.6 M). The solution was allowed to warm to room temperature with stirring for 3 h. Hexane (15 mL) was added, and the resulting white solid was isolated by filtration, rinsed with hexane, and dried in vacuo. The resulting product is spectroscopically pure, but can be recrystallized from CH_3CN: yield 0.37 g (70%); mp 243–244 °C; IR (KBr) $\nu_{P=O}$ 1178, 1117 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 30.6; ^{13}C NMR ($CDCl_3$) δ 133.5 (d, $^1J_{PC} = 98$ Hz, Ph-ipso), 132.9 (d, $^1J_{PC} = 97$ Hz, Ph-ipso), 131.4 (d, $^4J_{PC} = 2$ Hz, Ph-para), 130.65 (d, $^2J_{PC} = 8.5$ Hz, Ph-ortho), 130.60 (d, $^2J_{PC} = 8.5$ Hz, Ph-ortho), 128.6 (d, $^3J_{PC} = 11.5$ Hz, Ph-meta), 34.6 (m, CH), 32.1 (dd, $^1J_{PC} = 69$ Hz, $^3J_{PC} = 9$ Hz, CH_2); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (ddd, $^3J_{PH} = 11.5$ Hz, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.5$ Hz, 8 H, Ph-ortho), 7.58 (ddd, $^3J_{PH} = 11.5$ Hz, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 1.5$ Hz, 8 H, Ph-ortho), 7.46–7.30 (m, Ph-meta,para), 2.96 (ddd, $^2J_{HH} = 15.0$ Hz, $^2J_{PH} = 12.5$ Hz, $^3J_{HH} = 6.5$ Hz, 4 H, CH_2), 2.70–2.55 (m, 6 H, CH, CH_2). Anal. Calcd for $C_{54}H_{50}P_4O_4$: C, 73.13; H, 5.68; P, 13.97. Found: C, 72.53; H, 5.68; P, 13.67.

Preparation of 2,3-Bis[(diphenylthiophosphoryl)methyl]-1,4-bis(diphenylthiophosphoryl)butane (7). A solution of **5** (0.500 g, 0.607 mmol) and S_8 (0.083 g, 0.32 mmol) in 15 mL of toluene was refluxed for 1 h to yield a white mixture. The solid was isolated by filtration and was then eluted on a silica gel column with CH_2Cl_2. The pure product-containing fractions were combined, and the solvent was removed in vacuo. The product was recrystallized from CH_2Cl_2/hexane to yield white crystals: yield 0.56 g (96%); mp 275–276 °C; HRMS (EI) *m/z* for $C_{54}H_{50}P_4S_4$ (M^+), calcd 950.17461, found 950.17659; ^{31}P NMR (CD_2Cl_2) δ 40.1; ^{13}C NMR ($CDCl_3$) δ 133.7 (d, $^1J_{PC} = 82$ Hz, Ph-ipso), 131.8 (d, $^1J_{PC} = 78$ Hz, Ph-ipso), 131.7 (d, $^2J_{PC} = 10.5$ Hz, Ph-ortho), 131.3 (d, $^4J_{PC} = 2.6$ Hz, Ph-para), 131.0 (d, $^4J_{PC} = 2.7$ Hz, Ph-para), 130.7 (d, $^2J_{PC} = 10.5$ Hz, Ph-ortho), 128.5 (d, $^3J_{PC} = 12.2$ Hz, Ph-meta), 36.9 (m, CH), 35.8 (dd, $^1J_{PC} = 53.4$ Hz, $^3J_{PC} = 7.3$ Hz, CH_2); ^1H NMR (CD_2Cl_2) δ 7.86 (ddd, $^3J_{PH} = 13.0$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz, 8 H, Ph-ortho), 7.59 (ddd, $^3J_{PH} = 13.0$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz, 8 H, Ph-ortho), 7.46–7.33 (m, Ph-meta,para), 3.22 (m, 4 H, CH_2), 2.81 (m, 2 H, CH), 2.62 (m, 4 H, CH_2); $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 500 MHz) δ 3.22 (dd, $^2J_{HH} = 15.0$ Hz, $^3J_{HH} = 6.0$ Hz, 4 H, CH_2), 2.81 (quin, $^3J_{HH} = 6.0$ Hz, 2 H, CH_2), 2.62 (m, 4 H, CH_2). Anal. Calcd for $C_{54}H_{50}P_4S_4$: C, 68.19; H, 5.30; P, 13.03. Found: C, 67.53; H, 5.12; P, 12.61.

Preparation of $Cl_2Pd(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2PdCl_2$ (8). A solution of **5** (0.240 g, 0.292 mmol) in 20 mL of toluene was added dropwise to a solution of $(PhCN)_2PdCl_2$ (0.240 g, 0.626 mmol) in 50 mL of toluene. The resulting mixture was stirred for 5 h to ensure complete reaction. The pale yellow solid was isolated by filtration, rinsed with 10 mL of toluene followed by 10 mL of diethyl ether, and dried in vacuo;

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yield 0.30 g (87%). Recrystallization can be achieved by slow evaporation of a DMSO solution of **8** in air: ^{31}P NMR (DMSO) δ 21.7; ^{13}C NMR (DMSO-d_6) δ 134.4 (d, $^{2}J_{PC}$ = 10 Hz, Ph-ortho), 132.4 (d, $^{2}J_{PC}$ = 8 Hz, Ph-ortho), 131.9 (s, Ph-para), 131.4 (d, $^{1}J_{PC}$ = 61 Hz, Ph-ipso), 130.7 (s, Ph-para), 128.6 (d, $^{3}J_{PC}$ = 10 Hz, Ph-meta), 128.1 (d, $^{3}J_{PC}$ = 11 Hz, Ph-meta), 127.5 (d, $^{1}J_{PC}$ = 57 Hz, Ph-ipso), 38.2 (m, CH), 28.1 (d, $^{1}J_{PC}$ = 35 Hz, CH_2); ^{1}H NMR (DMSO-d_6) δ 7.70 (m, Ph-ortho), 7.5–7.3 (m, Ph-meta,para), 2.18–2.09 (m, CH, CH_2).

Preparation of $Br_2Pd(PPh_2CH_2)_2CHCH(CH_2Ph_2P)PdBr_2$ (9). A solution of **5** (0.33 g, 0.40 mmol) in 5 mL of CH_2Cl_2 was slowly added to a solution of (NBD)$PdBr_2$ (0.32 g, 0.89 mmol) in 15 mL of CH_2Cl_2, and the resulting mixture was stirred overnight. Filtration yielded a light yellow solid which was washed with CH_2Cl_2 and dried in vacuo: yield 0.40 g (74%); ^{31}P NMR (DMSO) δ 19.1; ^{13}C NMR (DMSO-d_6) δ 134.6 (d, $^{2}J_{PC}$ = 7 Hz, Ph-ortho), 132.5 (d, $^{1}J_{PC}$ = 57 Hz, Ph-ipso), 132.2 (d, $^{2}J_{PC}$ = 8 Hz, Ph-ortho), 131.9 (s, Ph-para), 130.6 (s, Ph-para), 128.5 (d, $^{3}J_{PC}$ = 11 Hz, Ph-meta), 128.0 (d, $^{3}J_{PC}$ = 11 Hz, Ph-meta), 127.7 (d, $^{1}J_{PC}$ = 52 Hz, Ph-ipso), 28.5 (m, CH_2).

Preparation of $I_2Pd(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2PdI_2$ (10). To a solution of $Pd(BF_4)_2\cdot 4CH_3CN$ (0.340 g, 0.766 mmol) in 10 mL of CH_3CN was added a solution of **5** (0.310 g, 0.377 mmol) in 5 mL of CH_2Cl_2. The ^{31}P NMR spectrum of this solution showed the presence of a complex mixture with sharp singlets at 24.0 and 22.5 ppm and broad resonances at 11.0, 7.9, 7.1, and 6.4 ppm. No resonances attributable to free phosphine or phosphine oxide were observed. To this complex solution was added excess Et_4NI, yielding a deep red solution, the ^{31}P NMR spectrum of which showed only two singlets at 11.4 and 11.7 ppm in a ratio of approximately 10:1 (see Results and Discussion).

Preparation of $Cl_2Ni(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2NiCl_2$ (11). To a suspension of anhydrous $NiCl_2$ (0.095 g, 0.73 mmol) in 30 mL of CH_3CN was added a solution of **5** (0.30 g, 0.36 mmol) in 15 mL of CH_2Cl_2 to give a deep orange-red mixture. This mixture was refluxed for 30 min in which time all solids dissolved to give a deep red solution which was cooled and reduced to a volume of 10 mL in vacuo. Diethyl ether (5 mL) was added to initiate precipitation, and the mixture was cooled overnight. The deep red product was isolated by filtration, washed with two 10-mL portions of diethyl ether, and dried in vacuo; yield 0.31 g (80%). Recrystallization from CH_3CN yields red crystals which crumble to a powder upon removal from their mother liquor; ^{31}P NMR (CD_3CN) δ 5 (br).

Preparation of $Cl_2Pt(PPh_2CH_2)CHCH(CH_2Ph_2P)_2PtCl_2$ (12). A solution of **5** (0.300 g, 0.365 mmol) in 5 mL of CH_2Cl_2 was added to a solution of (COD)$PtCl_2$ (0.270 g, 0.722 mmol) in 15 mL of CH_2Cl_2, and the resulting mixture was stirred overnight. The white product was isolated by filtration, washed with 5 mL of diethyl ether, and dried in vacuo: yield 0.34 g, 71:; ^{31}P NMR (CD_2Cl_2) δ 2.9 ($^{1}J_{Pt\text{-}P}$ = 3456 Hz).

Preparation of $(OC)_4Cr(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2Cr(CO)_4$ (13). (Norbornadiene)tetracarbonylchromium (0.191 g, 0.729 mmol) and **5** (0.300 g, 0.365 mmol) were refluxed in 30 mL of tetrahydrofuran for 30 min to yield a yellow solution. The solvent was removed in vacuo to yield a yellow solid which was washed with methanol and dried in vacuo: yield 0.30 g (71%); IR (CH_2Cl_2) ν_{CO} 2004, 1919, 1879 cm^{-1}; ^{31}P NMR (CD_2Cl_2 δ 49.0; ^{13}C NMR (CD_2Cl_2) δ 226.1 (a t,[17] separation 19 Hz, CO_{eq}), 221.5 (t, $^{2}J_{PC}$ = 14 Hz, CO_{ax}), 221.4 (t, $^{2}J_{PC}$ = 14 Hz, CO_{ax}), 139.0 (m, separation 44 Hz, Ph-ipso), 136.5 (m, separation 29 Hz, Ph-ipso), 132.7 (a t, separation 11 Hz, Ph-ortho), 131.2 (a t, separation 10 Hz, Ph-ortho), 130.5 (s, Ph-para), 129.7 (s, Ph-para), 128.7 (m, Ph-meta), 38.5 (tt, $^{3}J_{PC}$ = 11 Hz, $^{2}J_{PC}$ = 5 Hz, CH), 34.9 (a t, separation 19 Hz, CH_2).

Preparation of $(OC)_4Mo(PPh_2CH_2)_2CHCH(CH_2Ph_2P)Mo(CO)_4$ (14). Bis(piperidine)tetracarbonylmolybdenum (0.240 g, 0.610 mmol) and **5** (0.261 g, 0.304 mmol) were refluxed in 25 mL of CH_2Cl_2 for 30 min to yield a bright yellow solution. Volatiles were removed in vacuo to yield a pale yellow solid which was rinsed with methanol and dried in vacuo: yield 0.27 g (71%); IR (CH_2Cl_2) ν_{CO} 2017, 1927, 1909 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 28.4; ^{13}C NMR (CD_2Cl_2) δ 214.8 (m, separation 16 Hz, CO_{eq}), 210.6 (t, $^{2}J_{PC}$ = 9.5 Hz, CO_{ax}), 210.3 (t, $^{2}J_{PC}$ = 8.0 Hz, CO_{ax}), 138.9 (m, separation 41 Hz, Ph-ipso), 136.1 (m, separation 30 Hz, Ph-ipso), 132.8 (a t, separation 13 Hz, Ph-ortho), 131.3 (a t, separation 11 Hz, Ph-ortho), 130.6 (s, Ph-para), 129.6 (s, Ph-para), 128.7 (a t, separation 10 Hz, Ph-meta), 128.6 (a t, separation 10 Hz, Ph-meta), 38.77 (tt, $^{3}J_{PC}$ = 10 Hz, $^{2}J_{PC}$ = 5 Hz, CH), 35.7 (a t, separation 18 Hz, CH_2).

Preparation of $(OC)_4W(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2W(CO)_4$ (15). (Cyclooctadiene)tetracarbonyltungsten (0.200 g, 0.495 mmol) and **5** (0.205 g, 0.248 mmol) were refluxed in 30 mL of tetrahydrofuran for 30 min to yield a pale yellow solution. The solvent was removed in vacuo, and the resulting yellow solid was washed with methanol and dried in vacuo: yield 0.25 g (71%); IR (CH_2Cl_2) ν_{CO} 2014, 1917, 1880 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 8.2 ($^{1}J_{PW}$ = 227 Hz); ^{13}C NMR (CD_2Cl_2) δ 205.4 (m, separation 17 Hz, CO_{eq}), 203.2 (t, $^{2}J_{PC}$ = 8 Hz, CO_{ax}), 202.6 (t, $^{2}J_{PC}$ = 6 Hz, CO_{ax}), 138.5 (m, separation 47 Hz, Ph-ipso), 135.7 (m, separation 35 Hz, Ph-ipso), 132.9 (a t, separation 12 Hz, Ph-ortho), 131.4 (a t, separation 11 Hz, Ph-ortho), 130.8 (s, Ph-para), 129.9 (s, Ph-para), 128.4 (m, Ph-meta), 39.1 (tt, $^{3}J_{PC}$ = 10 Hz, $^{2}J_{PC}$ = 4 Hz, CH), 35.8 (a t, separation 30 Hz, CH_2).

Preparation of $(OC)_3Fe(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2Fe(CO)_3$ (16). (Benzylideneacetone)tricarbonyliron (0.450 g, 1.57 mmol) and **5** (0.600 g, 0.729 mmol) were stirred in 20 mL of toluene for 4 h at room temperature. The solvent was removed in vacuo to yield a red-orange residue. This residue was dissolved in toluene and eluted on a silica gel column to yield a yellow solution. Removal of the solvent in vacuo gave the product as a bright yellow solid: IR (CH_2Cl_2) ν_{CO} 1981, 1909, 1886, 1875 cm^{-1}; ^{31}P NMR (toluene) δ 54.7; ^{13}C NMR (CD_2Cl_2, 20 °C) δ 220.2 (t, $^{2}J_{PC}$ = 9 Hz, CO), 140.2 (a t, separation 51 Hz, Ph-ipso), 134.9 (a t, separation 38 Hz, Ph-ipso), 133.3 (a t, separation 12 Hz, Ph-ortho), 131.0 (a t, separation 9 Hz, Ph-ortho), 130.5 (s, Ph-para), 129.9 (s, Ph-para), 128.7 (m, Ph-meta), 38.9 (m, CH), 34.1 (a t, separation 27 Hz, CH_2); ^{1}H NMR (CD_2Cl_2) δ 7.4–7.1 (m, Ph), 2.13 (m, 4 H, CH_2), 1.92 (m, 4 H, CH_2), 1.13 (m, 2 H, CH).

Preparation of (5)$Mo(CO)_3$ (17). A solution of **5** (0.400 g, 0.486 mmol) and (η^6-cycloheptatriene)$Mo(CO)_3$ (0.134 g, 0.486 mmol) in 25 mL of toluene was stirred for 30 min at room temperature and was then refluxed for 1.5 h. The resulting yellow-brown solution was cooled, and the solvent was removed in vacuo. The remaining residue was dissolved in CH_2Cl_2 and eluted on a silica gel column. A light yellow fraction was collected and the solvent removed in vacuo to yield a pale yellow solid (see Results and Discussion): IR (KBr) ν_{CO} 1934 (br), 1830 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 17.7 (t, $^{2}J_{PP}$ = 19.6 Hz), 15.8 (t), 14.2 (t), −17.9 (s).

Preparation of $Cl_2Pd(PPh_2CH_2)_2CHCH(CH_2P(O)Ph_2)_2$ (21). A solution of the ligand **5** (0.235 g, 0.286 mmol) in 5 mL of toluene was added to a yellow solution of **8** (0.298 g, 0.253 mmol) in 25 mL of DMSO. This mixture was stirred for 3 days during which time ^{31}P NMR spectra showed two new resonances at 21.4 and −20.9 ppm assigned to the presence of $Cl_2Pd(PPh_2CH_2)_2CHCH(CH_2PPh_2)_2$ (**20**). This solution remained unchanged over the next 3 weeks as indicated by ^{31}P NMR spectra. The solution was then exposed to air and stirred for 5 days. DMSO was removed from the solution at 40 °C in vacuo to yield a yellow solid. This yellow solid was redissolved in 5 mL of CH_2Cl_2, and the resulting yellow solution was treated with 15 mL of MeOH to precipitate 50 mg of unreacted **8** which was isolated by filtration. The solvent was removed from the filtrate to yield a light yellow solid. Remaining traces of **8** were removed by eluting this material on a silica gel column with acetone. Removal of the solvent from the product-containing fractions in vacuo yielded 0.260 g of **21** as a creamy white solid, a 60% yield based on the quantity of **8** not recovered. (This is a minimum value for the percent yield since the unknown quantity of unreacted **8** not precipitated in the methanol addition step was subsequently removed by chromatography.) A pale yellow crystalline sample of **21** was obtained by layering methanol onto a DMSO solution: IR (KBr) $\nu_{P=O}$ 1184, 1119 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 31.4 ($P(O)Ph_2$), 20.4 (PPh_2); ^{13}C NMR (CD_2Cl_2) δ 134.8 (a t, separation 11.2 Hz, PPh_2-ortho), 133.5 (a t, separation 10.7 Hz, PPh_2-ortho), 133.1 (d, $^{1}J_{PC}$ = 98.9 Hz, $P(O)Ph_2$-ipso), 132.7 (d, $^{1}J_{PC}$ = 98.9 Hz, $P(O)Ph_2$-ipso), 132.2 (d, $^{4}J_{PC}$ = 2.7 Hz, $P(O)Ph_2$-para), 132.1 (s, $P(O)Ph_2$-para), 132.0 (s, PPh_2-para), 131.4 (s, PPh_2-para), 131.2 (d, $^{2}J_{PC}$ = 9.7 Hz, $P(O)Ph_2$-ortho), 130.8 (d, $^{2}J_{PC}$ = 9.1 Hz, $P(O)Ph_2$-ortho), 129.0 (d, $^{3}J_{PC}$ = 11.8 Hz, $P(O)Ph_2$-meta), 129.04 (a t, separation 10.7 Hz, PPh_2-meta), 128.9 (d, $^{3}J_{PC}$ = 11.8 Hz, $P(O)Ph_2$-meta), 128.7 (a t, separation 11.8 Hz, PPh_2-meta), 37.4 (tt, $^{3}J_{PC}$ = 12.0 Hz, $^{2}J_{PC}$ = 2.5 Hz, $\mathit{C}H(CH_2PPh_2)_2$), 36.0 (br s, $\mathit{C}H(CH_2P(O)Ph_2)_2$), 32.0 (dd, $^{1}J_{PC}$ = 69.3 Hz, $^{3}J_{PC}$ = 8.0 Hz, $\mathit{C}H_2P(O)Ph_2$), 30.9 (m, separation 37.1 Hz, $\mathit{C}H_2PPh_2$); ^{1}H NMR (CD_2Cl_2) δ 7.85 (ddd, $^{3}J_{PH}$ = 11.7 Hz, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 4 H, $P(O)Ph_2$-ortho), 7.70–7.59 (m, 8 H, $P(O)Ph_2$-ortho, PPh_2-ortho), 7.56–7.26 (m, Ph), 2.75–2.56 (m, $C\mathit{H}_2P(O)Ph_2$), 2.22 (m, CH), 2.10–1.94 (m, CH_2).

Reaction of 5 with $[Ni(CH_3CN)_6][BF_4]_2$. A solution of $[Ni(CH_3CN)_6][BF_4]_2$ was generated by treating $[Ni(H_2O)_6][BF_4]_2$ (0.083 g, 0.243 mmol) in 10 mL of CH_3CN with 0.5 mL of the dehydrating reagent 2,3-dimethoxypropane. The resulting blue solution was stirred for 15 min. Addition of a solution of **5** (0.200 g, 0.243 mmol) in 5 mL of CH_2Cl_2 resulted in the formation of a deep brown solution. A ^{31}P NMR spectrum of this solution showed only a very broad resonance centered at 5 ppm. No change in this solution was observed by ^{31}P NMR spectroscopy over a period of 2 weeks. Exposure of this solution to oxygen results in a change of color to pale yellow within 10 min. A ^{31}P NMR

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(17) Five-line multiplets of an AXX′ (A = ^{13}C; X, X′ = ^{31}P) spin system where the two outer lines are of low intensity are denoted here as apparent triplets, a t. The separation reported is that between lines 2 and 4.

Table I. Crystallographic Data for **6**, **8**, **11**, and **21**

	6	**8**	**11**	**21**
formula	$C_{54}H_{50}O_4P_4$	$C_{54}H_{50}Cl_4P_4Pd_2{\cdot}C_2H_6SO$	$C_{50}H_{54}Cl_4Ni_2P_4{\cdot}2C_6H_{12} + 2C_6H_{10}O$	$C_{54}H_{50}Cl_2O_2P_4Pd{\cdot}C_2H_6SO$
formula weight	886.83	1255.6	1090.47 (1455.08)	1126.3
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	*Pna*2, No. 33
a, Å	11.70 (3)	21.798 (8)	14.320 (5)	33.375 (5)
b, Å	21.80 (3)	13.927 (5)	14.601 (2)	11.125 (2)
c, Å	9.28 (6)	22.802 (9)	19.448 (15)	14.886 (3)
α, deg	94.0 (3)		92.39 (2)	
β, deg	102.7 (3)	115.81 (4)	99.83 (4)	
γ, deg	88.4 (2)		99.00 (1)	
V, Å^3	2302	6231 (4)	3947.6 (31)	5527 (3)
Z	2	4	4	4
d_{calc}, g/cm^3	1.28	1.34	1.47	1.35
crystal size, mm	0.10 × 0.10 × 0.12	0.08 × 0.10 × 0.15	0.60 × 0.50 × 0.45	0.20 × 0.20 × 0.60
μ(Mo Kα), cm^{-1}	2.04	8.56	9.07	6.2
data collectn instrum	DATEX	DATEX	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiatn (monochrom)	Mo Kα (λ = 0.71034 Å)	Mo Kα (λ = 0.71034 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
orientatn reflctns (no., range (2θ))	14, 22–35	12, 24–35	25, 17.8–31.9	25, 22–34
temperature, °C	17	17	−50 (1)	21
scan method	ω-scan	ω-scan	θ–2θ	θ–2θ
data collectn range, 2θ, deg	3.5–40.0	3.5–50.0	4.0–45.0	0–50.0
no. of total reflctns collected	3116	6287	6554	3896
no. of unique reflectns	1207 ($I > 2\sigma_I$)	1996 ($I > 2\sigma_I$)	5341 ($I > 3\sigma_I$)	3031 ($I > 3\sigma_I$)
no. of params refined	319	353	681	592
trans factors (max, min) (ψ-scans)	0.99, 0.94	0.99, 0.88	0.999, 0.699	0.999, 0.965
R^a	0.065	0.13	0.096	0.048
$R_w{}^b$	0.053	0.11	0.131	0.066
quality-of-fit indicator[c]			2.9	2.07
largest shift/esd, final cycle	0.01	0.01	0.01	0.03
largest peak, e/Å^3	0.8	2.5	1.82 (4)	2.2

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

spectrum of this solution showed only a singlet at 30.9 ppm, indicative of phosphine oxidation. Colorless crystals of **6** were obtained within 2 days as the solution slowly evaporated. Similar results were also obtained starting from $[Ni(DMSO)_6][BF_4]_2$ or $[Ni(CH_3CN)_6][ClO_4]_2$ without the addition of dimethoxypropane.

Preparation of (5)RhCl (22). A solution of **5** (0.830 g, 1.01 mmol) in 15 mL of THF was added to a stirred solution of $Rh_2Cl_2(COD)_2$ (0.250 g, 0.507 mmol) in 15 mL of THF. Within a few minutes a golden-yellow solid began to precipitate. The mixture was stirred for an additional 30 min, and **22** was isolated by filtration, rinsed with THF, and dried in vacuo: MS (FAB) *m*/*z* (relative intensity) 957.1 (M$^+$ + 2O, 6), 925.1 (M$^+$, 3), 887.2 (**6**, 15), 553 (28), 286.9 (79), 201.0 (100); Λ_m(EtOH) = 8.6 Ω^{-1} cm^2 mol^{-1}; $\Lambda_m(CH_3NO_2)$ = 37 Ω^{-1} cm^2 mol^{-1}.

Crystal and Molecular Structure Solution for ($Ph_2P(O)CH_2CHCH(CH_2P(O)Ph_2)_2$ (6). A suitable crystal for data collection, approximately 0.10–0.12 mm on a side, was selected, placed in a glass capillary, and mounted on a standard goniometer. All intensity data were collected at room temperature. The unit cell parameters were initially calculated using an automatic indexing procedure[18] and subsequently verified by oscillation photographs. Final lattice constants were determined by a least-squares fit to the ±2θ values of 14 higher angle reflections. The intensity data were corrected for Lorentz and polarization effects. Table I contains a tabulation of the pertinent information relevant to data collection and reduction.

The majority of the non-hydrogen atom positions were identified using direct-method routines.[19] The remaining non-hydrogen atoms were located via alternate cycles of least-squares calculations[20] and electron density difference density calculations.[21] The atomic scattering factors used were those found in the International Tables.[22] Positions of the hydrogen atoms were calculated using an assumed C–H bond distance of 1.0 Å and a C–H bond angle of 109°.

Analysis of residual electron density on an electron density difference map (maximum 0.4 e/Å^3) indicated that all atoms were accounted for by the model.

Crystal and Molecular Structure Solution for $Cl_2Pd(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2PdCl_2$ (8). A crystal suitable for data collection, approximately 0.08–0.15 mm on a side, was selected, attached to a glass fiber, and mounted on a standard goniometer. All intensity data were collected at room temperature. The unit cell dimensions and Bravais lattice type were initially calculated using an automatic indexing procedure[18] and subsequently verified by oscillation photographs. The observed systematic absences of 0*k*0, *k* = 2*n* + 1, and *h*0*l*, *h* + *l* = 2*n* + 1, indicated the space group $P2_1/n$. Final lattice constants were determined by a least-squares fit to the ±2θ values of 12 higher angle reflections. The intensity data were corrected for Lorentz and polarization effects. Table I contains a tabulation of the pertinent information relevant to data collection and reduction.

Analysis of palladium–palladium vectors from the three-dimensional Patterson map revealed the appropriate positions for the palladium atoms in the unit cell. The remaining non-hydrogen atoms were located via alternate cycles of least-squares calculations[20] and electron density difference density calculations.[21] The atomic scattering factors used were those found in the International Tables.[22a] Positions of the hydrogen atoms were calculated using an assumed C–H bond distance of 1.0 Å. Thermal parameters for the phenyl rings and the DMSO atoms were refined isotropically. The data were reweighted prior to the final least-squares cycle so that $\omega(|F_o| - |F_c|)^2$ was approximately constant as a function of sin θ.

Restraints[22b] were imposed upon the C–C bond distances in the phenyl

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(18) Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

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(20) Lapp, R. L.; Jacobson, R. A. *Alls: A Generalized Crystallographic Least Squares Program*; U.S. Department of Energy Report IS-4708; Iowa State University: Ames, IA, 1979.

(21) Powell, D. R.; Jacobson, R. A. *Four: A Generalized Crystallographic Fourier Program*; U.S. Department of Energy Report IS-4737; Iowa State University: Ames, IA, 1979.

(22) (a) Hydrogen scattering factors were taken from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. Atomic scattering factors were obtained from Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, pp 71–79. (b) Flippen-Anderson, J. L.; Gilardi, R.; Konnert, J. H. *Restrained Least-Squares Program (RESLSQ)*; NRL Memorandum Report 5042; Naval Research Laboratory: Washington, DC, 1983.

rings due to the relatively small contribution to the total scattering made by the individual carbon atoms when compared to the scattering power of the molecule and possible disorder in the ring positions. Analytical scattering factors were used, and the targets for the restrained phenyl distances were set to 1.40 Å. Residual electron density found on an electron density difference map indicated the possible presence of one or more highly disordered DMSO groups and some disorder in the phenyl ring orientations. These artifacts were not modeled due to the small occupancies of these disordered sites (<0.16). Since estimated standard deviations are not obtained from RESLSQ,[22b] the parameters were used without restraints in a full-matrix least-squares procedure. The estimated standard deviations (esd's) were obtained from the inverse of the normal equations matrix and therefore represent maxima for these values.

Crystal and Molecular Structure Solution for $Cl_2Ni(PPh_2CH_2)_2CHCH(CH_2Ph_2P)_2NiCl_2$ (11). An orange-colored crystal of the title compound was set on the tip of a glass fiber and the fiber mounted on the diffractometer for data collection at −50 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Several crystals were used initially to determine cell constants, and none were better than the one chosen for data collection. The error for the *c* cell parameter is noticeably high at 0.015 Å. Pertinent data collection and reduction information are given in Table I.

Lorentz and polarization corrections, a correction based on a decay in the standard reflections of 0.8%, and an absorption correction based on a series of ψ-scans were applied to the data. The agreement factor for the averaging of observed reflections was 4.2% (based on F). Generally this is twice the average merging agreement factor for CAD4 data collections.

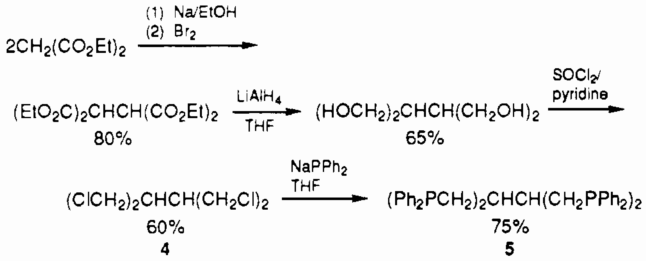
The centric space group $P\bar{1}$ was indicated initially by intensity statistics,[23] and later confirmed by successful refinement of the structure. About $^2/_3$ of the non-hydrogen atoms were placed directly from the E-map. The remaining non-hydrogen atoms were found in successive difference Fourier maps. Two cyclohexane and two cyclohexanone solvent molecules were placed in the asymmetric unit. It is suspected that solvent loss and/or disorder is the probable cause of the poor crystal quality discussed above. Only the non-hydrogen atoms of the nickel complex were allowed to refine anisotropically. All hydrogen atoms were placed at calculated positions 0.95 Å from the attached atom, with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of that atom. The hydrogen atom positions and isotropic temperature factors were not refined. The thermal ellipsoids for the phenyl rings of the complex visually indicate a high degree of thermal (vibrational) motion. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.[24]

Crystal and Molecular Structure Solution for $Cl_2Pd(PPh_2CH_2)_2CHCH(CH_2P(O)Ph_2)_2$ (21). A pale yellow pinacoidal crystal of approximate dimensions 0.20 × 0.20 × 0.60 mm was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $22 < 2\theta < 34$. The data were collected using the θ–2θ technique.

A total of 7783 reflections were collected, of which 3896 were unique and not systematically absent. As a check on crystal and electron stability, three representative reflections were measured every 60 min. No significant loss of intensity was observed throughout the data collection, so no decay correction was applied. Lorentz and polarization corrections and an empirical absorption correction, based on a series of ψ-scans, were applied to the data. Relative transmission coefficients ranged from 0.965 to 0.999 with an average value of 0.987. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 3896 observed and accepted reflections was 2.0% based on intensity and 1.7% based on F_o. Table I contains a tabulation of the pertinent information relevant to data collection and reduction.

The position of the Pd atom was given by a Patterson interpretation method.[23] The remainder of the non-hydrogen atoms were located from subsequent difference Fourier and least-squares refinement cycles. Following least-squares refinement of all the non-hydrogen atoms in the Pd complex, the oxygen atom of a water molecule and a partially disordered molecule of DMSO were located in the lattice. The DMSO molecule was disordered such that the oxygen atom and the two methyl groups defined a plane, on either side of which were located half-occupancy atoms. The total occupancy of the solvent molecule refined to a value of 0.88.

Scheme I



The parameters thus defined were refined in full-matrix least-squares calculations. Scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were included in F_c; the values of f and f' were those of Cromer.[24] Only those reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.[24]

Analysis of residual electron density on an electron density difference map (maximum 2.2 e/Å^3, located 0.23 Å from Pd) indicated all atoms were accounted for by the model.

Results and Discussion

Ligand Synthesis and Characterization. Previous work by Weinges and Spanig[16] provided a straightforward synthetic route to the tetrachloride **4** as outlined in Scheme I. Typical yields obtained by us are also given in this scheme. Diphenylphosphido groups are conveniently introduced into this framework by the reaction of **4** with $NaPPh_2$ in THF. Workup of the reaction mixture, followed by recrystallization of the resulting residue from THF/EtOH, gives **5** in yields ranging from 70% to 83% as an air-stable, crystalline white solid readily soluble in diethyl ether, toluene, and methylene chloride. Its constitution was confirmed by both analytical and high-resolution mass spectral data.

A ^{31}P NMR spectrum of **5** reveals a singlet resonance at −22.0 ppm, affirming the equivalence of all four phosphorus nuclei. The phenyl region of the ^1H NMR spectrum exhibits only uninformative multiplets from 7.35 to 7.10 ppm. The methylene protons are diastereotopic, and their ^1H NMR resonances appear at 2.26 and 2.03 ppm as part of an ABX spin system (X = CH; $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 7.0 Hz). The two methine protons appear as a multiplet at 2.12 ppm. The phosphorus coupling to the methylene protons was small and unresolved as confirmed by a 500-MHz $^1H\{^{31}P\}$ NMR spectrum.

Typical of tertiary phosphines, **5** is readily oxidized by *t*-BuOOH or S_8 in toluene to yield the white, crystalline phosphoryl and thiophosphoryl derivatives **6** and **7**, respectively. It was also found that partial oxidation of DMSO solutions of **5** occurs over a period of weeks to months. The oxidation of phosphines by DMSO with the liberation of dimethyl sulfide is well documented.[25] The reaction is typically quite slow for arylphosphines, but it is subject to acid catalysis. We have found that the rate of DMSO oxidation of **5** can be increased thermally or by sonication.

^{31}P NMR spectra of **6** and **7** exhibit singlet resonances at 30.6 and 40.1 ppm, respectively. In their ^1H NMR spectra the diastereotopic methylene protons exhibit an ABX pattern (X = CH). Unlike **5**, however, these resonances are complicated by strong coupling to the phosphorus nuclei with $^2J_{PH}$, evaluated with the aid of $^1H\{^{31}P\}$ spectra, of 12.5 Hz for one of the two diastereotopic methylene protons in **6**. This complication precludes complete assignment of these resonances. Similar difficulties also limit the utility of ^1H NMR spectroscopy in the characterization of the transition-metal complexes of **5**. The ^1H NMR spectra of **6** and **7** each exhibit two doublet of doublet of doublets in the phenyl

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(23) Sheldrick, G. M. SHELXS-86; Institut für Anorganische Chemie der Universität: Göttingen, FRG, 1986.

(24) *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland. Neutral atom scattering factors and anomalous scattering corrections were taken from Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B, Table 2.3.1.

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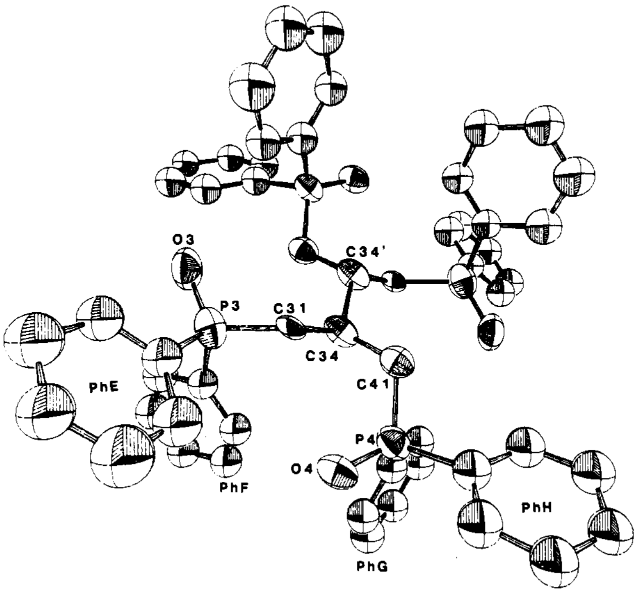

Figure 1. ORTEP drawing of **6**. The thermal ellipsoids are drawn at the 50% probability level.

region in addition to other phenyl proton multiplets. In the 500-MHz ^{1}H NMR spectrum of **7**, for example, these two unique resonances occur at 7.86 and 7.59 ppm each with the coupling constants $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, and $^3J_{PH}$ = 13.0 Hz. These resonances are assigned to ortho phenyl protons on the basis of integration and the collapse of these resonances to doublets of doublets in the ^{1}H{^{31}P} NMR spectra. Just as the methylene protons of **5–7** are diastereotopic, the two phenyl substituents on each phosphorus atom are stereochemically nonequivalent and hence give rise to the appearance of two Ph-ortho resonances in the ^{1}H NMR spectra of these compounds. This inequivalence is further demonstrated in the ^{13}C NMR spectra of **6** and **7** which clearly exhibit two phenyl ipso and ortho carbon resonances as doublets. For **7**, two phenyl para resonances are also resolved. As expected for P(V), the Ph-ipso carbon resonances each exhibit large one-bond coupling to phosphorus[26] with $^1J_{PC}$ values of 98 and 97 Hz for those in **6**, and 82 and 78 Hz for those in **7**. The methylene carbon resonances appear as doublets of doublets resulting from one-bond coupling to phosphorus of 69 and 53 Hz for **6** and **7**, respectively.

The identity of **6** was further confirmed by X-ray crystallography (Figure 1). The unit cell is comprised of two unique molecules of **6** which differ by the orientation of the phenyl rings with respect to the remainder of each molecule. The greatest deviation lies between the pairs of phenyl rings C, D and E, F which are rotated by almost 60° relative to one another. Half of each molecule is related to the second half by an inversion center at the midpoint of the HC–CH vector. The phosphoryl groups are oriented in a paddle wheel fashion around both molecules with P=O distances of 1.468 (1), 1.511 (1), 1.547 (2), and 1.515 (1) Å at P(1), P(2), P(3), and P(4), respectively. These distances do not differ significantly from the previously observed range of 1.47–1.50 Å for P=O bond distances.[27] For example, the distances reported for bis(diphenylphosphoryl)methane, which also crystallizes with two unique molecules in the unit cell, range from 1.484 (5) to 1.500 (5) Å.[27a] The paddle wheel orientation of the phosphoryl groups in **6** is presumably the result of crystal packing forces. It is interesting to note, however, that the phosphoryl oxygen atoms are each directed in the vicinity of a methylene proton of a neighboring "arm". Although the O···C distances between each phosphoryl oxygen atom and a neighboring methylene carbon atom (which range from 3.16 (1) to 3.20 (1) Å) may potentially be in the range allowable for a weak C–H···O hydrogen bonding interaction,[28] we do not believe it to be significant in **6**. (The positions of the hydrogen atoms were not located.)

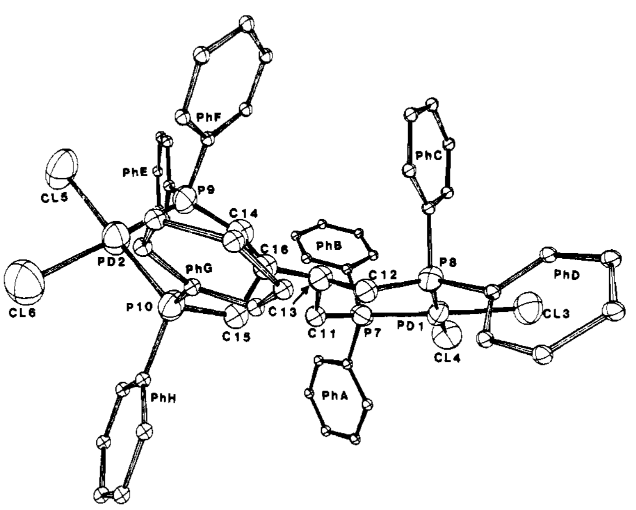

Figure 2. ORTEP drawing of **8** with thermal ellipsoids drawn at the 50% probability level. All phenyl carbons have been drawn at an arbitrary size.

Synthesis and Characterization of Bimetallic Complexes of 5. In the initial investigations of the transition-metal chemistry of **5** it quickly became apparent that this ligand favors bis(bidentate) coordination to two metals to form homobimetallic complexes. The addition of **5** to a toluene solution of $(PhCN)_2PdCl_2$ results in the precipitation of an air-stable, pale yellow solid, **8**, regardless of the stoichiometry of the reactants. This product, soluble only in DMSO or pyridine, exhibits a singlet in its ^{31}P NMR spectrum at 21.7 ppm. Analytical data for **8** indicate the presence of two $PdCl_2$ units per ligand **5**, suggesting that the ligand coordinates to two $PdCl_2$ fragments in a bis(bidentate) manner. The ^{13}C NMR spectrum of **8** is consistent with a structure of either type A or B.

Slow evaporation of a concentrated DMSO solution of **8** yielded crystals suitable for X-ray analysis (Figure 2). The structural solution suffers from highly disordered DMSO molecules and some disorder in the phenyl ring orientations leading to R and R_w values of 0.11 and 0.13, respectively. Despite the disorder present in the structure, the location of the heavy atom positions confirms the presence of two palladium atoms, each in an essentially square-planar environment comprised of two chloride ligands and two phosphorus donors from **5**. The Pd–P distances of 2.23 (1)–2.26 (1) Å are in the range reported previously for $(dppm)PdCl_2$, $(dppe)PdCl_2$, and $(dppp)PdCl_2$,[29] but the P–Pd–P angles of 93.7 (4)° and 94.5 (5)° are significantly larger than those found for $(dppp)PdCl_2$ and $(dppp)Pd(NCS)_2$[30] of 90.58 (5)° and 89.32°, respectively. The ORTEP drawing in Figure 2 shows that **5** chelates to the two $PdCl_2$ fragments with the formation of six-membered rings, rather than the isomeric product containing seven-membered chelate rings (vide infra).

In addition to forming complexes with $PdCl_2$, the bromide and iodide analogues $(\mu\text{-}5)(PdBr_2)_2$ (**9**) and $(\mu\text{-}5)(PdI_2)_2$ (**10**) have been prepared. The physical and spectroscopic characteristics of **9** are similar to those of **8**, but the ^{31}P NMR spectrum of **10** reveals resonances at 11.7 and 11.4 ppm in a ratio of 1:10. The solubility of **10** in acetonitrile and methylene chloride allows the separation of these two components by fractional crystallization, yielding **10a** (δ 11.7 ppm) as dark red needles and **10b** (δ 11.4 ppm) as orange hexagonal plates. X-ray crystallography reveals that the molecular

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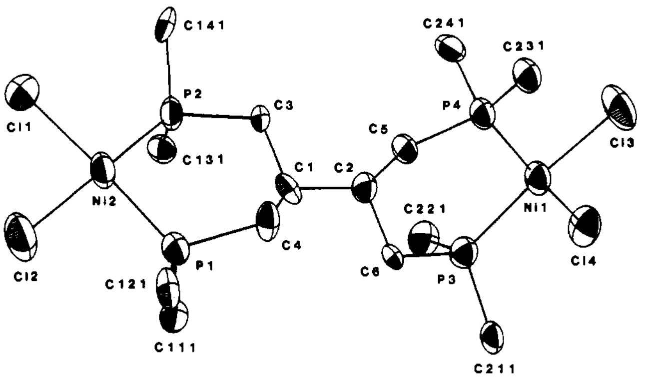

Figure 3. ORTEP drawing of **11** with all phenyl carbons, except for Ph-ipso carbons, omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

structure of **10b** is analogous to that for **8** where **5** coordinates to two palladium atoms with the formation of six-membered rings.[31] It is tempting to speculate that the minor component **10a** may be of type B, where **5** coordinates to two palladium atoms with the formation of seven-membered chelate rings (vide infra).

Reaction of **5** with 2 equiv of $NiCl_2$ yields a deep red solid, **11**, whose ^{31}P NMR spectrum exhibits a paramagnetically broadened, almost unobservable resonance at 5 ppm, consistent with a tetrahedral geometry at nickel. Complex **11** dissolves in pyridine to form a bright yellow solution, but the ^{31}P NMR spectrum of this solution indicates dissociation of the ligand has occurred to yield uncoordinated **5**. The nickel-containing material in this solution is presumably $Ni(py)_4Cl_2$.[32] We are unaware of previous reports concerning the dissociation of nickel phosphine complexes in pyridine, but this observation is consistent with the trend for first-row transition metals to prefer "hard" donors such as nitrogen whereas the second- and third-row transition metals display a preference for "soft" donors such as phosphines. In accord with these trends, complex **8** does not dissociate detectably in pyridine. Complex **11** is stable to dissociation in other solvents in which it is soluble (e.g., CH_3CN, DMSO, acetone) and forms red crystals upon concentration of an acetonitrile solution of the complex. Upon removal of these crystals from their mother liquor they immediately lose solvent to form a red powder. Crystals of **11** obtained from acetone were also plagued by rapid solvent loss. However, layering cyclohexane onto a cyclohexanone solution of **11** afforded red crystals sufficiently stable with respect to solvent loss to allow for the structure of this complex to be determined by X-ray crystallography. The molecular structure of **11** is depicted in Figure 3. Ligand **5** coordinates to two $NiCl_2$ fragments, each incorporated into a six-membered chelate ring. The nickel atoms adopt a slightly distorted square-planar geometry, with the sum of the angles around each nickel atom totaling 358°. The P–Ni–P angles are 96.79 (9)° and 94.52 (9)°. The Ni–P distances of 2.189 (3), 2.170 (3), 2.181 (3), and 2.178 (3) Å for P(1), P(2), P(3), and P(4), respectively, fall in the range of 2.145 (2)–2.321 (3) Å reported previously for (dppe)$NiCl_2$,[33a] $\{Ph_2P(CH_2)_2O(CH_2)_2PPh_2\}NiCl_2$,[33b] and $(Ph_3P)_2NiCl_2$.[33c] The square-planar geometry around nickel in the solid state and the paramagnetism exhibited in solution are reminiscent of (dppp)$NiCl_2$ which undergoes a square-planar ⇄ tetrahedral isomerization in solution, but is square-planar in the solid state on the basis of spectroscopic data.[34] Also of interest in this structure are the large number of solvent molecules incorporated into the crystalline lattice, two each of cyclohexane and cyclohexanone. This observation helps to rationalize why crystals obtained from more common, lower boiling solvents rapidly lose solvent to yield powders.

Table II. ^{31}P NMR Spectroscopic Data[a]

	δ, ppm
5	−22.0
6, (**5**)O_4	30.6
7, (**5**)S_4	40.1
8, (μ-**5**)$\{PdCl_2\}_2$	21.7[b]
9, (μ-**5**)$\{PdBr_2\}_2$	19.1[b]
10a, (μ-**5**)$\{PdI_2\}_2$	11.4
10b, (μ-**5**)$\{PdI_2\}_2$	11.7
11, (μ-**5**)$\{NiCl_2\}_2$	5 (br)[c]
12, (μ-**5**)$\{PtCl_2\}_2$	2.9 ($^1J_{Pt-P}$ = 3456 Hz)
13, (μ-**5**)$\{Cr(CO)_4\}_2$	49.0
14 (μ-**5**)$\{Mo(CO)_4\}_2$	28.4
15, (μ-**5**)$\{W(CO)_4\}_2$	8.2 ($^1J_{PW}$ = 227 Hz)
16, (μ-**5**)$\{Fe(CO)_3\}_2$	54.7[d]
17, (**5**-*P*,*P′*,*P″*)$Mo(CO)_3$[k]	17.7 (t),[e] 15.8 (t), 14.2 (t), −17.9 (s)[f]
18, (**5**-*P*,*P′*,*P″*)$Mo(CO)_3$[k]	20.1 (t),[g] 18.4 (t), 16.1 (t), 32.7 (s)[h]
19, (**5**-*P*,*P′*,*P″*)$Mo(CO)_3$[k]	17.1 (t),[i] 15.7 (t), 13.6 (t), 40.5 (s)[j]
20, (**5**-*P*,*P′*)$PdCl_2$	21.4, −20.7[f]
21, (**5**-*P*,*P′*)$PdCl_2$[k]	31.4,[h] 20.4

[a] Spectra taken in CH_2Cl_2 unless indicated otherwise. [b] DMSO. [c] CH_3CN. [d] Toluene. [e] $^2J_{PP}$ = 19.6 Hz. [f] Corresponds to uncoordinated PPh_2 group. [g] $^2J_{PP}$ = 19.1 Hz. [h] $P(O)Ph_2$ resonance. [i] $^2J_{PP}$ = 19.3 Hz. [j] $P(S)Ph_2$ resonance. [k] The fourth PPh_2 group of **5** is uncoordinated in **17**. This group is bonded to O in **18** and to S in **19**. In **21**, the third and fourth PPh_2 groups of **5** are each bonded to O.

Table III. Infrared Spectroscopic Data[a]

	ν_{CO}, cm^{-1}			
13, (μ-**5**)$\{Cr(CO)_4\}_2$	2004	1919	1879	
14, (μ-**5**)$\{Mo(CO)_4\}_2$	2017	1927	1909	
15, (μ-**5**)$\{W(CO)_4\}_2$	2014	1917	1880	
16, (μ-**5**)$\{Fe(CO)_3\}_2$	1981	1909	1886	1875
17, (**5**-*P*,*P′*,*P″*)$Mo(CO)_3$[b]		1934	1830	

[a] Obtained on CH_2Cl_2 solutions unless otherwise indicated. [b] KBr.

The platinum chemistry of **5** generally yielded insoluble white precipitates believed to be oligomeric in nature when starting from $(PhCN)_2PtCl_2$, $(PhCN)_2PtI_2$, or $(Me_2S)_2PtCl_2$. The reaction of **5** with 2 equiv of (COD)$PtCl_2$ yields a white solid (**12**) which does, however, exhibit slight solubility in CH_2Cl_2 and DMSO. The ^{31}P NMR spectrum of **12** exhibits a singlet at 2.9 ppm flanked by platinum satellites. The ^{195}Pt–^{31}P coupling constant of 3456 Hz is typical for a cis arrangement of phosphorus donors around platinum.[35] As for **8**–**10**, these data are consistent with a bimetallic complex wherein **5** coordinates to two square-planar $PtCl_2$ units.

Ligand **5** was also found to form bimetallic complexes when group VI metal carbonyl precursors were employed. Reaction of **5** with 2 equiv of $L_2M(CO)_4$ wherein M = Cr, Mo, and W and wherein L_2 = NBD, 2-piperidine, and COD, respectively, yields the creamy white complexes $[CH(CH_2PPh_2)_2M(CO)_4]_2$, M = Cr (**13**), Mo (**14**), and W (**15**). The ^{31}P NMR spectra of these complexes exhibit singlets with the tungsten analogue displaying satellites with $^1J_{PW}$ = 227 Hz (see Table II). The carbonyl stretches in the infrared spectra of **13**–**15** are consistent with those previously reported for *cis*-phosphine-substituted tetracarbonyl complexes[36] and are tabulated in Table III. The ^{13}C NMR

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(31) Crystals of **10b** are monoclinic, space group *C*2/*c*, with unit cell dimensions *a* = 37.541 Å, *b* = 14.622 Å, *c* = 27.353 Å, β = 113.212°, and *Z* = 8. The crystal had a calculated density of 1.53 g/cm^3. The structure was refined to *R* = 0.129 on the basis of 9665 reflections of which 2613 were unique with $I > 3\sigma(I)$. Phenyl rings were refined as rigid groups. Disorder in the DMSO molecule of crystallization and the low number of observed reflections presumably are the cause of the poor refinement. Data were collected at −80 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12 kW rotating anode generator.

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Table IV. Phosphorus Coordination Chemical Shifts[a] ($\Delta(\delta^{31}P)$) for (ligand)$M(CO)_4$ Complexes

	ligand					
M	dppm[b]	dppe[b]	dppp[b]	dppb[b]	**5**[c]	$Ph_2PCH_2CMe_2CH_2PPh_2$
Cr	49.6	91.9	58.3	63.0	71.0	
Mo	25.1	67.2	37.3	44.2	50.4	44.0[c]
W	0.1	52.6	17.2	26.3	30.2	25.3[d]

[a] $\Delta(\delta^{31}P) = \delta^{31}(P_{complex}) - \delta^{31}(P_{ligand})$; see ref 42. [b] Values taken from ref 39. [c] This work. [d] Value determined from data in ref 36c.

spectra of **13**–**15** are consistent with a bis(bidentate) coordination mode of either type A or B. Complex **15**, for example, exhibits triplet resonances at 203.2 ppm ($^{2}J_{PC}$ = 8 Hz) and 202.6 ppm ($^{2}J_{PC}$ = 6 Hz) assigned to the two nonequivalent axial carbonyls. The expected five-line multiplet of an AXX′ (A = ^{13}C; X, X′ = ^{31}P) spin system is observed at 205.4 ppm for the two equivalent equatorial carbonyls. In octahedral metal complexes where **5** coordinates in a bidentate manner, the two axial sites on each metal are stereochemically nonequivalent owing to the presence of two different exocyclic substituents on the methine carbons. The triplet multiplicities of these resonances as well as their $^{2}J_{PC}$ coupling constants[37] confirm the orientation of these two carbonyl ligands as cis to two phosphorus donors. The appearance of a five-line multiplet[38] for the two equivalent equatorial carbonyls and the dependence of the appearance of these multiplets on the variation of $^{2}J_{PP}$ in analogous complexes of chromium, molybdenum, and tungsten have been previously discussed for the series $(Ph_2P(CH_2)_nPPh_2)M(CO)_4$ where n = 1–4 and M = Cr, Mo, and W.[39] As was discussed earlier herein for the phosphoryl and thiophosphoryl derivatives of **5**, the complexes **13**–**15** exhibit two resonances in their ^{13}C NMR spectra for the phenyl ipso, ortho, meta, and para carbons of the two stereochemically nonequivalent phenyl substituents on phosphorus. These phenyl resonances for **13**–**15** appear as "apparent" triplets resulting from phosphorus coupling of the AXX′ spin system.[37] In contrast, the phenyl resonances for the palladium complexes **8** and **9** appear as slightly broadened doublets, which requires that $^{2}J_{PP}$ and $^{n}J_{PC}$ be small. Other complexes of the type $(R_3P)_2PdX_2$ have also been reported to exhibit doublet resonances in their ^{13}C NMR spectra.[40]

The complex $[CH(CH_2PPh_2)_2Fe(CO)_3]_2$ (**16**) was also prepared and characterized by infrared and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, and its spectral features are similar to those of the complexes discussed previously. It is worthy to note that the carbonyl ligands in **16** are fluxional on the ^{13}C NMR time scale and exhibit only one triplet resonance down to −60 °C where some broadening of the resonance occurs. Similar behavior has been previously reported for complexes of the type $(R_3P)_2Fe(CO)_3$.[41]

On the basis of the structural results obtained for **8**, **10b**, and **11** as well as the infrared and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data presented, compounds **8**–**18** are all assigned structure type A where **5** chelates to two metal fragments with the formation of six-membered chelate rings. The possible exception to this assignment may be the minor component **10a**, although we have as yet no evidence to support this claim. Because of this question, we were interested in finding a spectroscopic tool which could distinguish compounds of type A from those of type B without having to rely on X-ray crystallography. With this aim we pursued the differentiation of chelate ring size by measuring the phosphorus coordination chemical shift of the complexes, $\Delta(\delta^{31}P)$, which is defined as the difference in the ^{31}P NMR chemical shifts of the complex and the free ligand.[42] As discussed by Grim et al.,[42b] ^{31}P NMR chemical shifts for phosphine transition-metal complexes vary considerably with chelate size. Five-membered chelate rings exhibit large downfield shifts, four-membered chelate rings are shifted upfield, and six-membered chelate rings display normal chemical shift behavior in comparison to monodentate phosphine analogues. Literature data for a series of group VI metal carbonyl chelate complexes as well as data for complexes **13**–**15** are given in Table IV. These data show that the differences in $\Delta(\delta^{31}P)$ values for six- vs seven-membered rings range from only 5 to 9 ppm, with the larger $\Delta(\delta^{31}P)$ values associated with the seven-membered rings. These differences are much smaller than those observed between four-, five-, and six-membered rings. Unfortunately, the phosphorus coordination chemical shifts for **13**–**15** are considerably larger than those for either the six- or seven-membered chelate ring model complexes. Even more unsatisfying are the coordination chemical shifts of 25.3 ppm calculated for $(Ph_2PCH_2CMe_2CH_2PPh_2)W(CO)_4$ on the basis of data reported by Kraihanzel et al.[36c] and the value of 44.0 ppm which we obtained for its molybdenum analogue. Using these $\Delta(\delta^{31}P)$ values in the usual way would erroneously suggest the presence of seven-membered chelate rings in these two complexes, obviously leading us to discard this method for the differentiation of structural types A and B in our complexes. The determination of the configuration of **10a** must await growth of a crystal suitable for X-ray crystallography.

Synthesis and Characterization of Monometallic Complexes of 5: Tridentate Coordination Mode. Several attempts were made to synthesize complexes of type C utilizing group VI metal carbonyl precursors. Reactions of **5** with $Mo(CO)_6$ led to the formation of **14**. The bidentate coordination mode also prevailed when **5** was reacted with 1 equiv of $Mo(CO)_3(NCEt)_3$,[43] yielding a partially characterized complex of type A (e.g., $\{fac\text{-}(EtCN)(OC)_3Mo\}_2(\mu\text{-}\mathbf{5})$) based on the symmetry implied by its spectroscopic features. Ligand **5** was found, however, to slowly replace cycloheptatriene from (η^6-cycloheptatriene)$Mo(CO)_3$ at 60 °C to yield the new complex **17** as a creamy white solid. The ^{31}P NMR spectrum of **17** is most informative about its structure, exhibiting triplets at 17.7, 15.8, and 14.2 ppm and a singlet at −17.9 ppm indicative of an uncoordinated phosphine group, but shifted 4.4 ppm downfield from uncoordinated **5**. This spectrum is consistent with a complex of type C where ligand **5** adopts a tridentate coordination mode. Each of the four phosphine groups are inequivalent, accounting for the appearance of three triplets for the coordinated phosphine groups. The ^{13}C NMR spectrum is very complicated since all eight phenyl rings are inequivalent. An attempt to grow crystals of this complex by layering hexane onto a CH_2Cl_2 solution yielded thin colorless needles of a new complex, **18**, within 3 weeks. The ^{31}P NMR spectrum of this new complex shows three triplets, similar to **17**, but the free phosphine group has apparently been oxidized as indicated by a singlet at 32.7 ppm. Presumably this oxidation occurs because of the presence of adventitious oxygen. Darensbourg has similarly reported that, upon prolonged standing at room temperature, solutions of $W(CO)_3(dppm)(\eta^1\text{-}dppm)$ yield the new complex $W(CO)_3(dppm)(Ph_2PCH_2P(O)Ph_2)$, presumably due to the presence of adventitious oxygen.[44] Oxidation of the uncoordinated phosphine group in **17** with S_8 in toluene gives the new complex **19** as indicated by its ^{31}P NMR (Table II).

Attempted Synthesis of Monometallic Complexes of 5: Tetradentate Coordination Mode. Divalent nickel, palladium, and platinum, as well as monovalent rhodium, are known to favor a square-planar geometry for phosphine complexes. The square-planar complexes $[M(dppe)_2]^{2+}$ are well known for M = Ni, Pd, and Pt, and the palladium and platinum complexes have been

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characterized by X-ray crystallography.[45] Similarly, the series of square-planar complexes $[\{Ph_2P(CH_2)_nPPh_2\}_2Rh]^+$ where n = 2–4 have been synthesized and characterized spectroscopically and structurally.[46] Thus, these metals were chosen to explore the tendency of **5** to form square-planar complexes of type D.

In our first attempt, complex **8** was reacted with 1 equiv of **5** in DMSO in hopes of achieving ligand redistribution. The ^{31}P NMR spectrum of this reaction solution indicates the presence of a small quantity of unreacted **8** as well as new resonances at 21.4 and −20.7 ppm assigned to the new complex **20**. Occasionally additional resonances in the regions of 32–30, 23–20, and −18 to −23 ppm were observed. The 32–30 ppm region is indicative of phosphine oxidation and most likely arises from the presence of adventitious oxygen. Samples of this reaction solution are stable under argon for up to a month with no evidence of further reaction or oxidation. Exposure of this solution to air results in oxidation within several days to cleanly yield complex **21**, exhibiting ^{31}P NMR chemical shifts at 31.4 and 20.4 ppm. This complex was isolated as a pale yellow solid which exhibits good solubility in CH_2Cl_2. The ^{31}P NMR chemical shift of 31.4 ppm indicates the presence of phosphoryl groups, which are further substantiated by a split phosphoryl stretch in the infrared spectrum at 1184 and 1119 cm^{-1}. For comparison, the phosphoryl compound **6** exhibits a split phosphoryl stretch at 1178 and 1117 cm^{-1}. Such splitting of phosphoryl and thiophosphoryl stretches in infrared spectra is apparently relatively common.[47]

The ^{13}C NMR spectrum of **21** exhibits resonances for four distinct phenyl groups. Two of these obviously belong to a phosphoryl group on the basis of the doublet nature of their resonances and on the large coupling to phosphorus of 99 Hz observed for the two Ph-ipso carbons. The two remaining non-equivalent phenyl groups belong to two equivalent phosphine groups coordinated to a single palladium atom. This assignment is based on the apparent triplet multiplicity of these resonances indicative of an AXX′ spin system. The presence of two phosphine and two phosphoryl groups is also confirmed by the observation of two methylene carbon resonances, with the resonance for the methylene carbons adjacent to a phosphoryl group appearing as a doublet of doublets with $^1J_{PC}$ = 69 Hz. On the basis of the spectroscopic data presented above, **21** is assigned a structure of type E. The presence of two methine carbon resonances in the ^{13}C NMR spectrum of **21** clearly indicates the structure must contain a six-membered chelate ring.

Crystals of **21** were obtained as a DMSO solvate by slow evaporation of a DMSO solution in air, and their structure was confirmed by X-ray crystallography. The ORTEP diagram shown in Figure 4 shows that **21** is comprised of half each of compounds **6** and **8**. Figure 4 also reveals that **5** coordinates to palladium with the formation of a six-membered chelate ring as suggested by ^{13}C NMR spectroscopic data. The palladium atom is square-planar and lies 0.034 Å out of the P_2Cl_2 plane. The Pd–P distances of 2.243 (3) and 2.229 (3) Å as well as the P–Pd–P angle of 94.6 (1)° are quite similar to the analogous values found for **8**. The P–O distances of 1.480 (9) and 1.485 (9) Å lie in the normal range discussed earlier. Unlike the molecular structure of **6**, **23** has no close intramolecular contacts between phosphoryl oxygen atoms and neighboring methylene groups.

The formation of **21** upon exposure of the reaction solution of **5** and **8** to air is consistent with a metal-catalyzed oxidation of the uncoordinated phosphine groups. This oxidation does not appear to be the result of reaction with DMSO since solutions of **5** in DMSO exposed to air and the reaction solution of **5** and **8** in DMSO under argon show no oxidation according to their ^{31}P NMR spectra. Several other examples of metal-catalyzed oxidation of phosphines have been reported.[48] The precursor to **21**, formed in the reaction solution of **5** and **8** prior to exposure to air, is presumably $Cl_2Pd(Ph_2PCH_2)_2CHCH(CH_2PPh_2)_2$, **20**. This assignment is based on the two ^{31}P NMR chemical shifts of 21.4 and −20.7 ppm observed in this solution as well as the fact that exposure of solutions of **20** to air yields **21**. Although we have not yet attempted to isolate this complex, it could provide a convenient entry into heterobimetallic complexes of this ligand.

To avoid the formation of complexes **20** and **21**, we chose a palladium starting material with a noncoordinating anion. Reaction of **5** with 1 equiv of $Pd(BF_4)_2 \cdot 4CH_3CN$ in CH_2Cl_2/CH_3CN yields a yellow solution whose ^{31}P NMR spectrum consists mainly of a singlet at 6.7 ppm. A shoulder on the upfield side of this resonance as well as a broad peak centered at ~11 ppm was also present. Raising the temperature of this solution to 325 K results in a sharpening of the resonance at 11 ppm and splitting of the shoulder on the 6.7 ppm resonance into two additional resonances. These additional resonances suggest the presence of more than one species in solution. We have been unable to identify the complex giving rise to the resonance at 6.7 ppm and have been unable to isolate a complex which appears by ^{31}P NMR spectra to consist of only one species in solution.

The addition of 1 equiv of **5** to a light blue solution of $[Ni(NCCH_3)_6][ClO_4]_2$ or $[Ni(DMSO)_6][BF_4]_2$ in acetonitrile results in the formation of an immediate deep brown solution. The ^{31}P NMR spectrum of this solution exhibits only one small singlet at −22.0 ppm assigned to uncoordinated **5**. The lack of resonances for a nickel complex of **5** indicates the nickel complex may be tetrahedral and paramagnetic, inconsistent with a complex of type D. A nickel complex of type D would have to be square-planar and as such should be diamagnetic. This brown solution is stable indefinitely under argon, but similarly to **20**, this solution undergoes a metal-catalyzed oxidation within 10 min in the presence of air to yield a light yellow solution. Oxidation is indicated by a ^{31}P NMR chemical shift of 30.9 ppm and the formation of clear crystals of **6** upon allowing this solution to stand for several days.

Reaction of **5** with 0.5 equiv of $Rh_2Cl_2(COD)_2$ in THF yields a pale yellow powder (**22**) which does not contain cyclooctadiene. A FAB mass spectrum of **22** shows a small molecular ion peak for $(5)Rh^+$ at m/e 925.1 and peaks at me 957.1 and 973.1 corresponding to the molecular ion plus two and three oxygen atoms, respectively, arising from oxidation of the complex while in the glycerol matrix. Additionally, numerous smaller peaks corresponding to higher mass fragments were observed above m/e 1000. Conductivity measurements on CH_3NO_2 solutions of **22** provide a molar conductance of only 37 Ω^{-1} cm^2 mol^{-1} on the basis of a mononuclear species of composition [(**5**)Rh]Cl. This is considerably lower than the commonly accepted range[49] of 75–95 Ω^{-1} cm^2 mol^{-1} for 1:1 electrolytes in CH_3NO_2 and may indicate partial coordination of chloride to rhodium or the presence of dimeric species.

The ^{31}P NMR spectrum of **22** in acetonitrile shows a broadened resonance consisting of two doublets of unequal intensity at 18.3 and 15.9 ppm with coupling to rhodium of 130 and 135 Hz, respectively. In DMSO, **22** exhibits only one very broad resonance centered at 12.7 ppm. Removal of the chloride anion using $AgBF_4$ had no effect on the ^{31}P NMR spectrum of **22** in either solvent, indicating that chloride is probably not coordinated to rhodium in solution. Variable-temperature ^{31}P NMR spectra taken in CH_3CN/CH_2Cl_2 between 225 and 325 K shows complicated, unassigned resonances at both extremes. On the basis of this ^{31}P NMR data as well as the conductivity and mass spectral results, it is clear that **22** is not a mononuclear species of type D, and may

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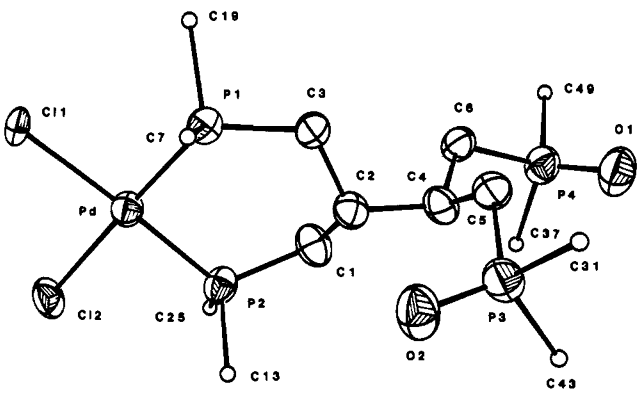

Figure 4. ORTEP drawing of **21** with thermal ellipsoids drawn at the 50% probability level. All phenyl carbons, except for Ph-ipso carbons, have been omitted for clarity.

well be dimeric or oligomeric in solution. We have no information concerning its structure in the solid state.

On the basis of the results of nickel, palladium, and rhodium reactions with an equimolar quantity of **5**, we believe that complex mixtures, which may contain interconverting dimeric or oligomeric complexes as well as solvated species, are present in these reaction solutions. Since we have shown that this ligand is capable of acting as a bidentate ligand to two metals, the formation of oligomeric materials seems quite plausible.

Work by Pignolet and Shaw offers some support for this proposal as well as a rationale for these results. Pignolet[46a] has published an informative paper concerning the series of complexes $[Rh(Ph_2P(CH_2)_nPPh_2)_2]BF_4$ ($n = 2$–4). These complexes are all reported to exhibit doublet resonances in their ^{31}P NMR spectra with couplings to rhodium of 132–137 Hz. In the low-temperature spectra for these complexes, however, only the $n = 2$ complex continued to exhibit a doublet resonance. The $n = 3$ complex exhibited an A_2B_2X pattern consistent with a five-coordinate solvated complex, and for the $n = 4$ complex the low-temperature spectrum was complex and unassignable, presumably due to the presence of solvated and dinuclear species. The researchers concluded that this temperature-dependent behavior was the result of *increasing steric interactions with increasing chelate size* throughout the series $n = 2$–4. Consistent with this argument was the appearance of the same trend in the molecular structures of these complexes. Furthermore, in the reaction of CO with the complex in which $n = 4$, a dppb ligand readily dissociates to form the dimeric species $[Rh_2(dppb)_3(CO)_4]^{2+}$, the structure of which has been confirmed by X-ray crystallography.[50] In solution, this complex exhibits two broad ^{31}P NMR resonances at 20 and 23 ppm and its low-temperature spectrum becomes complex. These spectra indicate that this complex does not retain its solid-state structure in solution. This is of direct relevance to our system since a complex of type D would contain both six-membered and seven-membered chelate rings. The results described by Pignolet for the complexes $n = 3$ and 4 suggest the presence of steric repulsions in our system, and they support our proposal for a complex solution chemistry with the potential formation of solvated and oligomeric species. Models indicate that four severe Ph–Ph interactions occur in complexes of type D. Unlike the bidentate ligands dppp and dppb, **5** offers little structural flexibility to allow for minimization of these steric interactions when all four phosphine groups are coordinated to a single metal atom.

Work by Shaw, McAuliffe, and others has shown that chelating phosphines of the type $R_2P(CH_2)_nPR_2$ require a minimum of five methylene units ($n = 5$) between the donor atoms in order to span trans positions on the same metal.[51] In fact, several structural studies on complexes of the type *trans*-$Cl_2Pd(R_2P(CH_2)_nPR_2)$ where $n > 5$ have shown many of these complexes to be cyclic dimers or trimers, forming rings as large as 45 atoms.[51h,i,l] In our system, a complex of structural type D has two trans pairs of phosphorus donors. There are only four backbone carbon atoms between either trans pair of phosphorus donors in **5**, thereby leaving the minimum requirement proposed by Shaw unfulfilled. This argument is also supported by attempts to build space-filling models of type D. Thus, it is apparent that attempts to form complexes of type D are hindered by (i) steric repulsions of the eight phenyl substituents in **5**, (ii) a ligand backbone structurally incapable of spanning two trans sites in a metal complex, and (iii) the ease of formation of dinuclear complexes wherein **5** readily acts as a bis(bidentate) ligand as in complexes **8–16**.

Conclusions. We have synthesized the new tetratertiary phosphine **5** which readily forms homobimetallic complexes with a variety of transition metals. The formation of **20** in solution may provide a convenient route to the synthesis of heterobimetallic complexes. Ligand **5** also coordinates to molybdenum tricarbonyl fragments as a tridentate ligand, with one phosphine group remaining uncoordinated. Steric hindrance and structural limitations were found, however, to preclude the formation of monometallic complexes of Ni(II), Pd(II), and Rh(I) wherein **5** coordinates as a tetradentate ligand. Removal of these steric and structural limitations in derivatives of **5** may yield a novel class of new tetradentate phosphine ligands, and studies aimed at this goal are underway.

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Supplementary Material Available: Tables of isotropic and anisotropic thermal parameters, positional parameters, bond lengths, and bond angles (35 pages); listings of calculated and observed structure factors (43 pages). Ordering information is given on any current masthead page.

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