Palladium and Platinum Complexes Containing the Linear Tetraphosphine Bis[((diphenylphosphino)ethyl)phenylphosphino]methane

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The linear tetraphosphine bis[((diphenylphosphino)ethyl)phenylphosphino]methane (DPPEPM) has been prepared and separated into its meso and racemic forms. Each has been reacted with elemental sulfur, and the structure of the meso compound DPPEPM-S_4 has been determined crystallographically. The meso or racemic form of DPPEPM reacts with 2 equiv of $[MCl_2(cod)]$ (M = Pd, Pt) or $[PtR_2(cod)]$ (R = Me, Ph, CH_2Ph, C_6H_4Me-4) to give complexes of the form $[M_2X_4(\mu\text{-DPPEPM})]$, in which DPPEPM acts as both a chelating and a bridging ligand. Complexes containing additional chloride bridges, $[M_2R_2(\mu\text{-Cl})(\mu\text{-DPPEPM})]PF_6$, have been prepared from DPPEPM and [PtClR(cod)] (R = Me, Ph, CH_2Ph), [PdClR(cod)] (R = Me, CH_2Ph), or $[Pd_2R_2(\mu\text{-Cl})_2(AsPh_3)_2]$ (R = Ph, COMe), followed by $TlPF_6$. Chloride-bridged compounds could also be prepared by treatment of $[M_2Cl_4(\mu\text{-DPPEPM})]$ with 1 equiv of $TlPF_6$. Addition of Bu_4NI to $[M_2Me_2(\mu\text{-Cl})(\mu\text{-DPPEPM})]PF_6$ resulted in bridge opening, and further treatment with $TlPF_6$ gave the corresponding iodide-bridged species. The compounds have been characterized by NMR spectroscopy and by elemental analysis or high-resolution mass spectrometry. The solid-state structures of $[Pd_2Cl_4(\mu\text{-DPPEPM})]$ and $[Pt_2Ph_4(\mu\text{-DPPEPM})]$ are also reported.

Introduction

Bis(diphenylphosphino)methane (dppm) and related ligands have been used extensively in the construction of homobimetallic complexes.[1] In certain cases $R_2PCH_2PR_2$ (R = Me, OR) ligands form bimetallic complexes of the form $[M_2X_4(\mu\text{-}R_2PCH_2PR_2)_2]$, in which the bridging phosphino groups lie cis to one another,[2] but, most commonly, the phosphino groups occupy mutually trans sites. This is found for the side-by-side dimers $[M_2X_2(\mu\text{-dppm})_2]$ (M = Pd, Pt)[3] and the many A-frame structures involving rhodium, iridium, palladium, and platinum.[4] One or two dppm ligands have been employed also in the synthesis of heterobimetallic complexes.[5] Indeed, we have used the $[PtR(dppm\text{-}PP)(dppm\text{-}P)]^+$ cations as precursors to a range of heterobimetallic derivatives.[6]

We have made extensive studies of A-frame complexes of palladium and platinum. These include symmetrical and unsymmetrical species, with bridging halides[7] or hydrides.[8] The hydride-bridged species $[M_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ are stable at ambient temperature in the solid state and in solution, and they undergo reductive elimination of RH in solution only at elevated temperatures.[9] It is likely that the thermal stability of these complexes is due to the favored trans orientation of the phosphino groups, which prevents the R and H groups from occupying the adjacent sites needed for elimination, except perhaps transiently at high temperatures. To increase the potential catalytic activity of the bimetallic systems, we sought to maintain the M_2P_4 unit but to constrain the phosphino groups in mutually cis

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positions. We decided to investigate the chemistry of palladium and platinum complexes of the linear tetraphosphine ligands reported by Stanley,[10] in which a pair of phosphino groups can form a five-membered chelate ring with each metal center and the two square-planar units are held together by a single methylene bridge. This is in contrast to the all-ethylene-bridged tetraphosphine reported by Brüggeller, which is capable of wrapping round a square-planar platinum(II) center.[11] Whereas much of Stanley's work has focused on the ethyl-substituted derivative $Et_2PCH_2CH_2PPhCH_2PPhCH_2CH_2PEt_2$, eLTTP, we chose to make use of the all-phenyl analogue, $Ph_2PCH_2CH_2PPhCH_2PPhCH_2CH_2PPh_2$ (bis[((diphenylphosphino)ethyl)phenylphosphino]methane, DPPEPM). A preliminary report of the synthesis and structures of a series of platinum complexes of this ligand has appeared.[12]

Experimental Section

All reactions were carried out under an atmosphere of argon. All the solvents were distilled prior to use. Neutral alumina and Hyflo Supercel were obtained from Fisher and Fluka, respectively. $[PtCl_2(cod)]$,[13] $[PdCl_2(cod)]$,[14] $[PtR_2(cod)]$ (R = Me, Ph, CH_2Ph, 2-tolyl), $[PtClR(cod)]$ (R = Me, Ph, CH_2Ph),[15,16] and $[PdClMe(cod)]$[17] were prepared as reported previously. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX-500 or Avance 300 instrument or a Varian Unity Plus 300 or XL-300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra were obtained in FAB mode, on a JEOL M Station-JMS700 instrument, using nitrobenzyl alcohol (NBA) as solvent. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of $PhHPCH_2PHPh$.[18] Phenylphosphine (5.0 g, 0.045 mol) and CH_2Cl_2 (1.95 g, 0.023 mol) were added to a flask containing DMF (55 mL). The mixture was cooled in an ice bath. Then 7 mL of aqueous KOH (9.35 g in 7.5 mL of water) was added dropwise over a period of 1 h. As the addition proceeded, the solution gradually turned deep yellow. The solution was stirred for 7−12 h. During this time the solution became colorless, with a white solid sticking to the sides of the flask. Water (36.5 mL) was added, and a cloud of hydrogen gas was produced. The resulting mixture was then washed with pentane (3 × 50 mL). The solvent was evaporated under reduced pressure to give the product as a clear, viscous liquid (2.55 g, 48%). The product consisted of a mixture of *meso* and *rac* diastereomers. $^{31}P\{^1H\}$ NMR (C_6D_6): δ(P) −54.8, −53.9.

Synthesis of DPPEPM. Bis(phenylphosphino)methane (2.3 g, 0.010 mol), vinyldiphenylphosphine (4.26 g, 0.020 mol), and cyclohexane (40 mL) were added to a flask fitted with a bent tube containing 2,2′-azobis(isobutyronitrile) (AIBN; 0.03 g). A reflux condenser was attached to the flask, and the AIBN was tipped into the solution. The reaction mixture was refluxed overnight and then cooled. The solvent was evaporated under reduced pressure to leave a viscous, colorless liquid. This was dissolved in ether (20 mL) and kept at −40 °C overnight. The ether was evaporated to give a sticky solid. This was washed several times with small amounts of cold methanol to give DPPEPM (4.89 g, 75%) as a 1:1 mixture of *meso* and *rac* diastereomers.

Separation of the *meso* and *rac* Diastereomers of DPPEPM. A 1:1 mixture of the *meso* and *rac* diastereomers of DPPEPM (3.0 g) was stirred in benzene/MeOH (1:4) for several hours, leading to the exclusive extraction of the *rac* diastereomer. The less soluble *meso* diastereomer was filtered off and dried under vacuum (1.32 g, 88%). The *rac* form was isolated by removal of the solvents and crystallized from CH_2Cl_2/EtOH (0.97 g, 65%).

meso form: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ(P) −25.5 (dd, J_{PP} = 13, 18 Hz, 2P, internal), −12.0 (dd, J_{PP} = 13, 18 Hz, 2P, external); ^1H NMR ($CDCl_3$): δ(H) 1.80−2.11 (br m, PCH_2CH_2P), 2.32 (br, PCH_2P), 7.25−7.40 (m, C_6H_5).

rac form: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) −24.8 (dd, J_{PP} = 13, 17 Hz, 2P, internal), −11.9 (dd, J_{PP} = 13, 17 Hz, 2P, external); ^1H NMR ($CDCl_3$): δ(H) 1.63−1.84 (br m, PCH_2CH_2P), 2.04 (t, $^2J_{PH}$ = 12 Hz, PCH_2P), 7.25−7.34 (m, C_6H_5).

Synthesis of *meso*-DPPEPM-S_4. A solution of *meso*-DPPEPM (0.22 g, 0.34 mmol) in CH_2Cl_2 (10 mL) was treated with elemental sulfur (0.44 g, 0.17 mmol), and the mixture was allowed to react for 1 h. It was then passed through a silica gel column, and the column was eluted with more CH_2Cl_2. The fractions were combined, and the solvent was removed in vacuo. The product was redissolved in CH_2Cl_2, and addition of pentane gave the product as a white powder. Crystals suitable for X-ray diffraction were grown by slow evaporation of a $CDCl_3$ solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 41.5 (m, 2P, internal), 44.7 (m, 2P, external). The spectrum was simulated successfully using the following coupling constants: $^3J_{P1-P2} = {}^3J_{P3-P4}$ = 65.4 Hz, $^5J_{P1-P3} = {}^5J_{P2-P4}$ = 0.5 Hz, $^2J_{P2-P3}$ = 13.2 Hz. ^1H NMR ($CDCl_3$): δ(H) 2.00−2.06, 2.32−2.38, 2.63−2.69, 2.83−2.89 (br m, 8H, PCH_2CH_2P), 2.99−3.08 (two overlapping pseudoquartets, $^2J_{HH} = {}^2J_{PH}$ = 13 Hz, PCH_2P), 7.30−7.72 (m, C_6H_5).

Synthesis of *rac*-DPPEPM-S_4. This complex was prepared similarly and obtained in 92% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 41.8 (m, 2P, internal), 44.8 (m, 2P, external). The spectrum was simulated successfully using the following coupling constants: $^3J_{P1-P2} = {}^3J_{P3-P4}$ = 65.4 Hz, $^5J_{P1-P3} = {}^5J_{P2-P4}$ = 0.5 Hz, $^2J_{P2-P3}$ = 14.2 Hz. ^1H NMR ($CDCl_3$): δ(H) 2.07−2.13, 2.70−2.75, 2.82−2.87 (br m, 8H, PCH_2CH_2P), 2.97−3.08 (t, $^2J_{PH}$ = 13 Hz, 2H, PCH_2P), 7.37−7.80 (m, C_6H_5).

Synthesis of $[Pd_2Cl_4(\mu$-*meso*-DPPEPM)]. *meso*-DPPEPM (0.12 g, 0.18 mmol) was dissolved in CH_2Cl_2 (15 mL), and $[PdCl_2(cod)]$ (0.10 g, 0.36 mmol) was added. The solution was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was washed several times with pentane and dried in vacuo. The product was isolated as a light yellow powder (0.122 g, 67%). Anal. Calcd for $C_{41}H_{40}Cl_4P_4Pd_2$: C, 48.69; H, 3.98. Found: C, 48.72; H, 4.15. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 61.8 (internal P), 62.6 (external P). ^1H NMR ($CDCl_3$): δ(H) 1.67−2.02, 2.49−2.70, 3.17−3.37 (PCH_2CH_2P), 3.87 (q, $^2J_{HH} = {}^2J_{PH}$ = 14 Hz, 1H, PCH_2P), 4.33 (q, $^2J_{HH} = {}^2J_{PH}$ = 12 Hz, 1H, PCH_2P), 7.31−8.34 (m, C_6H_5). Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a $CDCl_3$ solution.

Synthesis of $[Pd_2Cl_4(\mu$-*rac*-DPPEPM)]. This complex was prepared similarly and obtained in 63% yield. Anal. Calcd for $C_{41}H_{40}Cl_4P_4Pd_2$: C, 48.69; H, 3.98. Found: C, 48.04; H, 4.11. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 64.3 (internal P), 67.4 (external P). ^1H NMR ($CDCl_3$): δ(H) 2.79, 3.20, 3.29, 3.46 (PCH_2CH_2P), 4.02 (t, $^2J_{PH}$ = 14 Hz, PCH_2P), 7.16−8.13 (m, C_6H_5).

Synthesis of $[Pt_2Cl_4(\mu$-*meso*-DPPEPM)]. *meso*-DPPEPM (0.26 g, 0.40 mmol) was dissolved in CH_2Cl_2 (25 mL), and $[PtCl_2(cod)]$ (0.30 g, 0.80 mmol) was added. The solution was stirred for 15 min, and the solvent was removed under reduced pressure. The residue was washed several times with pentane,

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and the product was isolated as a colorless powder (0.301 g, 63%). Anal. Calcd for $C_{41}H_{40}Cl_4P_4Pt_2$: C, 41.42; H, 3.92. Found: C, 41.67; H, 3.52. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 37.6 (s, $^1J_{PtP}$ = 3575 Hz, $^2J_{PP}$ = 22 Hz, internal P), 38.7 (s, $^1J_{PtP}$ = 3680 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 2.06−3.08 (m, PCH_2CH_2P), 3.92 (q, $^2J_{HH}$ = $^2J_{PH}$ = 14 Hz, PCH_2P), 4.45 (q, $^2J_{HH}$ = $^2J_{PH}$ = 13 Hz, PCH_2P), 7.31−8.34 (m, C$_6H_5$).

Synthesis of [Pt_2Cl_4(*μ-rac*-DPPEPM)]. This complex was prepared similarly and obtained in 61% yield. Anal. Calcd for $C_{41}H_{40}Cl_4P_4Pt_2$: C, 41.42; H, 3.92. Found: C, 42.41; H, 3.58. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 40.0 ($^1J_{PtP}$ = 3556 Hz, internal P), 41.9 ($^1J_{PtP}$ = 3558 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 2.06−3.08 (m, PCH_2CH_2P), 4.14 (t, $^2J_{PH}$ = 14 Hz, PCH_2P), 7.36−8.64 (m, C$_6H_5$).

Synthesis of [Pt_2Me_4(*μ-meso*-DPPEPM)]. *meso*-DPPEPM (0.11 g, 0.17 mmol) was dissolved in CH_2Cl_2 (15 mL), and [$PtMe_2$(cod)] (0.11 g, 0.33 mmol) was added. The solution was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was washed several times with pentane, and the product was isolated as an off-white powder (0.10 g, 55%). Anal. Calcd for $C_{45}H_{52}P_4Pt_2$: C, 48.86; H, 4.74. Found: C, 48.95; H, 4.66. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 37.9 (br s, $^1J_{PtP}$ = 1737 Hz, $^3J_{PtP}$ = 44 Hz, $^2J_{PP}$ = 24 Hz, internal P), 46.8 (d, $^2J_{PP}$ = 6 Hz, $^1J_{PtP}$ = 1806 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 0.64 (d, $^3J_{PH}$ = 8 Hz, $^1J_{PtH}$ = 70 Hz, CH_3), 0.76 (d, $^3J_{PH}$ = 8 Hz, $^1J_{PtH}$ = 70 Hz, CH_3), 1.40−1.45, 1.55−1.75, 1.77−2.06 (br m, PCH_2CH_2P), 2.95 (br m, PCH_2P), 3.41 (br m, PCH_2P), 6.87−7.86 (m, C$_6H_5$).$^1H\{^{31}P\}$ NMR ($CDCl_3$): δ(H) 0.55 (s, $^1J_{PtH}$ = 70 Hz, CH_3), 0.67 (s, $^1J_{PtH}$ = 70 Hz, CH_3), 1.47−1.53, 1.60−1.65, 2.00−2.06, 2.19−2.25 (br m, PCH_2CH_2P), 2.89 (d, $^2J_{HH}$ = 15 Hz, PCH_2P), 3.37 (d, $^2J_{HH}$ = 15 Hz, PCH_2P), 6.90−7.58 (m, C$_6H_5$).

Synthesis of [Pt_2Me_4(*μ-rac*-DPPEPM)]. This complex was prepared similarly and obtained in 55% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 39.3 (m, $^1J_{PtP}$ = 1795 Hz, internal P), 46.6 (m, $^1J_{PtP}$ = 1799 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 0.67 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 66 Hz, CH_3), 0.81 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 64 Hz, CH_3), 1.68−1.81, 2.09−2.41, 2.84 (br m, PCH_2CH_2P), 3.27 (t, $^2J_{PH}$ = 11 Hz, PCH_2P), 6.67−7.76 (m, C$_6H_5$).

Synthesis of [Pt_2Ph_4(*μ-meso*-DPPEPM)]. *meso*-DPPEPM (0.11 g, 0.17 mmol) was dissolved in CH_2Cl_2 (20 mL), and [$PtPh_2$(cod)] (0.159 g, 0.34 mmol) was added. The solution was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was washed several times with pentane, and the product was isolated as a light yellow powder (0.13 g, 54%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 36.1 (br s, $^1J_{PtP}$ = 1712 Hz, $^3J_{PtP}$ = 41 Hz, $^2J_{PP}$ = 23 Hz, internal P), 39.7 (d, $^2J_{PP}$ = 6 Hz, $^1J_{PtP}$ = 1705 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 1.64−1.81, 1.94−2.06 (br, m, PCH_2CH_2P), 3.46, 3.60 (br m, PCH_2P), 6.42−7.97 (m, C$_6H_5$). Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a $CDCl_3$/Et_2O solution.

Synthesis of [Pt_2Ph_4(*μ-rac*-DPPEPM)]. This complex was prepared similarly and obtained in 55% yield. Anal. Calcd for $C_{65}H_{60}P_4Pt_2$: C, 57.60; H, 4.43. Found: C, 57.03; H, 4.75. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 39.8 (d, $^2J_{PP}$ = 7 Hz, $^1J_{PtP}$ = 1712 Hz, internal P), 41.5 (d, $^2J_{PP}$ = 7 Hz, $^1J_{PtP}$ = 1687 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 1.68−1.81, 2.09−2.41, 2.84 (br m, PCH_2CH_2P), 3.04 (t, $^2J_{PH}$ = 12 Hz, PCH_2P), 6.67−7.76 (m, C$_6H_5$).

Synthesis of [$Pt_2(CH_2Ph)_4$(*μ-meso*-DPPEPM)]. *meso*-DPPEPM (0.086 g, 0.13 mmol) was dissolved in CH_2Cl_2 (15 mL) and [$Pt(CH_2Ph)_2$(cod)] (0.127 g, 0.26 mmol) was added. The solution was stirred for 15 min, then the solvent was removed under reduced pressure. The residue was washed several times with pentane, and the product was isolated as a light yellow powder (0.105 g, 57%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 33.1 (br s, $^1J_{PtP}$ = 1842 Hz, $^3J_{PtP}$ = 36 Hz, $^2J_{PP}$ = 24 Hz, internal P), 44.7 (d, $^2J_{PP}$ = 4 Hz, $^1J_{PtP}$ = 1879 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 1.43−1.50, 1.60−1.74, 2.10−2.21 (br m, PCH_2-CH_2P, PtCH_2Ph), 2.65−2.88 (br m, PCH_2P), 6.22−6.82 (m, C$_6H_5$), 7.08−7.31 (m, PPh_2).

Synthesis of [$Pt_2(CH_2Ph)_4$(*μ-rac*-DPPEPM)]. This complex was prepared similarly and obtained in 51% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 34.9 (d, $^2J_{PP}$ = 10 Hz, $^1J_{PtP}$ = 1855 Hz, internal P), 43.5 (d, $^2J_{PP}$ = 10 Hz, $^1J_{PtP}$ = 1869 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 1.42−1.50, 1.60−1.65, 2.36−2.91 (br m, PCH_2CH_2P, PtCH_2Ph), 3.24 (t, $^2J_{PH}$ = 12 Hz, PCH_2P), 6.56−6.93 (m, C$_6H_5$) 7.05−7.40 (PPh_2).

Synthesis of [$Pt_2(C_6H_4CH_3$-4)$_4$(*μ-meso*-DPPEPM)]. *meso*-DPPEPM (0.080 g, 0.12 mmol) was dissolved in CH_2Cl_2 (15 mL), and [$Pt(C_6H_5CH_3$-4)$_2$(cod)] (0.118 g, 0.24 mmol) was added. The solution was stirred for 30 min, and then the solvent was removed under reduced pressure. The residue was washed several times with pentane, and the product was isolated as a yellow powder (0.101 g, 59%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 36.9 (br s, $^1J_{PtP}$ = 1703 Hz, $^3J_{PtP}$ = 37 Hz, $^2J_{PP}$ = 24 Hz, internal P), 40.0 (d, $^2J_{PP}$ = 7 Hz, $^1J_{PtP}$ = 1690 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 2.09 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 1.58−1.73, 1.81−1.87, 2.03−2.08 (br m, PCH_2CH_2P), 2.58, 3.45 (br m, PCH_2P), 6.61 (d, $^3J_{HH}$ = 7 Hz, 4H, C*H-2,6*), 6.83, (d, $^3J_{HH}$ = 7 Hz, 4H, C*H-2,6*), 7.01 (d, $^3J_{HH}$ = 7 Hz, 4H, C*H-3,5*), 7.07 (d, $^3J_{HH}$ = 7 Hz, 4H, C*H-3,5*), 7.18−7.41 (m, C$_6H_5$). HRMS (CsI added): exact mass calcd for $^{12}C_{69}H_{68}P_4Cs^{195}Pt_2^+$, 1543.2622; obsd, 1543.2593.

Synthesis of [$Pt_2(C_6H_4CH_3$-4)$_4$(*μ-rac*-DPPEPM)]. This complex was prepared similarly and obtained in 51% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 40.1 (d, $^2J_{PP}$ = 7 Hz, $^1J_{PtP}$ = 1721 Hz, internal P), 41.8 (d, $^2J_{PP}$ = 7 Hz, $^1J_{PtP}$ = 1699 Hz, external P). ^1H NMR ($CDCl_3$): δ(H) 2.12 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.03−2.08, 3.47−3.54, 3.73−3.75 (br m, PCH_2CH_2P), 3.14 (t, $^2J_{PH}$ = 10 Hz), 6.65−7.47 (m, C$_6H_5$).

Synthesis of [Pt_2Me_2(*μ*-Cl)(*μ-meso*-DPPEPM)]PF_6. [PtClMe(cod)] (0.105 g, 0.29 mmol) and *meso*-DPPEPM (0.097 g, 0.15 mmol) were dissolved in acetone (10 mL). To this stirred solution was added dropwise $TlPF_6$ (0.052 g, 0.14 mmol) in acetone (1 mL). A white precipitate began to form, and the reaction was allowed to run overnight. The solvent was removed under vacuum, and the resulting solid was washed with pentane. The solid was then extracted with acetone and passed down a short column of alumina. The column was washed with small portions of acetone. The total effluent was collected, and the solvent was removed to leave the product as a white powder (0.104 g, 56%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 44.0 (s, $^1J_{PtP}$ = 4643 Hz, external P), 47.0 (s, $^1J_{PtP}$ = 1773 Hz, $^2J_{PP}$ = 37 Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 0.63 ($^2J_{PtH}$ = 40 Hz, CH_3), 1.68−1.78, 2.51−2.60, 2.87−3.17 (br m, PCH_2CH_2P), 4.42, 4.46 (pseudoquartets, $^2J_{HH}$ = $^2J_{PH}$ = 13 Hz, PCH_2P), 6.69−7.59 (m, C$_6$H$_5$). HRMS: exact mass calcd for $^{12}C_{43}H_{46}{}^{35}ClP_4{}^{195}Pt_2^+$, 1111.1534; obsd, 1111.1472.

Synthesis of [Pt_2Ph_2(*μ*-Cl)(*μ-meso*-DPPEPM)]PF_6. [PtClPh(cod)] (0.080 g, 0.19 mmol) and *meso*-DPPEPM (0.0634 g, 0.097 mmol) were dissolved in THF (10 mL). To this stirred solution was added dropwise $TlPF_6$ (0.052 g, 0.14 mmol) in THF (1 mL). A white precipitate started to form, and the reaction was allowed to run overnight. The solvent was removed under vacuum, and the resulting solid was washed with pentane several times. The solid was then extracted with THF and passed down a short column of alumina, with small portions of THF as eluent. The total effluent was collected, and the solvent was removed to give the product as an off-white solid (0.060 g, 55%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 39.0 (s, $^1J_{PtP}$ = 4525 Hz, external P), 42.2 (s, $^1J_{PtP}$ = 1724 Hz, $^2J_{PP}$ = 24 Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 1.83−1.85, 2.16−2.31, 2.99−3.03 (br m, PCH_2CH_2P), 3.57, 4.67 (pseudoquartets, $^2J_{HH}$ = $^2J_{PH}$ = 14 Hz, PCH_2P), 6.69−7.59 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{53}H_{50}{}^{35}ClP_4{}^{195}Pt_2^+$, 1236.1851; obsd, 1236.1815.

Synthesis of [$Pt_2(CH_2Ph)_2$(*μ*-Cl)(*μ-meso*-DPPEPM)]PF_6. [PtCl(CH_2Ph)(cod)] (0.060 g, 0.092 mmol) and *meso*-DPPEPM (0.079 g, 0.18 mmol) were dissolved in acetone (7 mL). To this

stirred solution was added dropwise $TlPF_6$ (0.032 g, 0.092 mmol) in MeOH (1 mL). The reaction was allowed to run overnight, and the solvent was removed under vacuum. The resulting solid was washed with pentane, extracted with acetone, and passed down a short column of alumina, with small portions of acetone as eluent. The total effluent was collected, and the solvent was removed, giving the product as a light yellow solid (0.077 g, 59%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 42.1 (s, $^1J_{PtP} = 4732$ Hz, external P), 43.3 (s, $^1J_{PtP} = 1809$ Hz, $^2J_{PP} = 26$ Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 2.72−2.97, 3.15−3.21, 3.60−3.66 (br m, PCH_2CH_2P, PtCH_2Ph), 3.98−4.11, 4.42−4.47 (br m, PCH_2P), 6.65−7.75 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{55}H_{54}{}^{35}ClP_4{}^{195}Pt_2{}^+$, 1263.2160; obsd, 1263.2159.

Synthesis of [Pt_2Cl_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. [Pt_2Cl_4(μ-*meso*-DPPEPM)] (0.075 g, 0.063 mmol) was dissolved in THF (7 mL), and $TlPF_6$ (0.022 g, 0.063 mmol) was added. A white precipitate started to form, and the reaction was allowed to proceed overnight. The mixture was passed through a short column of Hyflo Supercel to remove TlCl. The solvent was removed under vacuum, and the product was obtained as a light yellow powder (0.044 g, 54%).$^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 44.0 (br, $^1J_{PtP} = 3557$ Hz, internal P), 46.5 (br, $^1J_{PtP} = 3896$ Hz, external P). ^1H NMR (acetone-d_6): δ(H) 2.21−2.70, 2.85−3.17, 3.65−3.75 (br m, PCH_2CH_2P), 3.88−4.12 (br m, PCH_2P), 7.01−7.83 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{41}H_{40}{}^{35}Cl_3P_4{}^{195}Pt_2{}^+$, 1151.0442; obsd, 1151.0482.

Synthesis of [Pd_2Me_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. [PdClMe(cod)] (0.088 g, 0.33 mmol) and *meso*-DPPEPM (0.108 g, 0.17 mmol) were dissolved in CH_2Cl_2 (10 mL). To this stirred solution was introduced $TlPF_6$ (0.058 g, 0.17 mmol) in methanol (1 mL). A yellow precipitate started to form, and the reaction mixture was stirred for 15 min. The solvent was removed under vacuum. The resulting solid was washed with pentane and then extracted with CH_2Cl_2 and passed down a short column of alumina. The column was washed with small portions of CH_2Cl_2. The total effluent was collected, and the solvent was removed to leave the product as a yellow solid (0.112 g, 63%). Anal. Calcd for $C_{43}H_{46}P_5Pd_2ClF_6$: C, 47.81; H, 4.29. Found: C, 47.24; H, 4.39. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 33.1 (dd, $J_{PP} = 16$, 11 Hz, external P), 62.2 (dd, $J_{PP} = 16$, 11 Hz, internal P). ^1H NMR ($CDCl_3$): δ(H) 0.63 (s, CH_3), 1.98−2.21, 2.73−2.80, 2.82−2.93 (br m, PCH_2CH_2P), 3.70 (pseudo-quartet, $^2J_{HH} = 14$ Hz, $^2J_{PH} = 14$ Hz, 1H, PCH_2P), 3.51 (br m, 1H, PCH_2P), 6.84−7.63 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{43}H_{46}{}^{35}ClP_4{}^{106}Pd_2{}^+$, 933.0308; obsd, 933.0320.

Synthesis of [Pd_2Me_2(μ-Cl)(μ-*rac*-DPPEPM)]PF_6. This complex was prepared similarly and obtained in 55% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 36.3 (dd, $J_{PP} = 16$, 11 Hz, external P), 61.5 (dd, $J_{PP} = 16$, 11 Hz, internal P). ^1H NMR ($CDCl_3$): δ(H) 0.46 (s, CH_3), 1.81−2.21, 2.73−2.80 (br m, PCH_2CH_2P), 3.10 (t, $^2J_{PH} = 9$ Hz, PCH_2P), 6.71−7.63 (m, C$_6H_5$).

Synthesis of [Pd_2(CH_2Ph)$_2$(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. [Pd_2(CH_2Ph)$_2$(μ-Cl)$_2$($AsPh_3$)$_2$] (0.068 g, 0.063 mmol) and *meso*-DPPEPM (0.041 g, 0.063 mmol) were dissolved in THF (7 mL). To this stirred solution was added dropwise $TlPF_6$ (0.022 g, 0.063 mmol) in THF (1 mL). A precipitate began to form, and the reaction was allowed to run for 1 h. The solvent was removed under vacuum. The resulting solid was washed several times with pentane, and then extracted with THF and passed down a short column of Hyflo Supercel. The column was washed with small portions of THF. The total effluent was collected, and the solvent was removed, leaving the product as a yellow powder (0.045 g, 59%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ(P) 34.8 (dd, $J_{PP} = 29$, 12 Hz, external P), 58.7 (dd, $J_{PP} = 29$, 12 Hz, internal P). ^1H NMR (C_6D_6): δ(H) 1.88−2.24 (br m, PCH_2CH_2P, PdCH_2Ph), 2.84, 3.18 (br m, PCH_2P), 6.61−7.73 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{55}H_{54}{}^{35}ClP_4{}^{106}Pd_2{}^+$, 1085.0934; obsd, 1085.0945.

Synthesis of [Pd_2Ph_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. This complex was prepared analogously from [Pd_2Ph_2(μ-Cl)$_2$($AsPh_3$)$_2$] (0.060 g, 0.057 mmol) and *meso*-DPPEPM (0.036 g, 0.057 mmol), and isolated as an orange powder (0.045 g, 65%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 33.8 (dd, $J_{PP} = 17$, 10 Hz, external P), 58.7 (dd, $J_{PP} = 17$, 10 Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 2.17−2.50, 2.71−2.74, 2.94−2.98 (br m, PCH_2CH_2P), 3.18 (br m, 1H, PCH_2P), 3.56 (br m, 1H, PCH_2P), 6.23−7.80 (m, C$_6H_5$). HRMS: exact mass calcd. for $^{12}C_{53}H_{50}{}^{35}ClP_4{}^{106}Pd_2{}^+$, 1057.0621; observed, 1057.0588.

Synthesis of [Pd_2(COMe)$_2$(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. [Pd_2Me_2(μ-Cl)$_2$($AsPh_3$)$_2$] (0.070 g, 0.075 mmol) was dissolved in CH_2Cl_2 (10 mL). Carbon monoxide was bubbled through the solution for 2 h, then *meso*-DPPEPM (0.049 g, 0.075 mmol), methanol (1 mL), and $TlPF_6$ (0.026 g, 0.075 mmol) were added, and the mixture was stirred overnight. The solvent was removed under vacuum. The resulting solid was washed several times with pentane and then extracted with CH_2Cl_2. The solution was passed through a column of neutral alumina, with CH_2Cl_2 as eluent. The solvent was evaporated to give a dark yellow solid (0.040 g, 47%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 22.9 (dd, $J_{PP} = 21$, 22 Hz, external P), 40.3 (dd, $J_{PP} = 21$, 22 Hz, internal P). ^1H NMR ($CDCl_3$): δ(H) 2.19 (s, COCH_3), 1.92−2.09, 2.19−2.29, 2.61−2.75 (br m, PCH_2CH_2P), 3.34−3.40 (br m, PCH_2P), 7.00−7.53 (m, C$_6H_5$). IR (neat solid): 1684 cm^{-1} (ν_{CO}). HRMS: exact mass calcd for $^{12}C_{45}H_{46}{}^{35}ClP_4O_2{}^{106}Pd_2{}^+$ 989.0206; obsd, 989.0232.

Synthesis of [Pd_2Cl_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6. [Pd_2Cl_4(μ-*meso*-DPPEPM)] (0.080 g, 0.079 mmol) was dissolved in THF (7 mL), and $TlPF_6$ (0.027 g, 0.079 mmol) was added. A yellow precipitate started to form, and the reaction was allowed to proceed overnight. The mixture was passed through a short column of Hyflo Supercel to remove TlCl. The solvent was removed under vacuum, and the product was obtained as a yellow powder (0.060 g, 68%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 68.5 (s, internal P), 72.3 (s, external P). ^1H NMR (acetone-d_6): δ(H) 2.35−2.56, 2.86−3.00, 3.05−3.21 (br m, PCH_2CH_2P), 3.23−3.34, (br m, PCH_2P), 7.28−7.71 (m, C$_6H_5$). Anal. Calcd for $C_{41}H_{40}Cl_3P_5Pd_2$·0.5THF: C, 44.64; H, 3.83. Found: C, 44.75; H, 4.40. HRMS: exact mass calcd for $^{12}C_{41}H_{40}{}^{35}Cl_3P_4{}^{106}Pd_2{}^+$, 972.9216; obsd, 972.9222.

Synthesis of [Pt_2Me_2(μ-I)(μ-*meso*-DPPEPM)]PF_6. [Pt_2Me_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6 (0.040 g, 0.031 mmol) was dissolved in acetone (8 mL), and Bu_4NI (0.012 g, 0.031 mmol) in acetone (1 mL) was added by syringe. The mixture turned dark red. To this stirred solution was introduced $TlPF_6$ (0.011 g, 0.031 mmol) in acetone (1 mL). A precipitate started to form, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The resulting solid was washed several times with water and *sec*-butyl alcohol and then extracted with acetone and passed down a short column of alumina. The column was washed with small portions of acetone. The total effluent was collected, and the solvent was removed to leave the product as a light yellow solid (0.030 g, 71%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) 47.2 ($^1J_{PtP} = 4297$ Hz, external P), 48.9 ($^1J_{PtP} = 1808$ Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 0.71 (s, $^2J_{PtH} = 47$ Hz, CH_3), 1.55−1.85, 2.29−2.36, 2.47−2.51 (br m, PCH_2CH_2P), 3.80−4.01 (br m, PCH_2P), 6.93−7.77 (m, C$_6H_5$). HRMS: exact mass calcd for $^{12}C_{43}H_{46}{}^{127}IP_4{}^{195}Pt_2{}^+$, 1203.0891; obsd, 1203.0842.

Synthesis of [Pd_2Me_2(μ-I)(μ-*meso*-DPPEPM)]PF_6. [Pd_2Me_2(μ-Cl)(μ-*meso*-DPPEPM)]PF_6 (0.080 g, 0.074 mmol) was dissolved in acetone (8 mL). To this solution was added Bu_4NI (0.027 g, 0.074 mmol) in acetone (1 mL), and the mixture turned dark red. An acetone solution (1 mL) of $TlPF_6$ (0.026 g, 0.074 mmol) was introduced, and a precipitate started to form. The reaction mixture was stirred overnight, and the solution turned olive green. The solvent was removed under vacuum. The resulting solid was washed several times with water and *sec*-butyl alcohol and then extracted with acetone and passed down a short column of alumina. The column was washed with small portions of acetone. The total effluent was collected, and the solvent was removed to leave the product

Table 1. Crystallographic Data for *meso*-DPPEPM-S_4, [Pd_2Cl_4(*μ-meso*-DPPEPM)], and [Pt_2Ph_4(*μ-meso*-DPPEPM)

	meso-DPPEPM-S_4	[Pd_2Cl_4(*μ-meso*-DPPEPM)]	[Pt_2Ph_4(*μ-meso*-DPPEPM)]
cryst syst	orthorhombic	monoclinic	monoclinic
space group, *Z*	$Pna2_1$, 4	$P2_1/c$, 8	$P2_1/c$, 4
a, Å	12.1988(11)	20.0126(2)	29.1088(8)
b, Å	8.9786(8)	30.1998(3)	12.3862(3)
c, Å	35.885(3)	16.5381(2)	17.8170(5)
α, deg	90	90	90
β, deg	90	91.039(1)	96.055(2)
γ, deg	90	90	90
cell vol, Å^3	3930.4(6)	9993.60(19)	6388.0(3)
D(calcd), Mg/m^3	1.326	1.662	1.609
temp, K	223(2)	213(2)	223(2)
abs coeff, mm^{-1}	0.434	1.414	4.643
θ range, deg	2.27−27.61	1.40−26.00	1.79−25.68
no. of rflns collected	50 037	183 477	87 744
no. of indep rflns	8999	19 651	12 111
abs cor	none	empirical	empirical
no. of params refined	442	1126	730
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0663, 0.1171	0.0365, 0.0749	0.0712, 0.1198
$R(F)$, $R_w(F^2)$ (all data)	0.0735, 0.1201	0.0555, 0.817	0.1153, 0.1319
goodness of fit	1.272	1.057	1.108
largest diff peak and hole, e Å^{-3}	0.418 and −0.377	0.832 and −0.937	2.402 and −2.328

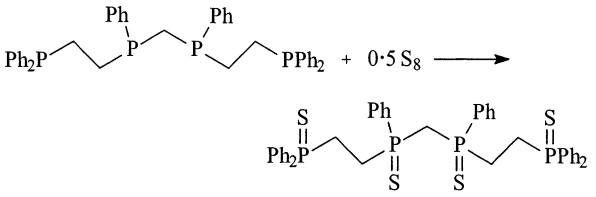
as a pale green solid (0.065 g, 75%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ(P) 38.8 (dd, J_{PP} = 16, 9 Hz, external P), 64.1 (dd, J_{PP} = 16, 9 Hz, internal P). ^1H NMR (acetone-d_6): δ(H) 0.78 (s, CH_3), 1.97−2.08, 2.36−2.52, 2.82−3.00 (br m, PCH_2CH_2P), 3.11 (br m, 1H, PCH_2P), 3.77 (br m, 1H, PCH_2P), 7.15−7.69 (m, C_6H_5). HRMS: exact mass calcd for $^{12}C_{43}H_{46}{}^{127}IP_4{}^{106}Pd_2{}^+$, 1024.9664; obsd, 1024.9637.

X-ray Structure Determinations. Preliminary examination and data collection were performed using a Siemens SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (50 kV × 40 mA) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package[19] was used for data collection, and SAINT[19] was used for frame integration. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections. An empirical absorption correction was applied using SADABS.[20] Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[21] Crystallographic data are collected in Table 1.

Results and Discussion

We have prepared the linear tetraphosphine ligand bis[((diphenylphosphino)ethyl)phenylphosphino]methane (DPPEPM) as reported previously, by addition of KPHPh to CH_2Cl_2, followed by reaction of the resulting bis(phenylphosphino)methane with $Ph_2PCH{=}CH_2$ in the presence of AIBN.[18] The ligand was obtained as an approximately 1:1 ratio of *meso* and *rac* diastereomers. These could be separated by extraction with a 4:1 methanol/benzene solvent mixture; the *rac* form dissolved, and the *meso* diastereomer could be separated by filtration. The latter was obtained as a colorless solid, and after solvent removal, the *rac* form was isolated as an oily solid. Both compounds were characterized by NMR spectroscopy. The *meso* form exhibits two doublets of doublets in its $^{31}P\{^1H\}$ NMR spectrum, the internal P atoms producing a resonance at −25.5 ppm and the external P atoms at −12.0 ppm. The *rac* isomer gives rise to an almost identical spectrum, with doublets of doublets at −24.8 and −11.9 ppm. Both isomers have broad resonances in their ^1H NMR spectra due to the ethylene and aromatic hydrogens. The *meso* form shows a broad signal due to the nonequivalent hydrogens of the central CH_2 group, whereas the *rac* isomer may be distinguished by its magnetically equivalent CH_2 hydrogens that give rise to a triplet at 2.04 ppm.

When a CH_2Cl_2 solution of *meso*- or *rac*-DPPEPM was stirred with elemental sulfur, the corresponding tetrasulfide was formed in high yield (eq 1). In each case,



(1)

the product was characterized by NMR spectroscopy, and the structure of the *meso* isomer was determined by X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectra are second order, but they appear as two approximate doublets of triplets. The spectra have been simulated successfully (see Experimental Section). The ^1H NMR spectrum of the *meso* form shows two overlapping pseudoquartets for the central CH_2 group, whereas the magnetically equivalent hydrogens of the central methylene group in the *rac* isomer appear as a simple triplet at 3.0 ppm.

The solid-state structure of *meso*-DPPEPM-S_4 is shown in Figure 1, and selected bond distances and angles are given in Table 2. The figure illustrates the linear nature of the ligand backbone. The pair of sulfur atoms on P(1) and P(2), and those on P(3) and P(4), point in opposite directions. Such an arrangement of substituents on phosphorus is evidently preferred here, but if it were maintained in solution, it would preclude chelation to a metal through these pairs of P atoms. The

(19) SMART and SAINT; Siemens Analytical X-ray Division, Madison, WI.
(20) SADABS: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(21) Sheldrick, G. M. SHELXTL-PLUS (5.03) Software Package; Siemens Analytical X-ray Division, Madison, WI, 1995.

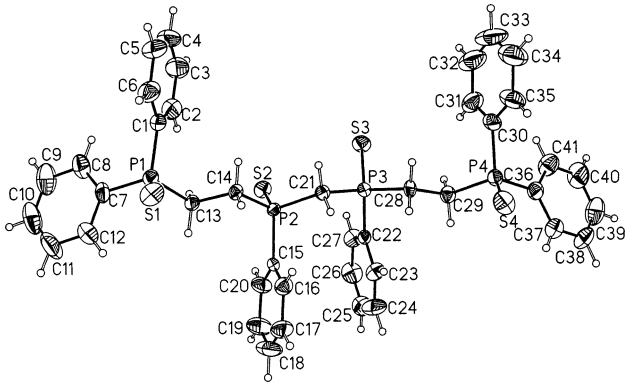


Figure 1. Molecular structure of *meso*-DPPEPM-S_4, with atoms represented by thermal ellipsoids at the 50% level.

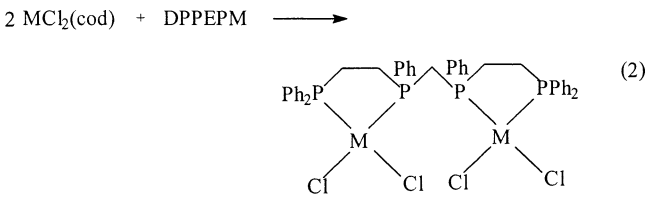
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for DPPEPM-S_4

P(1)−S(1)	1.9369(17)	P(2)−S(2)	1.9293(13)
P(3)−S(3)	1.9364(13)	P(4)−S(4)	1.9402(16)
P(1)−C(1)	1.801(4)	P(1)−C(7)	1.802(4)
P(1)−C(13)	1.818(4)	P(2)−C(14)	1.812(4)
P(1)−C(15)	1.805(3)	P(2)−C(21)	1.831(4)
P(3)−C(21)	1.821(4)	P(3)−C(22)	1.803(4)
P(3)−C(28)	1.808(4)	P(4)−C(29)	1.795(4)
P(4)−C(30)	1.806(4)	P(4)−C(36)	1.804(5)

C(1)−P(1)−C(7)	107.0(2)	C(1)−P(1)−C(13)	104.7(2)
C(7)−P(1)−C(13)	104.77(19)	C(1)−P(1)−S(1)	114.40(16)
C(7)−P(1)−S(1)	113.03(17)	C(13)−P(1)−S(1)	112.08(15)
C(15)−P(2)−C(14)	105.59(18)	C(15)−P(2)−C(21)	106.57(17)
C(14)−P(2)−C(21)	102.72(17)	C(15)−P(2)−S(2)	113.31(13)
C(14)−P(2)−S(2)	111.76(13)	C(21)−P(2)−S(2)	115.88(12)
C(22)−P(3)−C(28)	106.02(18)	C(22)−P(3)−C(21)	105.58(17)
C(28)−P(3)−C(21)	103.75(17)	C(22)−P(3)−S(3)	116.18(13)
C(28)−P(3)−S(3)	110.82(14)	C(21)−P(3)−S(3)	113.48(13)
C(29)−P(4)−C(36)	106.50(19)	C(29)−P(4)−C(30)	105.2(2)
C(36)−P(4)−C(30)	106.0(2)	C(29)−P(4)−S(4)	111.65(15)
C(36)−P(4)−S(4)	112.40(16)	C(30)−P(4)−S(4)	114.49(17)
P(2)−C(21)−P(3)	116.56(18)		

P−S bond distances are all 1.93−1.94 Å, which is typical of such bonds in P(V) compounds.[23] The P−C bond distances all lie between 1.79 and 1.83 Å, the longest bonds being to the central CH_2 group. The P atoms exhibit pseudo-tetrahedral geometry, the larger angles being those involving the S atom. The P−C−P angle, involving the central methylene carbon, is 116.6(2) Å.

When *meso*-DPPEPM was allowed to react with 2 equiv of $[MCl_2(cod)]$ (M = Pd, Pt) in CH_2Cl_2 solution, bimetallic complexes of the form $[M_2Cl_4(\mu\text{-}meso\text{-}DPPEPM)]$ were produced (eq 2). After solvent removal



(2)

and washing with pentane, the palladium or platinum complex was isolated in good yield as a yellow or colorless solid, respectively. The $^{31}P\{^1H\}$ NMR spectrum of $[Pd_2Cl_4(\mu\text{-}meso\text{-}DPPEPM)]$ exhibits signals at δ(P) 61.8 and 62.6, corresponding to $\Delta\delta$(P) values of 87.3 and 74.6 ppm, respectively. This indicates that, on coordination to the metal, there is very little difference in the electronic environment of the internal and external P atoms. Its ^1H NMR spectrum contains two broad pseudoquartets at 3.87 and 4.33 ppm due to the central CH_2 group. The platinum complex exhibits signals at δ(P) 37.6 ($^1J_{PtP}$ = 3575 Hz) and 38.7 ppm ($^1J_{PtP}$ = 3680 Hz), due to the internal and terminal P atoms, respectively. The ^{195}Pt satellites for the resonance due to the internal P atoms exhibit a $^2J_{PP}$ value of 22 Hz, and observation of this coupling (and in other cases, $^3J_{PtP}$ (vide infra)) allows identification of the signals due to the internal P atoms. The central CH_2 group again gives rise to two pseudoquartets, at 3.92 and 4.45 ppm. The complexes are air-stable, either as solids or in solution. The coordination behavior of the *rac* ligand is similar. The palladium complex gives rise to ^{31}P resonances at 64.3 and 67.4 ppm and a ^1H resonance at 4.02 ppm, due to the magnetically equivalent methylene hydrogens. $[Pt_2Cl_4(\mu\text{-}rac\text{-}DPPEPM)]$ exhibits ^{31}P resonances at 40.0 ($^1J_{PtP}$ = 3556 Hz, internal P) and 41.9 ppm ($^1J_{PtP}$ = 3558 Hz, terminal P).

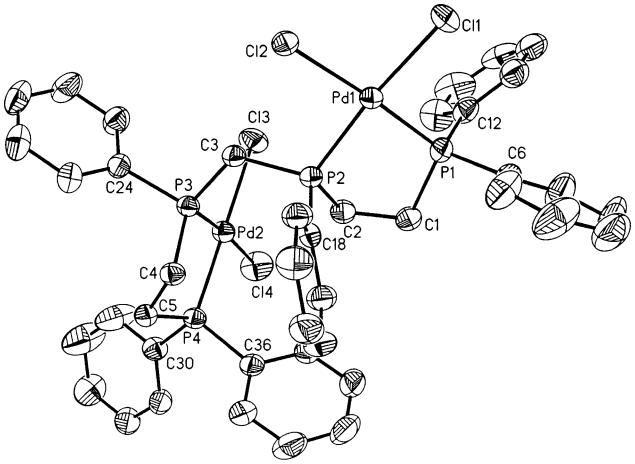


Figure 2. Molecular structure of $[Pd_2Cl_4(\mu\text{-}meso\text{-}DPPEPM)]$, with atoms represented by thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

The solid-state structure of $[Pd_2Cl_4(\mu\text{-}meso\text{-}DPPEPM)]$ has been determined by X-ray crystallography. Its molecular structure is shown in Figure 2, and selected bond distances and angles are given in Table 3. The structure reveals that it is a bimetallic complex, in which each palladium is coordinated by two P atoms and two chlorides. The *cis*-$PdCl_2P_2$ unit is almost perfectly planar (the sums of the angles about Pd(1) and Pd(2) being 359.96 and 360.22°), although the angles deviate slightly from the ideal 90°. The largest angle in each molecule is that between the two chlorides, whereas the smallest angle is between the two P atoms of the five-membered chelate ring, as expected. The chelating nature of the coordinated diphosphine unit imposes a cis geometry at each metal center and the "halves" of the molecule are held together by the single PCH_2P bridging group. The molecule is free to rotate about this

(22) Laneman, S. A.; Fronczek, F. R.; Stanley, G. G. *J. Am. Chem. Soc.* **1988**, *110*, 5585.

(23) (a) Codding, P. W.; Kerr, K. A. *Acta Crystallogr., Sect. B* **1978**, *34*, 3785. (b) Tkachev, V. V.; Shvets, A. A.; Tokina, L. M.; Osipov, O. A. *Zh. Strukt. Khim.* **1987**, *28*, 1496. (c) Lobana, T. S.; Sandhu, M. K.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1988**, 1401. (d) Weichmann, H.; Meunier-Piret, J. *Organometallics* **1993**, *12*, 4097. (e) Apperley, D. C.; Bricklebank, N.; Hursthouse, M. B.; Light, M. E.; Coles, S. J. *Polyhedron* **2001**, *20*, 1907.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for One of the Molecules of [Pd_2Cl_4(*μ-meso*-DPPEPM)]

Pd(1)−P(1)	2.2364(10)	Pd(1)−P(2)	2.2272(9)
Pd(1)−Cl(1)	2.3606(10)	Pd(1)−Cl(2)	2.3604(9)
Pd(2)−P(3)	2.2331(10)	Pd(2)−P(4)	2.2349(9)
Pd(2)−Cl(3)	2.3675(10)	Pd(2)−Cl(4)	2.3568(11)
P(2)−C(3)	1.827(4)	P(3)−C(3)	1.830(3)
P(1)−Pd(1)−P(2)	85.38(4)	P(1)−Pd(1)−Cl(1)	90.13(4)
P(1)−Pd(1)−Cl(2)	173.96(4)	P(2)−Pd(1)−Cl(1)	174.43(4)
P(2)−Pd(1)−Cl(2)	90.04(3)	Cl(2)−Pd(1)−Cl(1)	94.67(4)
P(3)−Pd(2)−P(4)	85.75(3)	P(3)−Pd(2)−Cl(3)	91.33(4)
P(3)−Pd(2)−Cl(4)	173.54(4)	P(4)−Pd(2)−Cl(3)	176.82(4)
P(4)−Pd(2)−Cl(4)	88.06(4)	Cl(3)−Pd(2)−Cl(4)	94.82(4)
Pd(1)−P(2)−C(3)	114.53(11)	Pd(2)−P(3)−C(3)	116.66(12)
P(2)−C(3)−P(3)	120.99(19)		

single bridge in solution, but in the solid state the two $PdCl_2P_2$ planes are rotated away from each other such that the Pd−Pd distance is 6.08 Å. This metal−metal distance is comparable to those found in the platinum analogue (5.931 Å),[12] [Ni_2Cl_4(*meso*-eLTTP)] (6.272(1) Å),[18] and [$Rh_2Cl_2(CO)_2$(*rac*-eLTTP)] (5.813(2) Å).[22] It is slightly shorter than the Pt−Pt distance of 6.338(1) Å found in [Pt_2Cl_4(*rac*-1,2-DPPEPE)] (DPPEPE = bis-[((diphenylphosphino)ethyl)phenylphosphino]ethane), in which the internal P atoms are connected by a two-carbon unit.[24] The central P−C−P angles in the palladium and platinum complexes [M_2Cl_4(*μ-meso*-DPPEPM)] are 120.99(19) and 118.0(4)°, respectively, increased from 116.6(2)° in the sulfide, and the opening of this angle may contribute to the large M−M distances. The P−C−P angles in [Ni_2Cl_4(eLTTP)] are 121.7(4) and 119.3(3)° for the *meso* and *rac* forms,[18] although the angle is only 113(1)° in [$Rh_2Cl_2(CO)_2$-(*rac*-eLTTP)].[22]

Treatment of *meso*-DPPEPM with 2 equiv of [PtR_2-(cod)] (R = Me, Ph, CH_2Ph, C_6H_4Me-4) in CH_2Cl_2 solution also produced bimetallic complexes [Pt_2R_4(*μ-meso*-DPPEPM)]. These were isolated as off-white to yellow, air-stable solids. In each case, the $^{31}P\{^1H\}$ NMR spectrum consists of two resonances with one-bond couplings to platinum in the range 1700−1900 Hz, as expected for P atoms lying trans to organic substituents.[25] As noted above for [Pt_2Cl_4(*μ-meso*-DPPEPM)], the ^{195}Pt satellites for the internal P atoms exhibit additional couplings, and this allows ready assignment of resonances to these atoms. In each of the four complexes [Pt_2R_4(*μ-meso*-DPPEPM)], the central resonance for the internal P atoms is flanked by two sets of doublet satellites corresponding to $^1J_{PtP}$ and $^3J_{PtP}$, due to the isotopomer containing one ^{195}Pt nucleus. In the ^1H NMR spectrum of the methyl complex, two pseudotriplets ($^3J_{PH}$ = 8 Hz) are observed at 0.64 and 0.76 ppm, due to the methyl groups lying trans to the internal and external P atoms. The 4-tolyl complex similarly shows two signals for the methyl substituents on the tolyl rings. The coordinated CH_2 groups in the benzyl complex are obscured by the CH_2 groups of the DPPEPM ligand. In all four complexes, the central CH_2 group of the DPPEPM ligand gives rise to two pseudoquartets, typical of the *meso* form of the ligand. The high-resolution mass spectrum of the 4-tolyl complex, obtained in the presence of CsI, shows the parent species complexed by one Cs^+ ion; presumably the Cs^+ ion interacts with one of the aryl rings in the complex. Reactions of the *rac* form of the ligand proceed analogously, and the NMR spectra of the [Pt_2R_4(*μ-rac*-DPPEPM)] complexes are qualitatively similar to those of the *meso* derivatives.

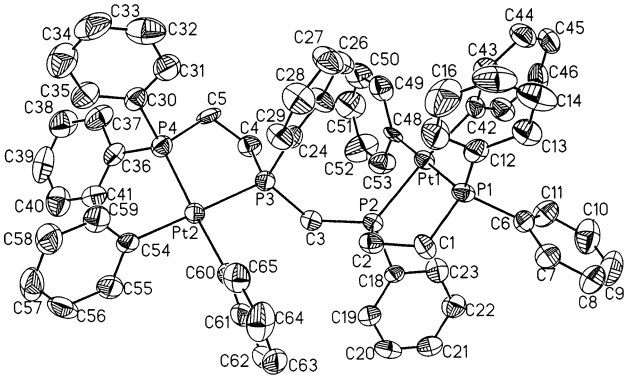


Figure 3. Molecular structure of [Pt_2Ph_4(*μ-meso*-DPPEPM)], with atoms represented by thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for [Pt_2Ph_4(*μ-meso*-DPPEPM)]

Pt(1)−P(1)	2.284(3)	Pt(1)−P(2)	2.274(3)
Pt(1)−C(42)	2.077(11)	Pt(1)−C(48)	2.082(10)
Pt(2)−P(3)	2.273(3)	Pt(2)−P(4)	2.296(3)
Pt(2)−C(54)	2.077(11)	Pt(2)−C(60)	2.060(11)
P(2)−C(3)	1.837(11)	P(3)−C(3)	1.836(11)
P(1)−Pt(1)−P(2)	83.92(10)	P(1)−Pt(1)−C(42)	93.5(3)
P(1)−Pt(1)−C(48)	177.9(3)	P(2)−Pt(1)−C(42)	175.6(3)
P(2)−Pt(1)−C(48)	95.6(3)	C(42)−Pt(1)−C(48)	86.9(4)
P(3)−Pt(2)−P(4)	83.88(11)	P(3)−Pt(2)−C(54)	177.8(3)
P(3)−Pt(2)−C(60)	94.5(3)	P(4)−Pt(2)−C(54)	96.4(3)
P(4)−Pt(2)−C(60)	177.4(3)	C(54)−Pt(2)−C(60)	85.1(4)
Pt(1)−P(2)−C(3)	124.0(4)	Pt(2)−P(3)−C(3)	119.7(4)
P(2)−C(3)−P(3)	123.3(6)		

Crystals of [Pt_2R_4(*μ-meso*-DPPEPM)] (R = Me, Ph) were isolated from $CDCl_3$ or $CDCl_3/Et_2O$ solution, respectively. The structure of the methyl derivative has been reported previously.[11] The molecular structure of the phenyl complex is shown in Figure 3, and selected bond distances and angles are presented in Table 4. The structure of [Pt_2Ph_4(*μ-meso*-DPPEPM)] consists of two planar PtC_2P_2 units (the sums of the angles around Pt(1) and Pt(2) each being 359.9°) connected via the PCH_2P linkage. In this case, the smaller angles are between the two P atoms and between the two phenyl groups, whereas the P−Pt−C angles exceed 90°. The average Pt−P distances in the methyl and phenyl derivatives are greater than in the analogous chloride complex (average 2.265 (Me) and 2.282 Å (Ph), compared with 2.238 Å), as expected from the greater trans influence of the organic groups.[25] The average Pt−C distance in [Pt_2Ph_4(*μ-meso*-DPPEPM)] is 2.074 Å. Again, the two platinum centers are rotated away from one another in the solid state, giving Pt−Pt distances of 6.732 and 6.632 Å in the methyl and phenyl derivatives, respectively, slightly greater than in the chloride complexes. The central P−C−P angles are 125.5(3) and 123.3(6)°, larger still than those found in the chloride complexes. The Pt−P−C−P torsion angles in [Pt_2Me_4-(*μ-meso*-DPPEPM)] are 58.9 and 137.9°, and the corre-

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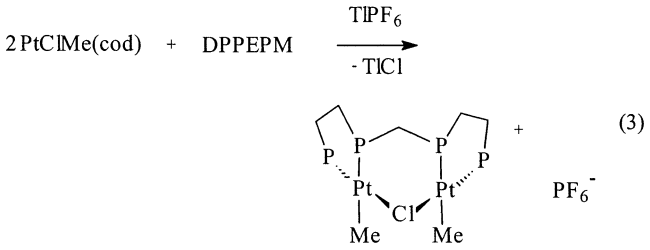
(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

sponding angles in $[Pt_2Ph_4(\mu\text{-}meso\text{-DPPEPM})]$ are 64.2 and 121.7°. If these angles are maintained in solution, they might account for the significant values of $^3J_{PtP}$ in these complexes. In contrast, the corresponding torsion angles in $[Pt_2Cl_4(\mu\text{-}meso\text{-DPPEPM})]$ are closer to 90° (73.7 and 82.1°), and the $^3J_{PtP}$ value is too small to be measured in this complex.

When *meso*-DPPEPM was added to a solution containing 2 equiv of [PtClMe(cod)], the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution was complicated, but the resonances could be assigned to the three possible isomers of [ClMePt(μ-DPPEPM)PtClMe]. When 1 equiv of $TlPF_6$ was added, however, a white precipitate of TlCl formed and, after filtration and purification, $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ was obtained as a yellow solid in moderate yield (eq 3). Its $^{31}P\{^1H\}$ NMR spectrum contains resonances at 44.0 ($^1J_{PtP} = 4643$ Hz) and 47.0 ppm ($^1J_{PtP} = 1773$ Hz), due to the P atoms lying trans to the bridging chloride and the terminal methyl groups, respectively.[25] Its ^1H NMR spectrum contains a single resonance at 0.55 ppm ($^2J_{PtH} = 44$ Hz), due to the two equivalent methyl groups, and the expected two pseudoquartets due to the central CH_2 group of the DPPEPM ligand. The phenyl- and benzylplatinum derivatives were formed similarly, by reaction of [PtClR(cod)] (R = Ph, CH_2Ph) with *meso*-DPPEPM and $TlPF_6$.



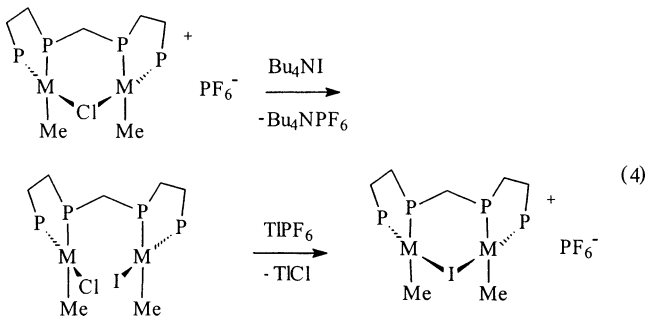
(3)

In another bridge-forming reaction, treatment of $[Pt_2Cl_4(\mu\text{-}meso\text{-DPPEPM})]$ with 1 equiv of $TlPF_6$ in THF solution produced the trichlorodiplatinum complex $[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ as a light yellow solid. In this case, the $^{31}P\{^1H\}$ NMR spectrum consists of two closely spaced resonances, each with a coupling to platinum in excess of 3500 Hz. Similar ^{31}P NMR parameters were observed for the related complex $[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-DPPEPE})]Cl$.[24]

The chloride-bridged palladium complexes $[Pd_2R_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ (R = Me, Ph, CH_2Ph) could also be prepared by reaction of 2 equiv of [PdClMe(cod)] with 1 equiv of *meso*-DPPEPM in CH_2Cl_2 solution, followed by addition of 1 equiv of $TlPF_6$ in methanol, or by reaction of equimolar amounts of $[Pd_2R_2(\mu\text{-Cl})_2(AsPh_3)_2]$, DPPEPM, and $TlPF_6$ in THF solution. The acetyl derivative $[Pd_2(COMe)_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ could be generated by treating $[Pd_2R_2(\mu\text{-Cl})_2(AsPh_3)_2]$ with CO prior to the addition of DPPEPM and $TlPF_6$. The product was isolated as a yellow or orange solid in each case. In contrast to the $^{31}P\{^1H\}$ NMR spectra of the platinum complexes, which consist of two resonances in the range 39−47 ppm, the spectra of the palladium derivatives are characterized by two widely separated resonances. In $[Pd_2R_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ (R = Me, Ph, CH_2Ph) the resonance due to the P atom lying trans to the bridging chloride appears at 33−35 ppm, whereas that due to the internal P atom appears in the range 58−62 ppm. The acetylpalladium complex exhibits resonances at 22.9 and 40.3 ppm. The ^1H NMR spectra exhibit the expected signals. Similarly, reaction of the *rac* ligand with [PdClMe(cod)], followed by addition of $TlPF_6$, gave $[Pd_2R_2(\mu\text{-Cl})(\mu\text{-}rac\text{-DPPEPM})]PF_6$.

We have been unable to obtain crystals of the chloride-bridged complexes, and they have proved difficult to obtain in analytically pure form because it is virtually impossible to remove all traces of TlCl. They have been characterized in each case by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, by high-resolution mass spectrometry, and, in a small number of cases, by elemental analysis. Although we do not have structural details, the presence of the chloride bridge in these instances would force the two metal centers into closer proximity than in the open forms found for $[M_2X_4(\mu\text{-DPPEPM})]$ derivatives.

Attempts to open the chloride bridges in the above compounds with tertiary phosphines gave complicated mixtures. Addition of iodide to $[M_2Me_2(\mu\text{-Cl})(\mu\text{-}meso\text{-DPPEPM})]PF_6$ (M = Pd, Pt), however, did produce the mixed halide derivative quite cleanly (eq 4). The bridge-opening reaction took place stereospecifically, with only one isomer of the intermediate [MeClM(μ-DPPEPM)MIMe] being formed. In each case, a single species with four nonequivalent P atoms was generated. Further addition of $TlPF_6$ gave the iodide-bridged complex in good yield. The $^{31}P\{^1H\}$ NMR data for the iodide-bridged complexes show slight shifts of both signals to higher frequencies, and in the platinum complex the $^1J_{PtP}$ value for the P atom lying trans to the bridging halide decreases from 4643 to 4297 Hz, a consequence of the greater trans influence of iodide compared to chloride.[25]



(4)

Summary

We have shown that the *meso* and *rac* forms of the linear tetraphosphine DPPEPM may be used to generate bimetallic palladium and platinum complexes of the type $[M_2Cl_4(\mu\text{-DPPEPM})]$ and organoplatinum derivatives of the form $[Pt_2R_4(\mu\text{-DPPEPM})]$. Solid-state structures of both compound types reveal bimetallic structures in which the two metal square planes are rotated away from each other about the single PCH_2P bridge, resulting in M−M distances of ca. 6 Å. Reactions of "MClR" sources with DPPEPM give the analogous complexes $[M_2Cl_2R_2(\mu\text{-DPPEPM})]$, but removal of one chloride gives a chloride-bridged species of the form $[M_2R_2(\mu\text{-Cl})(\mu\text{-DPPEPM})]^+$. Although we have been unable to obtain a crystal structure of one of these compounds, the presence of the bridging chloride would necessitate a much shorter M−M distance. The ability of these systems to move between open and closed,

bridged forms may have implications for their potential use as bimetallic catalysts, and we are currently evaluating their activity in a number of catalytic reactions.

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Supporting Information Available: Tables of crystal data, atomic coordinates and displacement parameters, and all bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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