complex. For $Ni(dppe)Br_2$, the five-membered chelate ring is puckered with the two carbon atoms lying out of the coordination plane by 0.404 (5) and 0.391 (5) Å.

Acknowledgment. We wish to thank Professor Glen C. Miller for the mass spectrum. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for financial support.

Supplementary Material Available: Listings of X-ray experimental parameters, bond distances and angles, hydrogen coordinates, and thermal parameters (6 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557,
and University of Warwick, Coventry CV4 7AL, England, and NMR Applications Laboratory,
Varian Instrument Division, Palo Alto, California 94303

Intramolecular [4 + 2] Diels-Alder Cycloaddition Reactions of Phospholes with Vinylphosphines Promoted by Palladium and Platinum

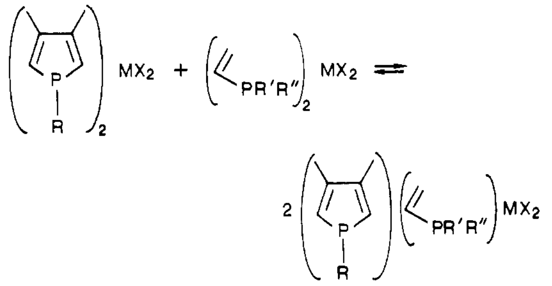
Jeffrey A. Rahn,[1a] Mark S. Holt,[1a] George A. Gray,[1b] Nathaniel W. Alcock,[1c] and John H. Nelson*,[1a]

Received June 20, 1988

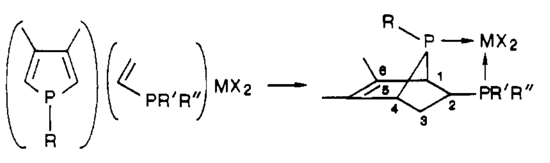
Reactions of $(vinylphosphine)_2MX_2$ complexes with $(1\text{-R-3,4-dimethylphosphole})_2MX_2$ complexes (where vinylphosphine = Ph_2VyP, $PhVy_2P$, Et_2VyP; R = Ph, Bzl, *t*-Bu; X = Cl, Br, I; M = Pd, Pt) produce dihalo[2-(R',R''-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]metal(II) complexes via an intramolecular Diels-Alder [4 + 2] cycloaddition. These reactions occur at ambient temperature with very high diastereoselectivity, providing a facile route to a new class of rigid chiral bidentate phosphines. These substituted 7-phosphanorbornene palladium and platinum complexes have been characterized by elemental analysis, physical properties, infrared spectroscopy, mass spectrometry, thermal analysis, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^1H/^{13}C$ HETCOR, COSY, and 2-D *J* nuclear magnetic resonance spectroscopy. The structures of two palladium complexes have been confirmed by X-ray crystallography. Dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) crystallizes in the monoclinic space group $P2_1/c$ in a unit cell of dimensions a = 11.184 (4) Å, b = 10.972 (5) Å, c = 23.351 (8) Å, β = 103.17 (3)°, and ρ(calcd) = 1.58 g cm^{-3}, with Z = 4. Refinement converged to R = 0.060 with 1886 independent observed ($I/\sigma(I) \geq 3.0$) reflections. The donor abilities of the two phosphorus donors are not significantly different; the PdP distances are 2.213 (4) and 2.251 (4) Å, the CPC angle for the bridging phosphorus is small (82.5 (6)°), and the PdCl distances (2.344 (4), 2.351 (4) Å) are not significantly different. The chelate ring is rigid, and the molecule contains four asymmetric centers. Dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) crystallizes in the orthorhombic space group *Fdd*2 in a unit cell of dimensions a = 28.737 (5) Å, b = 32.979 (8) Å, c = 10.253 (2) Å, and ρ(calcd) = 1.44 g cm^{-3}, with Z = 16. Refinement converged to R = 0.036 with 2011 independent observed reflections. The donor abilities of the two phosphorus donors are not significantly different; the PdP distances are 2.224 (2) and 2.236 (2) Å, the CPC angle for the bridging phosphorus is small (82.3 (4)°), and the PdCl distances (2.356 (2), 2.366 (2) Å) are not significantly different. The chelate ring is rigid, and the molecule contains five asymmetric centers. Two of the ligands have been liberated from the complexes and converted to their respective disulfides with retention of stereochemical configuration. Thermal analyses (TG and DSC) show that the complexes and disulfides polymerize upon melting, probably by extrusion of phosphinidine. A mechanism for the [4 + 2] Diels-Alder cycloaddition is proposed.

Introduction

In the course of our studies of the coordination chemistry of phospholes[2,3] and their novel reactions,[4-9] we have investigated the redistribution reactions[10] of palladium and platinum phosphole complexes with palladium and platinum complexes of vinylphosphines (reaction 1). We observed that these mixed phosphole-vinylphosphine complexes undergo a very facile [4 + 2] Diels-Alder cycloaddition reaction[11] (reaction 2) to produce a new class of rigid chiral diphosphines and report the details of these novel reactions herein.



(1)



(2)

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or sythesized as described below. Diphenylvinylphosphine, phenyldivinylphosphine, diethylvinylphosphine, and diallylphenylphosphine were obtained from Organometallics, Inc. The phospholes were prepared as previously described.[12] All reactions involving the phosphines were conducted under an N_2 atmosphere.

---

(1) (a) University of Nevada. (b) Varian Instrument Division. (c) University of Warwick.

(2) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding (Berlin)* **1983**, *55*, 153.

(3) Nelson, J. H.; Mathey, F. In *Methods of Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 8, Chapter 19.

(4) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.

(5) Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077.

(6) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.

(7) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

(8) Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 425.

(9) Mercier, F.; Mathev, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.* **1985**, *24*, 4141.

(10) Rahn, J. A.; Holt, M. S.; Nelson, J. H. *Polyhedron*, in press.

(11) A communication describing this reaction has appeared: Holt, M. S.; Nelson, J. H.; Savignac, P.; Alcock, N. W. *J. Am. Chem. Soc.* **1985**, *107*, 6936.

(12) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

0020-1669/89/1328-0217$01.50/0 © 1989 American Chemical Society

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Mass spectra were recorded on a MS30AEI spectrometer at 70 eV. Far-infrared spectra were recorded on a Perkin-Elmer 1800 FT infrared spectrophotometer as polyethylene pellets. $^{31}P\{^{1}H\}$ and some $^{13}C\{^{1}H\}$ NMR spectra were recorded at 40.26 and 25.00 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra were recorded at 500 or 300 MHz on one or more of the following: Varian VXR-300, Varian VXR-500, GE QE-300, and GE GN-300 spectrometers. $^{13}C\{^{1}H\}$ NMR spectra were recorded at 75 or 125 MHz on one or more of the above-mentioned spectrometers. Heteronuclear chemical shift correlated (HETCOR), hononuclear chemical shift correlated (COSY), and 2-D *J* NMR spectra were obtained as previously described.[13] Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4, with a positive value being downfield of the respective reference.

Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms were obtained under nitrogen at constant heating rates of 20 and 5 $°C^{-1}$ by using a Model 2000 DSC and TGA instrument coupled with a Model 3500 computer data station, all manufactured by Perkin-Elmer. DSC calibration was accomplished using pure indium metal.

(B) Synthesis. The complexes $(Ph_2VyP)_2PdX_2$,[14] $(PhVy_2P)_2PdX_2$,[14] $(PhVy_2P)_2PtX_2$,[15] $(DMPP)_2PtX_2$,[16] $(DMPB)_2PtI_2$,[16] $(DMPP)_2PdX_2$,[17] and $(DMTBP)_2PdBr_2$[17] (Vy = $-CH{=}CH_2$; X = Cl, Br, I; DMPP = 1-phenyl-3,4-dimethylphosphole; DMBP = 1-benzyl-3,4-dimethylphosphole; DMTBP = 1-*tert*-butyl-3,4-dimethylphosphole) were prepared as previously described.

Dichlorobis(diphenylvinylphosphine)platinum(II). To 2.51 g (5.30 mmol) of dichlorobis(benzonitrile)platinum(II) in 75 mL of $CHCl_3$ under N_2 was added 2.5 mL (10.6) mmol of diphenylvinylphosphine via syringe. The resultant solution was stirred magnetically for 4 h at ambient temperature and filtered and the solution volume reduced to approximately 35 mL on a rotary evaporator. Methanol was added to induce crystallization, and the pale yellow hexagonal plates that resulted were isolated by filtration, washed with cold methanol, and vacuum-dried overnight: yield 2.33 g (63.5%); mp 214–216 °C; IR ν_{PtCl} 306, 282 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.19 (ddd; $^{3}J_{PH}$ = 20.7, $^{3}J_{HH}$ = 18.0, $^{2}J_{HH}$ = 1.2 Hz; H_c, 2 H), 5.76 (ddd; $^{3}J_{PH}$ = 41.8, $^{3}J_{HH}$ = 12.0, $^{2}J_{HH}$ = 1.2 Hz H_b, 2 H), 6.38 (ddd; $^{2}J_{PH}$ = 22.5, $^{3}J_{HH}$ = 18.0, $^{3}J_{HH}$ = 12.0 Hz; H_a, 2 H), 7.25–7.7 (m; Ar H, 20 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 127.36 (m; $^{1}J_{PC}$ = 64.1, $^{2}J_{PtC}$ = 29.8, $^{3}J_{PC}$ = 2.4 Hz; C_i), 128.32 (m; $^{3}J_{PC}$ = 12.1, $^{5}J_{PC}$ = −0.7 Hz; C_m), 129.84 (m; $^{1}J_{PC}$ = 62.2, $^{2}J_{PtC}$ = 28, $^{3}J_{PC}$ = 0.3 Hz; C_α), 131.38 (t, "J_{PC}" = 2.7 Hz; C_p), 132.78 (s; $^{3}J_{PtC}$ = 31.0 Hz; C_β), 134.40 (t; "J_{PC}" = 10.8 Hz; C_o), "J_{PC}" = $|^{n}J_{PC} + {}^{n+2}J_{P'C}|$; ^{31}P NMR ($CDCl_3$) δ 2.66 (s, $^{1}J_{PtP}$ = 3633 Hz). Anal. Calcd for $C_{28}H_{26}Cl_2P_2Pt$: C, 48.72; H, 3.77. Found: C, 48.58; H, 3.85.

Dibromobis(diphenylvinylphosphine)platinum(II). Metathesis of 0.72 g of the chloride complex in $CH_2,Cl_2/CH_3OH/H_2O$ for 3 days with a mixture of NaBr and chloride complex in a 6:1 molar ratio gave 0.80 g (97.8%) of light yellow plates: mp 234–238 °C; IR ν_{PtBr} 216, 180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.21 (ddd; $^{3}J_{PH}$ = 20.6, $^{3}J_{HH}$ = 18.0, $^{2}J_{HH}$ = 1.1 Hz; H_c, 2 H), 5.75 (ddd; $^{3}J_{PH}$ = 41.9, $^{3}J_{HH}$ = 12.0, $^{2}J_{HH}$ = 1.1 Hz; H_b, 2 H), 6.42 (ddd; $^{2}J_{PH}$ = 22.4, $^{3}J_{HH}$ = 18.0, $^{2}J_{HH}$ = 12.0 Hz; H_a, 2 H), 7.2–7.7 (m; Ar H, 20 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 127.96 (m; $^{1}J_{PC}$ = 64.2, $^{3}J_{PC}$ = 1.3 Hz; C_i), 128.24 (m; $^{3}J_{PC}$ = 13.5, $^{5}J_{PC}$ = −2.0 Hz; C_m), 130.91 (d; "J_{PC}" = 61.3, $^{3}J_{PtC}$ = 26.7 Hz; C_α), 131.26 (s; C_p), 132.76 (s; $^{3}J_{PtC}$ = 31.7 Hz; C_β), 134.41 (t; "J_{PC}" = 10.7 Hz; C_o); ^{31}P NMR ($CDCl_3$) δ 2.30 (s; $^{1}J_{PtC}$ = 3582 Hz). Anal. Calcd for $C_{28}H_{26}Br_2P_2Pt$: C, 43.16; H, 3.34. Found: C, 43.30; H, 3.21.

Diiodobis(diphenylvinylphosphine)platinum(II). Metathesis of 0.64 g of the chloride complex in $CH_2Cl_2/CH_3OH/H_2O$ for 3 days with a mixture of NaI and chloride complex in a 6:1 molar ratio gave 0.60 g (73.7%) of bright yellow microcrystals: mp 228–229 °C; IR ν_{PtI} 164, 152, 148 cm^{-1}. ^{1}H NMR ($CDCl_3$): cis isomer, δ 5.26 (ddd; $^{3}J_{PH}$ = 19.9, $^{3}J_{HH}$ = 17.9, $^{2}J_{HH}$ = 1.0 Hz; H_c, 2 H), 5.73 (ddd; $^{3}J_{PH}$ = 41.5, $^{3}J_{HH}$ = 12.0, $^{2}J_{HH}$ = 1.0 Hz; H_b, 2 H), 6.46 (ddd, $^{2}J_{PH}$ = 22.2, $^{3}J_{HH}$ = 17.9, $^{3}J_{HH}$ = 12.0 Hz; H_a, 2 H); trans isomer, δ 5.38 (ddd; "J_{PH}" = 19.4, $^{3}J_{HH}$ = 18.2, $^{2}J_{HH}$ = 1.5 Hz; H_c, 2 H), 6.35 (ddd; "J_{PH}" = 40.9, $^{3}J_{HH}$ = 12.1, $^{2}J_{HH}$ = 1.5 Hz; H_b, 2 H), 7.2–7.7 (m; Ar H and H_a, 22 H); "J_{PH}" = $|^{n}J_{PH} + {}^{n+2}J_{P'H}|$. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): cis isomer, δ 127.82 (t; "J_{PC}" = 11.0 Hz; C_m), 129.45 (d; "J_{PC}" = 64.8 Hz; C_α), 130.58 (s; C_p), 132.64 (m; $^{3}J_{PC}$ = 48.4, $^{5}J_{PC}$ = 0.1 Hz; C_β), 134.85 (t; "J_{PC}" = 11.8 Hz; C_o); trans isomer, δ 128.08 (t; "J_{PC}" = 11.3 Hz; C_m), 130.45 (t; "J_{PC}" = 60.5 Hz; C_α), 131.08 (s; C_p), 132.62 (d; "J_{PC}" = 20.9 Hz; C_β), 134.48 (t; "J_{PC}" = 10.6 Hz; C_o). ^{31}P NMR ($CDCl_3$): δ −0.30 (s; $^{1}J_{PtP}$ = 3433 Hz, cis isomer), 0.48 (s, $^{1}J_{PtP}$ = 2454 Hz, trans isomer). Anal. Calcd for $C_{28}H_{26}I_2P_2Pt$: C, 38.52; H, 2.98. Found: C, 38.45; H, 2.86.

Dichlorobis(diethylvinylphosphine)platinum(II). To 2.10 g (4.45 mmol) of dichlorobis(benzonitrile)platinum(II) in 50 mL of CH_2Cl_2 under N_2 was added 1 mL of diethylvinylphosphine via syringe. The resultant solution was stirred magnetically for 24 h at ambient temperature and the solvent removed via rotary evaporation. The solid that remained was extracted with methanol to separate the product from unreacted benzonitrile complex. The methanol was removed via rotary evaporation, the residue was dissolved in hot benzene, the solution was filtered, and high-boiling petroleum ether was added to induce crystallization. The yellow plates that resulted were isolated by filtration, washed with anhydrous diethyl ether, and vacuum-dried overnight: yield 0.87 g (39.4%); mp 116–132 °C; IR ν_{PtCl} 308, 286 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (dt; "J_{PH}" = 18.6, $^{3}J_{HH}$ = 7.7 Hz; CH_3, 12 H), 2.02 (m; $^{2}J_{HH}$ = 14.8, "J_{PH}" = 12.0, $^{3}J_{HH}$ = 7.7 Hz; H_1, 4 H), 2.24 (m; $^{2}J_{HH}$ = 14.8, "J_{PH}" = 12.0, $^{3}J_{HH}$ = 7.7 Hz; H_2, 4 H), 5.90 (ddd; $^{3}J_{PH}$ = 18.6, $^{3}J_{HH}$ = 18.5, $^{2}J_{HH}$ = 1.1 Hz; H_c, 2 H), 5.99 (ddd; $^{3}J_{PH}$ = 37.6, $^{3}J_{HH}$ = 12.5, $^{2}J_{HH}$ = 1.0 Hz; H_b, 1 H), 6.21 (ddd; $^{2}J_{PH}$ = 19.5, $^{3}J_{HH}$ = 18.5, $^{3}J_{HH}$ = 12.5 Hz; H_a, 2 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 8.45 (t; $^{3}J_{PtC}$ = 46.6, "J_{PC}" = 3.2 Hz; CH_3), 17.87 (m; $^{1}J_{PC}$ = 41.8, $^{2}J_{PtC}$ = 27.6, $^{3}J_{PC}$ = 0.9 Hz; CH_2), 129.22 (m; $^{2}J_{PtC}$ = 54.9, $^{1}J_{PC}$ = 49, $^{3}J_{PC}$ = 3.3 Hz; C_α), 131.77 (s; $^{3}J_{PtC}$ = 38.3 Hz; C_β); ^{31}P NMR ($CDCl_3$) δ 0.12 (s, $^{1}J_{PtP}$ = 3528 Hz). Anal. Calcd for $C_{12}H_{26}Cl_2P_2Pt$: C, 28.94; H, 5.22. Found: C, 28.76; H, 5.12.

Dichlorobis(diallylphenylphosphine)platinum(II). To 3.66 g (7.75 mmol) of dichlorobis(benzonitrile)platinum(II) in 100 mL of CH_2Cl_2 under N_2 was added 3.1 mL (15.5 mmol) of diallylphenylphosphine via syringe. The resultant solution was stirred magnetically for 3 days at ambient temperature and the solvent removed via rotary evaporation. The solid was dissolved in ethanol, the solution was filtered, and water was added slowly to induce crystallization. The white prisms that resulted were isolated by fitlration, washed with anhydrous diethyl ether, and vacuum-dried overnight: yield 1.86 g (37.1%); mp 110–126 °C; IR ν_{PtCl} 306, 286 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.61 (m; $^{2}J_{HH}$ = 15 Hz; $H_{1^\bullet}$, 2 H), 2.78 (m; $^{2}J_{HH}$ = 15, $^{2}J_{PH}$ = 14 Hz; $H_{2^\bullet}$, 2 H), 4.80 (m; $^{3}J_{HH}$ = 17.0, $^{3}J_{PH}$ = 4.9, $^{2}J_{HH}$ = 1.7, $^{4}J_{HH}$ = 1.6 Hz; H_c, 2 H), 4.93 (m; $^{3}J_{HH}$ = 10.1, $^{3}J_{PH}$ = 3.8, $^{2}J_{HH}$ = 1.7, $^{4}J_{HH}$ = 1.0 Hz; H_b, 2 H), 5.44 (m; $^{3}J_{HH}$ = 17.0, $^{3}J_{HH}$ = 10.1, $^{3}J_{HH}$ = 7.6, $^{3}J_{HH}$ = 7.0, $^{3}J_{PH}$ = 6.0 Hz; H_a, 2 H), 7.0–7.3 (m; Ar H, 10 H), $H_{1^\bullet}$ and $H_{2^\bullet}$ correspond to the diastereotopic CH_2 protons; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 29.27 (m; $^{1}J_{PC}$ = 38.9, $^{2}J_{PtC}$ = 29.3, $^{3}J_{PC}$ = 0.5, $^{2}J_{PP}$ = 15.5 Hz; CH_2), 120.50 (m; $^{2}J_{PC}$ = 12.8, $^{4}J_{PC}$ = −0.6 Hz; C_β), 128.42 (m; $^{3}J_{PC}$ = 11.4, $^{5}J_{PC}$ = −1.3 Hz; C_m), 128.86 (m; "J_{PC}" = 57 Hz; C_i), 129.40 (t, "J_{PC}" = 6.8 Hz; C_α), 131.22 (s; C_p), 131.70 (t; "J_{PC}" = 8.8 Hz; C_o); ^{31}P NMR ($CDCl_3$) δ −7.84 (s; $^{1}J_{PtP}$ = 3552 Hz). Anal. Calcd for $C_{24}H_{30}Cl_2P_2Pt$: C, 44.61; H, 4.64. Found: C, 44.39; H, 4.48.

Dihalo[2-(R′,R″-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]metal(II). These complexes were prepared as previously described[11] by adding 1 equiv of the vinylphosphine complex to 1 equiv of the phosphole complex in $CHCl_3$ or CH_2Cl_2 at ambient temperature. The reactions were monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy and were normally complete in 24–48 h. The ^{1}H NMR and IR spectral data are given below. The $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR data are given in Tables I–III.

Dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (1): pale yellow microcrystals; yield 94.0%; mp 318–320 °C; IR ν_{PdCl} 314, 287 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49 (s; CH_3, 3 H), 1.67 (s; CH_3, 3 H), 1.88 (m; $^{3}J_{P'H}$ = 26.1, $^{3}J_{PH}$ = 22.2, $^{2}J_{HH}$ = 13.1, $^{3}J_{HH}$ = 9.1 Hz; H_4, 1 H), 2.45 (dd; $^{3}J_{PH}$ = 23.7, $^{2}J_{HH}$ = 13.1 Hz; H_3, 1 H), 2.98 (dt; $^{3}J_{P'H}$ = 48.2, $^{3}J_{HH}$ = 9.1, $^{2}J_{PH}$ = 6.9 Hz; H_2, 1 H), 3.04 (s; H_1, 1 H), 3.32 (s; H_5, 1 H), 7.2–8.2 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 48.96; H, 4.23; Cl, 21.41. Found: C, 48.68; H, 4.47; Cl, 21.20.

Dibromo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (2): bright yellow microcrystals; yield 91.2%; dp 323 °C, IR ν_{PdBr} 234, 215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s; CH_3, 3 H), 1.66 (s; CH_3, 3 H), 1.87 (m; $^{3}J_{P'H}$ = 25.8, $^{3}{}_{JPH}$ = 21.9, $^{2}J_{HH}$ = 13.2, $^{3}J_{HH}$ = 9.3 Hz; H_4, 1 H), 2.57 (dd; $^{3}J_{PH}$ = 24.9, $^{2}J_{HH}$ = 13.2 Hz; H_3, 1 H), 2.90 (dt; $^{3}J_{P'H}$ = 48.4, $^{3}{}_{JHH}$ = 9.3, $^{2}J_{PH}$ = 7.2 Hz; H_2, 1 H), 3.02 (s; H_1, 1 H), 3.41 (s; H_5, 1 H), 7.3–8.3 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}Br_2P_2Pd$: C, 46.84; H, 3.93. Found: C, 46.67; H, 3.91.

Diiodo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (3): bright orange microcrystals; yield

---

(13) Nelson, J. H.; Affandi, S.; Gray, G. A.; Alyea, E. C. *Magn. Reson. Chem.* **1987**, *25*, 774.

(14) Rahn, J. A.; Holt, M. S.; O'Neil-Johnson, M.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 1316.

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

(16) MacDougall, J. J.; Nelson, J. H.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 2145.

(17) MacDougall, J. J.; Nelson, J. H.; Mathey, F.; Mayerle, J. *Inorg. Chem.* **1980**, *19*, 709.

Table I. $^{31}P\{^1H\}$ NMR Data for Dihalo[2-(R′,R″-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]metal(II) Complexes

compd no.	R′, R″	R	M	X	$\delta(^{31}P)^a$ $(J_{PtP})^b$	$J_{PP}{}^b$
1	Ph, Ph	Ph	Pd	Cl	124.00, 34.60	7.3
2	Ph, Ph	Ph	Pd	Br	123.94, 35.42	0
3	Ph, Ph	Ph	Pd	I	121.40, 34.63	4.9
4	Ph, Vy	Ph	Pd	Cl	123.82, 35.42	4.9
					125.76, 34.03^c	4.9
5	Ph, Vy	Ph	Pd	Br	125.50, 35.48	1.5
					126.06, 33.42^c	0
6	Ph, Vy	Ph	Pd	I	120.73, 33.18	0
7	Ph, Vy	*t*-Bu	Pd	Br	148.88, 36.87	2.2
8	Ph, Ph	Ph	Pt	Cl	96.00 (3237), 20.46 (3474)	17
9	Ph, Ph	Ph	Pt	Br	97.87 (3137), 22.80 (3430)	12
10	Ph, Ph	Ph	Pt	I	99.09 (2932), 24.28 (3274)	10
11	Ph, Vy	Ph	Pt	Cl	96.09 (3254), 21.22 (3420)	17
					97.3 (-), 21.1 (-)^{c,d}	17
12	Ph, Vy	Ph	Pt	Br	97.75 (3159), 22.92 (3357)	15
					99.45 (-), 21.83 (-)^{c,d}	12
13	Ph, Vy	Ph	Pt	I	98.51 (2957), 23.12 (3188)	10
					101.40 (2959), 21.13 (3223)^c	10
14	Ph, Vy	Bzl	Pt	I	102.27 (2959), 23.95 (3201)	10
					103.90 (2944), 22.92 (3271)^c	10
15	Et, Et	Ph	Pt	Cl	95.67 (3359), 29.49 (3203)	15

^{a}In ppm in $CDCl_3$ at 300 K, relative to 85% H_3PO_4 (0 ppm). ^{b}In hertz. ^{c}Minor diastereomer. ^{d}Concentration too low to observe platinum satellites.

95.0%; dp 317 °C; IR ν_{PdI} 148, 134 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (s; CH_3, 3 H), 1.69 (s; CH_3, 3 H), 1.90 (m; $^3J_{P'H}$ = 26.4, $^3J_{PH}$ = 22.5, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 9.0 Hz; H_4, 1 H), 2.63 (dd; $^3J_{PH}$ = 23.3, $^2J_{HH}$ = 13.3 Hz; H_3, 1 H), 2.80 (dt; $^3J_{P'H}$ = 47.8, $^2J_{PH}$ = 11.1, $^3J_{HH}$ = 9.0 Hz; H_2, 1 H), 2.93 (s; H_1, 1 H), 3.44 (s; H_5, 1 H), 7.3–8.3 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}I_2P_2Pd$: C, 41.06; H, 3.45. Found: C, 41.03; H, 3.49.

Dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (4): pale yellow microcrystals; yield 74.9%; dp 320 °C; IR ν_{PdCl} 312, 290 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (s; CH_3, 3 H), 1.66 (s; CH_3, 3 H), 1.99 (m; $^3J_{P'H}$ = 27.9, $^3J_{PH}$ = 19.5, $^2J_{HH}$ = 14, $^3J_{HH}$ = 8.4 Hz; H_4, 1 H), 2.63 (dd; $^3J_{PH}$ = 23.7, $^2J_{HH}$ = 14 Hz; H_3, 1 H), 2.72 (dt; $^3J_{P'H}$ = 44, $^3J_{HH}$ = 8.4, $^2J_{PH}$ = 7.0 Hz; H_2, 1 H), 2.84 (s; H_1, 1 H), 3.43 (s; H_5, 1 H), 6.21 (dd; $^3J_{PH}$ = 21.5, $^3J_{HH}$ = 18.4 Hz; H_c, 1 H), 6.31 (dd; $^3J_{PH}$ = 43.6, $^3J_{HH}$ = 12.3 Hz; H_b, 1 H), 6.81 (ddd; $^2J_{PH}$ = 23.8, $^3J_{HH}$ = 18.4, $^3J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.2–8.1 (m; Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}Cl_2P_2Pd$: C, 48.85; H, 4.76; Cl, 13.00. Found: C, 48.72; H, 5.09; Cl 12.94.

Dibromo[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (5): yellow needles; yield 93.2%; mp 299–302 °C; IR ν_{PdBr} 234, 224 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (s; CH_3, 3 H), 1.66 (s; CH_3, 3 H), 2.00 (m; $^3J_{P'H}$ = 25.9, $^3J_{PH}$ = 22.8, $^2J_{HH}$ = 13.5, $^3J_{HH}$ = 8.7 Hz; H_4, 1 H), 2.62 (dd; $^3J_{PH}$ = 24.5, $^2J_{HH}$ = 13.5 Hz; H_3, 1 H), 2.66 (dt; $^3J_{P'H}$ = 47.4, $^2J_{PH}$ = 8.7, $^3J_{HH}$ = 8.7 Hz; H_2, 1 H), 2.77 (s; H_1, 1 H), 3.43 (s; H_5, 1 H), 6.11 (dd; $^3J_{PH}$ = 19.8, $^3J_{HH}$ = 18.3 Hz, H_c, 1 H), 6.27 (dd; $^3J_{PH}$ = 39.4, $^3J_{HH}$ = 12.3 Hz; H_b, 1 H), 6.91 (ddd; $^2J_{PH}$ = 21.9, $^3J_{HH}$ = 18.3, $^3J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.3–8.2 (m; Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}Br_2P_2Pd\cdot0.5CHCl_3$: C, 39.96; H, 3.65. Found: C, 39.82; H, 3.73.

Diiodo[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (6): brown-orange microcrystals; yield 99.9%; mp 288–292 °C; IR ν_{PdI} 136 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s; CH_3, 3 H), 1.65 (s; CH_3, 3 H), 2.00 (m; $^3J_{P'H}$ = 26, $^3J_{PH}$ = 23.4, $^2J_{HH}$ = 13.9, $^3J_{HH}$ = 9.8 Hz; H_4, 1 H), 2.57 (dd; $^3J_{PH}$ = 26, $^2J_{HH}$ = 13.9 Hz; H_3, 1 H), 2.59 (dt; $^3J_{P'H}$ = 46.8, $^2J_{PH}$ = 10.7, $^3J_{HH}$ = 9.8 Hz; H_2, 1 H), 2.70 (s; H_1, 1 H), 3.45 (s; H_5, 1 H), 6.04 (dd; $^3J_{PH}$ = 19.8, $^3J_{HH}$ = 18.8 Hz; H_c, 1 H), 6.23 (dd; $^3J_{PH}$ = 41.3, $^3J_{HH}$ = 12.3 Hz; H_b, 1 H), 7.03 (ddd; $^2J_{PH}$ = 24.7, $^3J_{HH}$ = 18.8, $^3J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.3–8.1 (m, Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}I_2P_2Pd\cdot0.5CHCl_3$: C, 35.08; H, 3.21. Found: C, 34.82; H, 3.13.

Dibromo[2-(phenylvinylphosphino)-5,6-dimethyl-7-*tert*-butyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (7): bright yellow prisms; yield 79.7%; dp 320 °C; IR ν_{PdBr} 232, 214 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (d; $^3J_{P'H}$ = 16.4 Hz; $C(CH_3)_3$, 9 H), 1.59 (s; CH_3, 3 H), 1.76 (s; CH_3, 3 H), 1.90 (m; $^3J_{P'H}$ = 24, $^3J_{PH}$ = 23, $^2J_{HH}$ = 12.8, $^3J_{HH}$ = 9 Hz; H_4, 1 H), 2.43 (s; H_1, 1 H), 2.50 (dt; $^3J_{P'H}$ = 41.2, $^3J_{HH}$ = 9, $^2J_{PH}$ = 7 Hz; H_2, 1 H), 2.73 (dd; $^3J_{PH}$ = 23.8, $^2J_{HH}$ = 12.8 Hz; H_3, 1 H), 3.24 (s; H_5, 1 H), 5.87 (ddd; $^3J_{PH}$ = 20.5, $^3J_{HH}$ = 18.6, $^2J_{HH}$ = 0.7 Hz; H_c, 1 H), 6.16 (ddd; $^3J_{PH}$ = 42.2, $^3J_{HH}$ = 12.4, $^2J_{HH}$ = 0.7 Hz; H_b, 1 H), 7.01 (ddd; $^3J_{PH}$ = 24.8, $^3J_{HH}$ = 18.6, $^3J_{HH}$ = 12.4 Hz; H_a, 1 H), 7.5–8.0 (m; Ar H, 5 H). Anal. Calcd for $C_{20}H_{28}Br_2P_2Pd$: C, 40.28; H, 4.70. Found: C, 40.15; H, 4.59.

Dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (8): white microcrystals; yield 46.9%; mp 361 °C; IR ν_{PtCl} 322, 284 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (s; CH_3, 3 H), 1.6 (m; H_4, 1 H), 1.67 (s; CH_3, 3 H), 2.43 (dd; $^3J_{PH}$ = 22.5, $^2J_{HH}$ = 13.3 Hz; H_3, 1 H), 2.90 (dt; $^3J_{P'H}$ = 40, $^3J_{HH}$ = 7.5, $^2J_{PH}$ = 6 Hz; H_2, 1 H), 2.93 (s; H_1, 1 H), 3.30 (s; H_5, 1 H), 7.3–8.2 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}Cl_2P_2Pt$: C, 46.86; H, 3.90; Cl, 10.64. Found: C, 47.12; H, 4.03; Cl, 10.58.

Dibromo[2-(dimethylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (9): white microcrystals; yield 45.5%; dp 320 °C; IR ν_{PtBr} 214, 188 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s; CH_3, 3 H), 1.6 (m; H_4, 1 H), 1.68 (s; CH_3, 3 H), 2.50 (dd; $^3J_{PH}$ = 22.2, $^2J_{HH}$ = 13.6 Hz; H_3, 1 H), 2.82 (dt; $^3J_{P'H}$ = 33.1, $^3J_{HH}$ = 9, $^2J_{PH}$ = 7 Hz; H_2, 1 H), 2.92 (s; H_1, 1 H), 3.38 (s; H_5, 1 H), 7.3–8.2 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}Br_2P_2Pt$: C, 41.34; H, 3.47. Found: C, 41.42; H, 3.56.

Diiodo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (10): pale yellow microcrystals; yield 74.2%; dp 290 °C; IR ν_{PtI} 154, 142 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (s; CH_3, 3 H), 1.6 (m; H_4, 1 H), 1.70 (s; CH_3, 3 H), 2.6 (dd; $^3J_{PH}$ = 23,

Table II. $^{13}C\{^1H\}$ NMR Data for Dihalo[2-(R′,R″-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) Complexes

	$\delta(^{13}C)^a$ $(J_{PC})^b$						
position	1	2	3	4	5	6	7^{d,e}
C_1	54.61 (35.4, 15.9)	55.00 (33.2, 16.5)	55.31 (30.8, 18.3)	54.07 (35.1, 16.6)	54.33 (33.6, 17.6)	54.44 (31.2, 19.1)	51.03 (28.3, 16.6)
C_2	32.27 (39.1, 35.4)	33.06 (39.7, 34.3)	34.01 (40.8, 31.4)	31.12 (39.4, 36.1)	31.69 (40.1, 34.5)	32.78 (40.7, 32.4)	30.46 (36.2, 27.7)
C_3	31.45 (19.6, 6.2)	31.61 (19.3, 5.1)	31.82 (20.5, 5.1)	31.34 (18.8, 4.7)	31.64 (19.2, 4.7)	31.83 (19.5, 9.3)	34.06 (16.7, 4.6)
C_4	47.15 (30.5)	47.26 (29.6)	47.56 (28.6)	47.54 (30.1)	47.57 (29.8)	47.65 (28.9)	46.67 (23.0)
C_5	137.55^c	137.31	136.6	137.24	137.02	136.35	129.90^c
C_6	137.53^c	137.31	136.6	137.24	137.02	136.35	130.18^c
5,6-CH_3	13.5	13.83	13.77	13.70 (3.1)	13.87	13.83	12.81 (3.1)
	15.0	14.94	14.89	14.78 (~3)	14.86	14.88	14.10 (3.1)
C_i	126.93 (48.9)	126.38 (74.8)	NO	NO	125.69 (47.8)	NO	125.94 (51.0)
	127.12 (53.7)	127.04 (68.4)	NO	NO	125.84 (50.8)	NO	NO
	NO	129.29 (82.5)	NO	NO	NO	NO	NO
C_o	132.86 (9.8)	132.80 (9.1)	132.70 (8.7)	132.84 (9.3)	132.81 (9.1)	132.69 (8.7)	134.42 (11.6)
	134.10 (11.0)	134.46 (11.0)	134.81 (9.3)	134.34 (11.6)	134.60 (11.6)	134.79 (11.8)	
	134.60 (9.7)	134.78 (10.0)	134.87 (10.4)				
C_m	128.31 (10.0)	128.19 (11.4)	127.94 (11.0)	128.37 (11.3)	128.29 (11.3)	128.07 (11.1)	129.29 (11.3)
	128.83 (11.0)	128.67 (11.3)	128.38 (11.1)	129.52 (11.4)	129.54 (11.3)	128.43 (10.6)	
	129.51 (11.0)	129.52 (11.0)	129.44 (10.5)				
C_p	131.76 (2.4)	131.65	131.36 (2.3)	131.83 (2.9)	131.73	131.50	132.72 (1.8)
	131.97 (2.5)	131.93	131.69 (2.4)	132.73 (2.7)	131.77	132.62	
	132.41 (2.4)	132.44	132.35 (1.4)				
C_α				125.91 (50.9)	127.41 (50.6)	126.53 (47.9)	128.48 (53.2)
C_β				135.35 (1.6)	134.53	133.56	133.99 (2.2)

^{a}In ppm. NO = not observed. ^{b}In hertz. The largest J_{PC} values for C_1, C_3, and C_4 correspond to coupling to P′; for C_2 the largest J_{PC} values correspond to coupling to P. Like phenyl carbons cannot be distinguished; therefore, J_{PC} values are not distinguishable. ^{c}May be reversed. ^{d}In DMSO-d_6. $^e\delta(C_a)$ (J_{PC}) = 35.04 (9.8) and $\delta(C_b)$ (J_{PC}) = 30.04 (1.7).

Table III. $^{13}C\{^{1}H\}$ NMR Data for Dihalo[2-(R′,R″-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) Complexes

	$\delta(^{13}C)^{a}$ $(J_{PC})^{b}$							
position	**8**	**9**	**10**	**11**	**12**	**13**	**14**[c]	**15**[d]
C_1	54.04 (45.4, 11.3)	53.35 (41.7, 11.0)	54.15 (38.5, 13.5)	53.40 (43.2, 11.4)	53.33 (41.9, 12.1)	53.12 (39.6, 13.8)	50.00 (41.0, 13.2)	53.67 (43.3, 8.9)
C_2	31.74 (39.1, 33.3)	30.27 (41.3, 32.7)	33.37	30.76 (42.3, 33.1)	31.10 (41.6, 33.6)	31.6 (NR)	31.05 (40.1, 34.9)	27.65 (37.2, 33.4)
C_3	31.46	30.47 (23.6, 7.7)	31.28	31.25 (16.2, 14.8)	31.45 (16.9, 3.9)	31.7 (NR)	33.27 (15.2, 3.8)	30.51 (16.32)
C_4	46.44 (33.2)	45.32 (36.3)	46.24 (35.6)	46.76 (37.6)	46.64 (31.1)	46.14 (34.8)	47.59 (29.3)	46.56 (37.9)
C_5	NO	136.86	NO	137.11 (~10)	137.0	NO	136.47	137.14
C_6	NO	136.86	NO	137.11 (~10)	137.0	NO	136.47	137.14
5,6-CH_3	13.77 14.81	13.08 (3.8) 14.20 (2.6)	13.69 14.81	13.83 (3.9) 14.74 (2.6)	13.83 14.76	13.82 14.80	13.76 (3.6) 14.75 (2.3)	13.78 (3.7) 14.94
C_i	NO NO NO	124.95 (58.6) 127.05 (56.2) 127.10 (56.2)	NO NO NO	NO NO	NO NO	NO NO	125.83 (58.1) 133.83 (7.1)[e]	123.30 (57.1)
C_o	132.92 (8.9) 133.79 (10.5) 134.56 (10.1)	132.63 (8.8) 133.72 (10.4) 134.34 (9.8)	132.84 (8.0) 134.56 (10.7) 134.88 (10.0)	132.87 (9.4) 134.10 (11.2)	132.82 (9.1) 134.33 (11.2)	132.79 (9.2) 134.61 (11.0)	134.28 (11.6) 129.46 (5.6)[e]	132.86 (9.2)
C_m	128.22 (11.4) 128.74 (11.3) 129.33 (11.3)	127.58 (11.3) 128.22 (11.3) 128.86 (10.9)	127.82 (11.4) 128.24 (11.3) 129.22 (11.0)	128.29 (11.1) 129.35 (11.4)	128.15 (11.4) 129.3 (11.3)	127.92 (11.0) 129.20 (11.0)	128.76 (11.3) 127.20 (3.0)[e]	128.24 (11.3)
C_p	131.74 131.89 (1.5) 132.12	131.06 (2.3) 131.54 (2.2) 131.87 (1.9)	131.44 131.70 132.12	131.84 (2.8) 132.49 (2.8)	131.73 (1.7) 132.49	131.54 132.41	132.2 (2.0) 128.76 (2.5)	131.66 (1.9)
C_α				125.78 (57.8)	125.80 (58.7)	126.25 (57.2)	127.82 (59.1)	
C_β				135.83	134.89	136.42 (1.5)	133.23 (2.0)	

[a] In ppm. NO = not observed; NR = not resolved. [b] In hertz. The largest J_{PC} values for C_1, C_3, and C_4 correspond to coupling to P′; for C_2, the largest J_{PC} values correspond to coupling to P. Like phenyls carbons cannot be distinguished; therefore, coupling to P′ or P cannot be assigned. [c] Carbon $\delta(C_a)$ (J_{PC}) = 28.18 (27.4). [d] Each ethyl group is different; therefore, there are four different chemical shifts, $\delta(C_a)$ (J_{PC}) = 14.89 (38.0) and 16.88 (33.7) and $\delta(C_b)$ (J_{PC}) = 8.23 (7.0) and 8.74 (3.3). [e] Benzyl phenyl resonances.

$^{2}J_{HH}$ = 13 Hz; H_3, 1 H), 2.75 (dt; $^{3}J_{P'H}$ = 41, $^{3}J_{HH}$ = 9, $^{2}J_{PH}$ = 7 Hz; H_2, 1 H), 2.86 (s; H_1, 1 H), 3.38 (s; H_5, 1 H), 7.3–8.3 (m; Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}I_2P_2Pt$: C, 36.77; H, 3.09. Found: C, 36.76; H, 3.17.

Dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (11): white microcrystals; yield 58.9%; dp 343 °C; IR ν_{PtCl} 312, 286 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s; CH_3, 3 H), 1.68 (s; CH_3, 3 H), 1.73 (m; $^{3}J_{P'H}$ = 24, $^{3}J_{PH}$ = 21, $^{2}J_{HH}$ = 13.3, $^{3}J_{HH}$ = 9 Hz; H_4, 1 H); 2.58 (dd; $^{3}J_{PH}$ = 23, $^{2}J_{HH}$ = 13.3 Hz; H_3, 1 H), 2.63 (dt; $^{3}J_{P'H}$ = 45, $^{3}J_{HH}$ = 9, $^{2}J_{PH}$ = 4.5 Hz; H_2, 1 H), 2.67 (s; H_1, 1 H), 3.34 (s; H_5, 1 H), 6.27 (ddd; $^{3}J_{PH}$ = 43.3, $^{3}J_{HH}$ = 12.3, $^{2}J_{HH}$ = 0.8 Hz; H_b, 1 H), 6.29 (ddd; $^{3}J_{PH}$ = 22.2, $^{3}J_{HH}$ = 18.5, $^{2}J_{HH}$ = 0.8 Hz; H_c, 1 H), 6.73 (ddd; $^{2}J_{PH}$ = 22.2, $^{3}J_{HH}$ = 18.5, $^{3}J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.2–8.1 (m; Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}Cl_2P_2Pt$: C, 42.88; H, 3.89; Cl, 11.51. Found: C, 43.04; H, 4.09; Cl, 11.34.

Dibromo[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (12): white plates; yield 62.6%; dp 310–316 °C; IR ν_{PtBr} 214, 186 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s; CH_3, 3 H), 1.69 (s; CH_3, 3 H), 1.75 (m; H_4, 1 H), 2.56 (m; H_3, 1 H), 2.6 (m; H_2, 1 H), 2.65 (s; H_1, 1 H), 3.37 (s; H_5, 1 H), 6.18 (ddd; $^{3}J_{PH}$ = 21.3, $^{3}J_{PH}$ = 18.6, $^{2}J_{HH}$ = 0.8 Hz; H_c, 1 H), 6.26 (ddd; $^{3}J_{PH}$ = 43.3, $^{3}J_{HH}$ = 12.3, $^{2}J_{HH}$ = 0.8 Hz; H_b, 1 H), 6.85 (ddd; $^{2}J_{PH}$ = 22.8, $^{3}J_{HH}$ = 18.6, $^{3}J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.2–8.1 (m; Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}Br_2P_2Pt \cdot CHCl_3$: C, 33.49; H, 3.06. Found: C, 33.56; H, 3.10.

Diiodo[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (13): pale yellow prisms; yield 33.9%; dp 280 °C; IR ν_{PtI} 150, 140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s; CH_3, 3 H), 1.70 (s; CH_3, 3 H), 1.80 (m; $^{3}J_{P'H}$ = 24, $^{3}J_{PH}$ = 20, $^{2}J_{HH}$ = 14, $^{3}J_{HH}$ = 9 Hz; H_4, 1 H), 2.52 (dt; $^{3}J_{P'H}$ = 43, $^{3}J_{HH}$ = 9, $^{2}J_{PH}$ = 4.8 Hz; H_2, 1 H), 2.56 (dd; $^{3}J_{PH}$ = 22, $^{2}J_{HH}$ = 14 Hz; H_3, 1 H), 2.60 (s; H_1, 1 H), 3.38 (s; H_5, 1 H), 6.16 (dd; $^{3}J_{PH}$ = 19.5, $^{3}J_{HH}$ = 18.6 Hz; H_c, 1 H), 6.23 (dd; $^{3}J_{PH}$ = 42.1, $^{3}J_{HH}$ = 12.3 Hz; H_b, 1 H), 7.00 (ddd; $^{2}J_{PH}$ = 23.1, $^{3}J_{HH}$ = 18.6, $^{3}J_{HH}$ = 12.3 Hz; H_a, 1 H), 7.3–8.1 (m, Ar H, 10 H). Anal. Calcd for $C_{22}H_{24}I_2P_2Pt$: C 33.06; H, 3.03. Found: C, 33.27; H, 3.07.

Diiodo[2-(phenylvinylphosphino)-5,6-dimethyl-7-benzyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (14): pale yellow needles; yield 19.7%; mp 258–266 °C; IR ν_{PtI} 152, 144 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.54 (s; CH_3, 3 H), 1.66 (m; H_4, 1 H), 1.78 (s; CH_3, 3 H), 2.19 (dt; $^{3}J_{P'H}$ = 39.4, $^{2}J_{PH}$ = 5.7, $^{3}J_{HH}$ = 5.7 Hz; H_2, 1 H), 2.52 (dd; $^{3}J_{PH}$ = 23.1, $^{2}J_{HH}$ = 12.9 Hz; H_3, 1 H), 3.12 (s; H_1, 1 H), 3.46 (ABX; $^{3}J_{PtH}$ = 29, $^{2}J_{HH}$ = 13.8, $^{2}J_{P'H}$ = 13.8 Hz; CH_2, 2 H), 4.86 (dd; $^{2}J_{PH}$ = 13.4, $^{3}J_{HH}$ = 6.8 Hz; H_5, 1 H), 5.95 (ddd; $^{3}J_{PH}$ = 20.1, $^{3}J_{HH}$ = 18.6, $^{2}J_{HH}$ = 0.7 Hz, H_c, 1 H), 6.19 (ddd; $^{3}J_{PH}$ = 41.8, $^{3}J_{HH}$ = 12.5, $^{2}J_{HH}$ = 0.7 Hz; H_b, 1 H), 7.04 (ddd; $^{2}J_{PH}$ = 23.8, $^{3}J_{HH}$ = 18.6, $^{3}J_{HH}$ = 12.5 Hz; H_a, 1 H), 7.2–7.6 (m; Ar H, 10 H). Anal. Calcd for $C_{23}H_{26}I_2P_2Pt$: C, 33.98; H, 3.20. Found: C, 33.82; H, 3.07.

Dichloro[2-(diethylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]platinum(II) (15): white microcrystals; yield 50%; mp 294–296 °C; IR ν_{PtCl} 306, 282 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (dt; $^{3}J_{PH}$ = 16.8, $^{3}J_{HH}$ = 7.7 Hz; CH_2CH_3, 3 H), 1.38 (dt; $^{3}J_{PH}$ = 17.7, $^{3}J_{HH}$ = 7.7 Hz; CH_2CH_3, 3 H), 1.65 (t; "J_{PH}" = 2.7 Hz; CH_3, 3 H), 2.0–2.8 (m; H_2, H_3, CH_2, 6 H), 2.74 (s; CH_3, 3 H), 3.01 (s; H_1, 1 H), 3.27 (s; H_5, 1 H), 7.35–7.6 (m; Ar H, 5 H). Anal. Calcd for $C_{18}H_{26}Cl_2P_2Pt$: C, 37.91; H, 4.59. Found: C, 38.16; H, 4.77.

2-(Diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene *P*,*P*′-Disulfide (16). The ligand was displaced from the palladium chloride complex and reacted with sulfur by a previously described procedure[9] to give a 58.1% yield of colorless crystals: mp 204–207 °C; ^{1}H NMR ($CDCl_3$) δ 1.54 (d; $^{4}J_{P'H}$ = 2.0 Hz; CH_3, 6 H), 2.32 (m; $^{3}J_{P'H}$ = 33.3, $^{2}J_{HH}$ = 12.7, $^{3}J_{HH}$ = 9.1, $^{3}J_{PH}$ = 5.06, $^{3}J_{HH}$ = 2.1 Hz; H_4, 1 H), 2.85 (m; $^{3}J_{P'H}$ = 20.4, $^{2}J_{PH}$ = 10.2, ^{3}JHH = 9.1, $^{3}J_{HH}$ = 8.0, $^{3}J_{HH}$ = 2.0 Hz; H_2, 1 H), 2.98 (m; ^{2}J$_{P'H}$ = 5.4, $^{4}J_{HH}$ = 2.1, $^{3}J_{HH}$ = 2.0, $^{3}J_{PH}$ = 1.5 Hz; H_1, 1 H), 3.10 (m; $^{3}J_{PH}$ = 17.9, $^{2}J_{HH}$ = 12.7, $^{3}J_{HH}$ = 8.0, $^{3}J_{P'H}$ = 4.0, $^{3}J_{HH}$ = 2.3 Hz; H_3, 1 H), 3.86 (m; $^{4}J_{PH}$ = 6.5, $^{2}J_{P'H}$ = 3.8, $^{3}J_{HH}$ = 2.3, $^{3}J_{HH}$ = 2.1, $^{4}J_{HH}$ = 2.1 Hz; H_5, 1 H), 7.2–7.8 (m; Ar H, 15 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 14.17 (d; $J_{P'C}$ = 3.0 Hz; CH_3), 14.62 (d; $J_{P'C}$ = 3.2 Hz; CH_3), 28.13 (d; $J_{P'C}$ = 19.2 Hz; C_3), 44.77 (dd; J_{PC} = 47.6, $J_{P'C}$ = 19.8 Hz; C_2), 51.72 (dd; $J_{P'C}$ = 44.4, J_{PC} = 5.0 Hz; C_1), 53.29 (d; $J_{P'C}$ = 51.2 Hz; C_4), 127.83 (d; *J$_{PC}$ = 12.4, C_m), 128.40 (d, $^{*}J_{PC}$ = 11.1, C_m), 128.54 (d, $^{*}J_{PC}$ = 11.1 Hz; C_m), 129.23 (d, $^{*}J_{PC}$ = 9.1 Hz; C_o), 130.21 (d; $^{*}J_{PC}$ = 3 Hz; C_p), 131.26 (d; $^{*}J_{PC}$ = 3 Hz; C_p) 131.34 (d; $^{*}J_{PC}$ = 3 Hz; C_p), 131.41 (d; $^{*}J_{PC}$ = 9.5 Hz; C_o), 133.37 (d; $^{*}J_{PC}$ = 10.1 Hz; C_o), 138.31 (d; $J_{P'H}$ = 9.9 Hz; C_5), 138.44 (d; $J_{P'H}$ = 9.9 Hz; C_6), since like phenyl carbons cannot be distinguished from one another, $^{*}J_{PC}$ designates the phosphorus coupling to either P or P′; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 46.1 (s; P), 89.4 (s; P′). Anal. Calcd for $C_{26}H_{26}P_2S_2$: C, 67.25; H, 5.60. Found: C, 67.15; H, 5.49.

2-(Phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene *P*,*P*′-Disulfide (17). The ligand was displaced from the palladium chloride complex with cyanide and reacted with sulfur[9] to give a 70.9% yield of colorless crystals: mp 172–174 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (d; $^{3}J_{P'H}$ = 1.2 Hz; CH_3, 3 H), 1.52 (d; $J_{P'H}$ = 1.1 Hz; CH_3, 3 H), 1.99 (m; $^{3}J_{P'H}$ = 33.9, $^{2}J_{HH}$ = 12.3, $^{3}J_{HH}$ = 10.1, $^{3}J_{PH}$ = 4.8, $^{3}J_{HH}$ = 2.1 Hz; H_4, 1 H), 2.37 (m; $^{3}J_{P'H}$ = 21.6, $^{2}J_{PH}$ = 14.1, $^{3}J_{HH}$ = 10.1, $^{3}J_{HH}$ = 7.2 Hz; H_2, 1 H), 2.97 (m; $^{3}J_{PH}$ = 17.4, $^{2}J_{HH}$ = 12.3, $^{3}J_{HH}$ = 7.2, $^{3}J_{P'H}$ = 4.1, $^{3}J_{HH}$ = 2.0 Hz; H_3, 1 H), 2.98 (m; $^{2}J_{P'H}$ = 5.9, $^{3}J_{PH}$ = 3.0, $^{4}J_{HH}$ = 2.0 Hz; H_1, 1 H), 3.68 (m; $^{4}J_{PH}$ = 6.9, $^{2}J_{P'H}$ = 3.0, $^{3}J_{HH}$ = 2.1, $^{3}J_{HH}$ = 2.0, $^{4}J_{HH}$ = 2.0 Hz; H_5, 1 H), 6.26 (ddd; $^{3}J_{PH}$ = 47.7, $^{3}J_{HH}$ = 11.7, $^{2}J_{HH}$ = 1.5 Hz; H_b, 1 H), 6.29 (ddd; $^{3}J_{PH}$ = 25.5, $^{3}J_{HH}$ = 17.7, $^{2}J_{HH}$ = 1.5 Hz; H_c, 1 H), 7.25–8.0 (m; Ar H, 10 H), 7.67 (ddd; $^{2}J_{PH}$ = 2.52, $^{3}J_{HH}$ = 17.7, $^{3}J_{HH}$ = 11.7 Hz; H_a, 1 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 13.61 (d; $J_{P'C}$ = 3.8 Hz; CH_3), 14.71 (d; $J_{P'C}$ = 3.8 Hz; CH_3), 26.95 (d; $J_{P'C}$ = 19.6 Hz; C_3) 48.19 (dd; J_{PC} = 49.8, $J_{P'C}$ = 20.4 Hz; C_2), 50.91 (dd; $J_{P'C}$ = 49.8, J_{PC} = 4.5 Hz; C_1), 51.8 (d; $J_{P'C}$ = 50.6 Hz; C_4), 128.47 (d; $^{*}J_{PC}$ = 12.1 Hz; C_m), 128.53 (d; $^{*}J_{PC}$ = 12.1 Hz; C_m), 129.14 (d; $^{*}J_{PC}$ = 9.8 Hz; C_o), 130.42 (d; $^{*}J_{PC}$ = 3.0 Hz; C_p), 130.74 (d; J_{PC} = 72.5 Hz; C_α),

Table IV. Crystal and Refinement Data for Compounds **1** and **4**[a]

	1	**4**
formula	$PdC_{26}H_{26}Cl_2P_2 \cdot CH_2Cl_2$	$PdC_{22}H_{23}Cl_2P_2$
fw	662.67	526.66
a, Å	11.184 (4)	28.737 (5)
b, Å	10.972 (5)	32.979 (8)
c, Å	23.351 (8)	10.253 (2)
β, deg	103.17 (3)	
space group	$P2_1/c$	*Fdd*2
Z	4	16
d(calcd), g cm^{-3}	1.58	1.44
μ, cm^{-1}	11.7	11.0
abs factor range	0.84–0.92	0.74–0.83
temp, K	298	298
final R_F	0.060	0.036
final R_{wF}	0.056	0.040

[a] Stationary background counts were taken before and after the scan for 0.25 of the scan time; Mo Kα radiation; graphite monochromator; $\lambda = 0.71069$ Å.

Table V. Atom Coordinates (×10^4) for $C_{26}H_{26}Cl_2P_2Pd \cdot CH_2Cl_2$ (**1**)

	x	*y*	*z*
Pd	5406.0 (9)	5065.6 (10)	6800.1 (4)
Cl(1)	7018 (3)	5747 (4)	6393 (2)
Cl(2)	4850 (4)	7062 (3)	6997 (2)
Cl(3)	8194 (7)	7166 (6)	5009 (3)
Cl(4)	7255 (9)	9352 (7)	5385 (3)
C(01)	7686 (26)	7933 (20)	5580 (10)
P(1)	5744 (3)	3185 (3)	6534 (2)
P(2)	4025 (3)	4152 (3)	7223 (2)
C(1)	6520 (11)	2139 (11)	7102 (6)
C(2)	6139 (12)	928 (11)	6821 (6)
C(3)	6993 (14)	−149 (12)	6918 (6)
C(4)	4963 (13)	946 (11)	6530 (6)
C(5)	4207 (13)	−75 (14)	6204 (7)
C(6)	4432 (12)	2210 (11)	6548 (6)
C(7)	5708 (13)	2315 (12)	7564 (6)
C(8)	4384 (12)	2491 (11)	7210 (7)
C(11)	6225 (12)	2978 (11)	5859 (6)
C(12)	5430 (15)	3336 (16)	5346 (7)
C(13)	5750 (16)	3210 (16)	4796 (7)
C(14)	6876 (17)	2771 (15)	4787 (7)
C(15)	7704 (16)	2427 (16)	5303 (8)
C(16)	7363 (13)	2544 (13)	5839 (6)
C(21)	2452 (11)	4411 (12)	6832 (7)
C(22)	1484 (13)	4104 (11)	7079 (6)
C(23)	285 (15)	4282 (13)	6792 (7)
C(24)	65 (13)	4776 (13)	6232 (7)
C(25)	996 (11)	5088 (14)	5973 (6)
C(26)	2200 (13)	4882 (13)	6269 (6)
C(27)	4068 (13)	4480 (13)	7983 (6)
C(28)	4096 (14)	5688 (15)	8180 (7)
C(29)	4132 (15)	5974 (16)	8753 (7)
C(210)	4122 (12)	5059 (16)	9142 (6)
C(211)	4062 (15)	3872 (15)	8980 (7)
C(212)	4047 (13)	3555 (16)	8402 (6)

Table VI. Atom Coordinates (×10^4) for $C_{22}H_{23}Cl_2P_2Pd$ (**4**)

	x	*y*	*z*
Pd	2331.6 (2)	5524.4 (1)	5000
P(1)	3021.3 (6)	5248.8 (5)	5429 (2)
P(2)	2747.7 (6)	6095.9 (5)	4874 (2)
Cl(1)	1953.5 (7)	4903.0 (6)	5400 (3)
Cl(2)	1638.1 (7)	5876 (1)	4479 (3)
C(1)	3264 (3)	5355 (2)	7045 (7)
C(2)	3779 (3)	5279 (2)	6810 (9)
C(3)	4062 (3)	5111 (3)	7919 (11)
C(4)	3910 (2)	5419 (2)	5688 (9)
C(5)	4384 (3)	5457 (3)	5094 (14)
C(6)	3493 (2)	5590 (2)	4906 (9)
C(7)	3206 (3)	5822 (2)	7066 (8)
C(8)	3304 (3)	5968 (2)	5642 (8)
C(11)	3123 (2)	4734 (2)	4987 (9)
C(12)	3201 (3)	4442 (2)	5959 (10)
C(13)	3240 (4)	4044 (3)	5559 (14)
C(14)	3226 (4)	3933 (3)	4301 (14)
C(15)	3161 (4)	4219 (3)	3347 (12)
C(16)	3101 (3)	4616 (3)	3683 (10)
C(21)	2869 (2)	6276 (2)	3246 (9)
C(22)	2834 (3)	6020 (2)	2187 (9)
C(23)	2936 (4)	6159 (3)	982 (11)
C(24)	3101 (4)	6549 (3)	767 (11)
C(25)	3144 (4)	6805 (3)	1797 (13)
C(26)	3036 (3)	6670 (2)	3061 (11)
C(27)	2497 (3)	6515 (2)	5697 (10)
C(28)	2698 (4)	6738 (3)	6620 (12)

Table VII. Selected Bond Distances (Å) for Compounds **1** and **4**

	1	**4**
Pd–P(1)	2.213 (4)	2.224 (2)
Pd–P(2)	2.251 (4)	2.236 (2)
Pd–Cl(1)	2.344 (4)	2.356 (2)
Pd–Cl(2)	2.351 (4)	2.366 (2)
P(1)–C(1)	1.818 (13)	1.832 (8)
P(1)–C(6)	1.823 (14)	1.843 (7)
P(1)–C(11)	1.792 (15)	1.781 (7)
P(2)–C(8)	1.868 (13)	1.832 (8)
P(2)–C(21)	1.810 (12)	1.806 (9)
P(2)–C(27)	1.800 (15)	1.774 (9)
C(1)–C(2)	1.500 (15)	1.520 (11)
C(1)–C(7)	1.574 (22)	1.551 (11)
C(2)–C(3)	1.504 (19)	1.506 (14)
C(2)–C(4)	1.335 (18)	1.296 (13)
C(4)–C(5)	1.502 (19)	1.498 (12)
C(4)–C(6)	1.513 (18)	1.547 (11)
C(6)–C(8)	1.588 (21)	1.554 (10)
C(7)–C(8)	1.535 (18)	1.563 (12)
C(27)–C(28)		1.329 (15)
Ph C–C[a]	1.381	1.378

[a] Average.

131.00 (d; $^*J_{PC} = 9.8$ Hz; C_o), 131.42 (d; $^*J_{PC} = 2.3$ Hz; C_p), 133.29 (d; $^*J_{PC} = 49.0$ Hz; C_i), 133.32 (dd; $J_{PC} = 64.2$, $J_{P'C} = 50.1$ Hz; C_i), 134.64 (s; C_β), 138.95 (d; $J_{PC} = 9.1$ Hz; C_6), 139.02 (d; $J_{PC} = 9.1$ Hz; C_5), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 42.02 (s; P), 88.04 (s; P′). Anal. Calcd for $C_{22}H_{24}P_2S_2$: C, 63.78; H, 5.79. Found: C, 63.84; H, 5.65.

(C) X-ray Data Collection and Processing. Pale yellow plates of dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II)–dichloromethane (**1**) and pale yellow blocklike crystals of dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (**4**) were isolated from dichloromethane/methanol solutions. For **1** the crystal chosen had a minor satellite, which was ignored. Crystal data and details of data collection are given in Table IV. Intensity data were taken with a Synthex $P2_1$ four-circle diffractometer and corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR.[18] Systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/c$ for **1** and (hkl, $h + l$, $k + l$, $l \neq h \neq 2n$; $0kl$, $k + l \neq 4n$; $h0l$, $h + l \neq 4n$) indicated space group *Fdd*2 for **4**. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. For **1** a few reflections were omitted that had $F_c \ll F_o$. These discrepancies may have resulted from reflections from the disoriented satellite being recorded. One molecule of CH_2Cl_2 was located during Fourier synthesis. The chiral **4** sponaneously resolved during crystallization. The hand of the individual crystal chosen was confirmed by refinement of a $\Delta f''$ multiplier. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors and were not refined, except for the methyl groups, which were treated as rigid bodies. Final refinement was by least-squares methods (minimizing $\sum w(F_o - F_c)^2$) in cascaded large blocks. Weighting schemes of the form $1/(\sigma^2(F) + gF^2)$ with $g = 6 \times 10^{-4}$ for **1** and $g = 2 \times 10^{-3}$ for **4** were shown to be satisfactory by weight analyses. Three standard reflections were monitored every 200 reflections, and if any changes were noted, then the data were scaled to correct for this. Computing was with the SHELXTL system[19] on a Data General NOVA 3 computer, following initial processing on a Burroughs B6800 computer. Scattering factors, including anomalous scattering, were taken from ref 20. Final atom coordinates

---

(18) Alcock, N. W. In *Crystallographic Computing*; Ahmed, F., Ed.; Munksgaard: Copenhagen, 1970.

(19) Sheldrick, G. M. *SHELXTL Users Manual*; Nicolet: Madison, WI, 1981.

Table VIII. Selected Bond Angles (deg) for Compounds 1 and 4

	1	4
P(1)–Pd–P(2)	83.5 (1)	83.1 (1)
P(1)–Pd–Cl(1)	89.2 (1)	91.2 (1)
P(1)–Pd–Cl(2)	173.6 (1)	174.3 (1)
P(2)–Pd–Cl(1)	171.4 (1)	171.9 (1)
P(2)–Pd–Cl(2)	95.2 (2)	91.4 (1)
Cl(1)–Pd–Cl(2)	92.6 (2)	94.5 (1)
Pd–P(1)–C(1)	117.9 (4)	116.1 (2)
Pd–P(1)–C(6)	110.6 (5)	110.4 (2)
Pd–P(1)–C(11)	118.0 (4)	119.0 (2)
Pd–P(2)–C(8)	104.8 (5)	104.4 (2)
Pd–P(2)–C(21)	113.2 (5)	115.7 (3)
Pd–P(2)–C(27)	118.5 (5)	114.4 (3)
C(1)–P(1)–C(6)	82.5 (6)	82.3 (4)
C(1)–P(1)–C(11)	111.9 (6)	110.5 (4)
C(6)–P(1)–C(11)	110.3 (6)	112.8 (3)
C(8)–P(2)–C(21)	109.5 (6)	107.7 (4)
C(8)–P(2)–C(27)	104.8 (7)	109.3 (4)
C(21)–P(2)–C(27)	105.7 (7)	105.2 (4)
P(1)–C(1)–C(2)	101.5 (8)	101.3 (5)
P(1)–C(1)–C(7)	99.7 (8)	99.3 (5)
P(1)–C(6)–C(4)	102.4 (9)	101.3 (5)
P(1)–C(6)–C(8)	96.3 (8)	95.2 (5)
P(1)–C(11)–C(12)	117.7 (12)	120.0 (7)
P(1)–C(11)–C(16)	122.7 (10)	120.2 (6)
P(2)–C(8)–C(6)	105.1 (9)	106.3 (5)
P(2)–C(8)–C(7)	107.3 (9)	108.3 (5)
P(2)–C(21)–C(22)	121.0 (11)	120.9 (6)
P(2)–C(21)–C(26)	120.2 (11)	119.8 (7)
P(2)–C(27)–C(28)	120.4 (11)	124.4 (8)
P(2)–C(27)–C(212)	122.5 (11)	
C(1)–C(2)–C(3)	121.5 (11)	117.9 (7)
C(1)–C(2)–C(4)	111.0 (11)	111.5 (7)
C(1)–C(7)–C(8)	106.4 (11)	105.9 (6)
C(2)–C(1)–C(7)	104.9 (11)	105.6 (6)
C(2)–C(4)–C(5)	128.5 (12)	130.9 (8)
C(2)–C(4)–C(6)	110.3 (11)	111.4 (7)
C(3)–C(2)–C(4)	127.3 (11)	130.2 (8)
C(4)–C(6)–C(8)	107.8 (10)	108.1 (7)
C(5)–C(4)–C(6)	121.2 (11)	117.6 (8)
C(6)–C(8)–C(7)	105.0 (11)	105.7 (6)
Ph C–C–C[a]	120.0	120.0

[a] Average.

for **1** and **4** are given in Tables V and VI and selected bond lengths and angles in Tables VII and VIII, respectively.

Results

Palladium and platinum vinylphosphine complexes react with palladium and platinum 1-R-3,4-dimethylphosphole complexes via an intramolecular [4 + 2] Diels–Alder cycloaddition to yield complexes of chiral diphosphines, the 2-phosphino-7-phosphabicyclo[2.2.1]hept-5-enes, by the sequence of steps illustrated in reactions 1 and 2. These reactions proceed to completion at room temperature in a period of 24–48 h to give a single distereomer when R′ = R″ and only two diastereomers in approximately a 20:1 molar ratio when R′ ≠ R″.

Discussion

Phosphorus NMR and Infrared Spectroscopy. All of the Diels–Alder products display two ν_{MX} stretching frequencies (see Experimental Section), as expected for a *cis*-MX_2 moiety.[21–25] All of these products display two resonances in their $^{31}P\{^1H\}$ NMR spectra (Table I), one for each unique phosphorus. The resonance

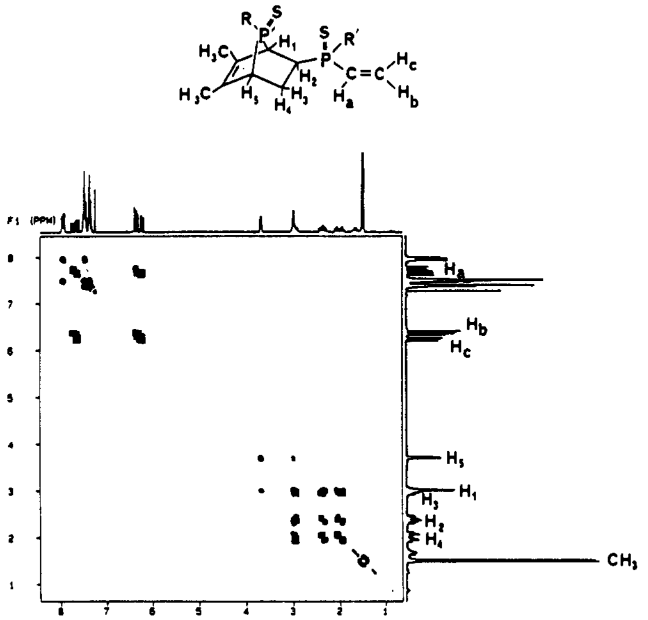
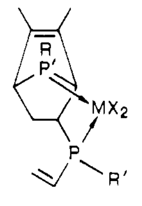
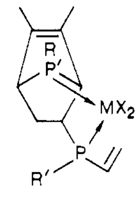


Figure 1. 300-MHz homonuclear chemical shift correlation spectrum of 2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene *P*,*P*′-disulfide (**17**) in $CDCl_3$ at 300 K.

corresponding to the bridgehead phosphorus is downfield[4,26–31] (95.7–148.9 ppm) while the other resonance lies in the region typical of a phosphine coordinated to palladium or platinum in a five-membered chelate ring[32] (21–35 ppm). The values of $^2J_{PP}$ are small (0–17 Hz), as usually found[33,34] for cis phosphines in square-planar palladium and platinum complexes. Within a series of compounds, the P–P coupling constant decreases in the order Cl > Br > I. The magnitude of $^1J_{PtP}$ observed for the platinum complexes is in the range expected for phosphorus trans to a halide.[35,36] In all but one case (compound **15**) $^1J_{PtP}$ is smaller for the 7-phospha phosphorus than for the 2-phosphino phosphorus. Within a series $^1J_{PtP}$ decreases in the order Cl > Br > I, consistent with the increasing trans influence[37] of the halides. Complexes **4**, **5**, and **11–14** were all formed in two diastereomeric forms schematically represented by A and B. In each of these cases



A



B

the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures showed two

---

(20) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(21) Shabatake, K.; Nakamoto, K. J. *J. Am. Chem. Soc.* **1970**, *92*, 3332.

(22) Goggin, P. L.; Goodfellow, R. J. *J. Chem. Soc. A* **1966**, 1492.

(23) Adams, D. M. *Metal Ligand and Related Vibrations*; Edward Arnold: London, 1976.

(24) Pfeffer, M.; Braunstein, P.; Dehand, J. *Spectrochim. Acta, Part A* **1974**, *30A*, 341.

(25) Goodfellow, R. J.; Evans, J. G.; Goggin, P. L.; Duddell, D. A. *J. Chem. Soc. A* **1968**, 1604.

(26) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 273.

(27) Katz, T. J.; Nicholson, C. R.; Reilly, C. A. *J. Am. Chem. Soc.* **1966**, *88*, 3832.

(28) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

(29) Mesch, K. A.; Quin, L. D. *Tetrahedron Lett.* **1980**, *21*, 4791.

(30) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 319.

(31) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(32) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(33) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; pp 28–34.

(34) Dixon, K. R. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; pp 394–396.

(35) Pidcock, A.; Richards, R. E.; Venanzi, L. *Proc. Chem. Soc., London* **1962**, 184.

(36) Grim, S. O.; Keiter, R. L.; McFarlane, E. *Inorg. Chem.* **1967**, *6*, 1133.

(37) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112. Gofman, M. M.; Nefedov, V. I. *Inorg. Chim. Acta* **1978**, *28*, 1.

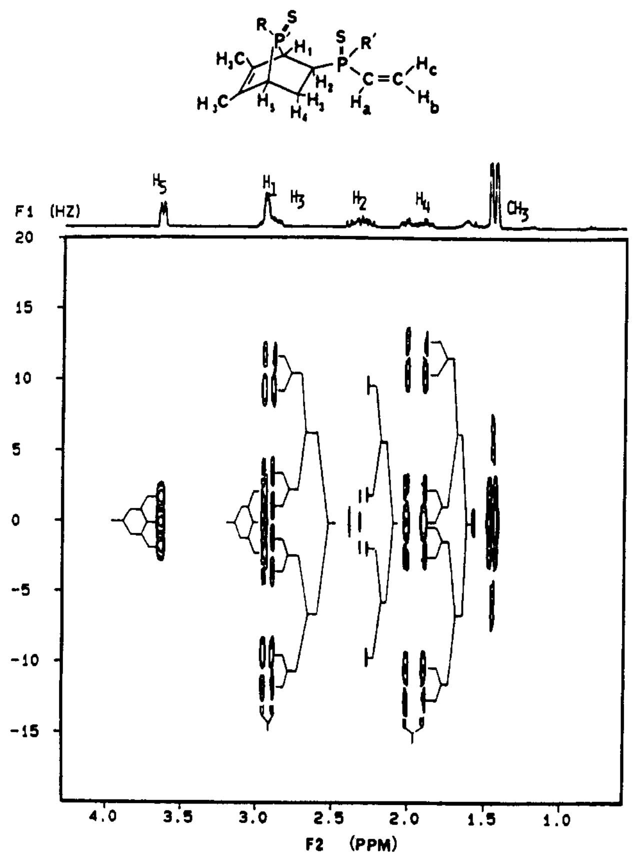


Figure 2. 300-MHz homonuclear 2-D *J* spectrum of **17** in $CDCl_3$ at 300 K. Spacings in F1 arise from H–H couplings, while the smaller splittings in F2 come from P–H couplings.

low-field and two high-field resonances representing these two diastereomers.[38,39] The relative integrated intensities of these resonances was generally about 20:1, showing that these reactions are highly diastereoselective. The crystal structure of **4** (vide infra) shows that for this compound the major diastereomer is A. For **4** the ^{31}P resonances corresponding to the 7-phospha and 2-phosphino phosphorus atoms of the minor diastereomer appear downfield and upfield, respectively, of the resonances for the major diastereomer. The same is true for compounds **5** and **11–14**, suggesting on the basis of ^{31}P NMR that the major diastereomer is A for all these compounds. Thus, neither the metal, Pd or Pt, nor the halide has a large influence on the diastereoselectivity of these particular reactions.

Proton and Carbon NMR Spectroscopy. Detailed analysis of the proton and carbon NMR spectra of these complexes provides additional information regarding the diastereoselectivity of these reactions. The $^{31}P\{^1H\}$ NMR spectra of the isolated products showed that the major diastereomer was in each case the isolated product. In order to obtain compounds with sufficient solubility for facile 2-D NMR studies, the ligands from compounds **1** and **4** were displaced with cyanide and converted into the disulfides by reaction with sulfur.

Selective $^1H\{^{31}P\}$ NMR experiments in combination with homonuclear chemical shift correlation (COSY) and 2-D *J* spectra enabled complete determination of H–H coupling constants and ^1H chemical shifts from both disulfides **16** and **17** in the following manner. The COSY spectrum (Figure 1) of **17** showed that the ring protons formed two tightly coupled spin sets of two and three members each. These logically divide into protons 1 and 5 and protons 2–4, respectively. From previous studies,[40] large values of $^3J_{PH}$ are expected for protons 2 and 4 and a smaller $^3J_{PH}$ value is expected for proton 3. The 2-D *J* spectrum (Figure 2) clearly shows two protons with large values for J_{PH} (protons 3 and 4); proton 2 has weaker intensity in this spectrum, and for it J_{PH} is not so evident. Selective $^1H\{^{31}P\}$ experiments (Figures 3–6) then established the values of the individual J_{PH} values. The 2-D *J* spectrum shows the large value of $^2J_{HH}$ expected for geminal coupling of protons 3 and 4 and the large vicinal $^3J_{HH}$ value for coupling of protons 2 and 4. The assignment of the chemical shift of proton 3 is corroborated by comparing the spectra of compounds **16** and **17**. Molecular models suggest that in **16** proton 3 is in the deshielding region of the neighboring magnetically anisotropic phenyl ring. Thus, the chemical shift for proton 3 in compound **16** (3.10 ppm) is, as expected, downfield of the chemical shift of proton 3 in compound **17** (2.97 ppm).

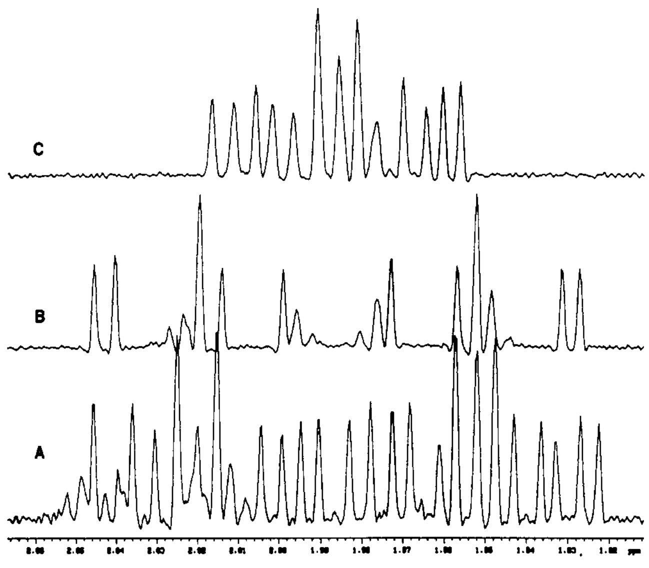


Figure 3. Resolution-enhanced 500-MHz $^1H\{^{31}P\}$ NMR spectra of **17** in $CDCl_3$ at 300 K: (A) normal ^1H spectrum of H_4 multiplet; (B) spectrum with the 2-phosphino phosphorus decoupled; (C) spectrum with the 7-phosphaphosphorus decoupled.

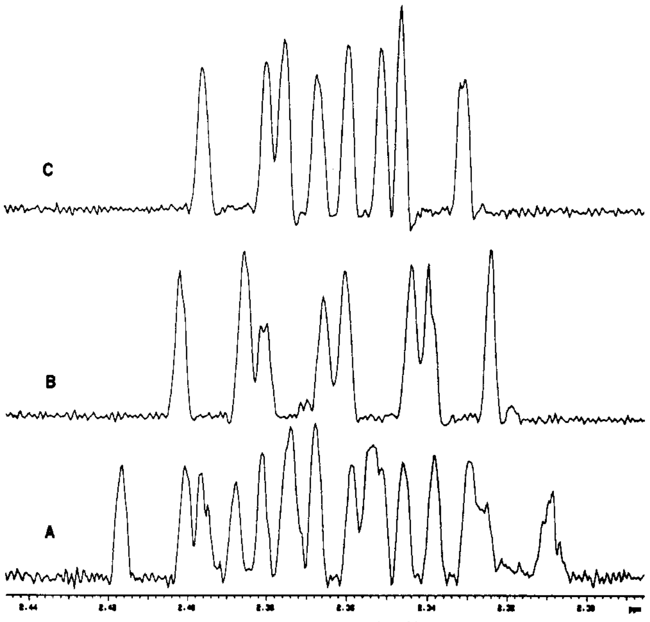


Figure 4. Resolution-enhanced 500-MHz $^1H\{^{31}P\}$ NMR spectra of **17** in $CDCl_3$ at 300 K: (A) normal ^1H spectrum of H_2 multiplet; (B) spectrum with the 2-phosphino phosphorus decoupled; (C) spectrum with the 7-phospha phosphorus decoupled.

The assignment of the carbon chemical shifts was then accomplished via the HETCOR spectrum (Figure 7). The ^{13}C spectral data are very similar for the two disulfides, with the only major differences arising from the substituents R′ and R″. The ^{13}C spectrum of **16** shows three sets of phenyl resonances and that of **17** two sets of phenyl resonances. The carbon C_1 and C_2

---

(38) Payne, N. C.; Stephan, D. W. *J. Organomet. Chem.* **1981**, *221*, 203.
(39) Kyba, E. P.; Pines, S. P. *J. Org. Chem.* **1982**, *47*, 4800.
(40) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley-Interscience: New York, 1981.

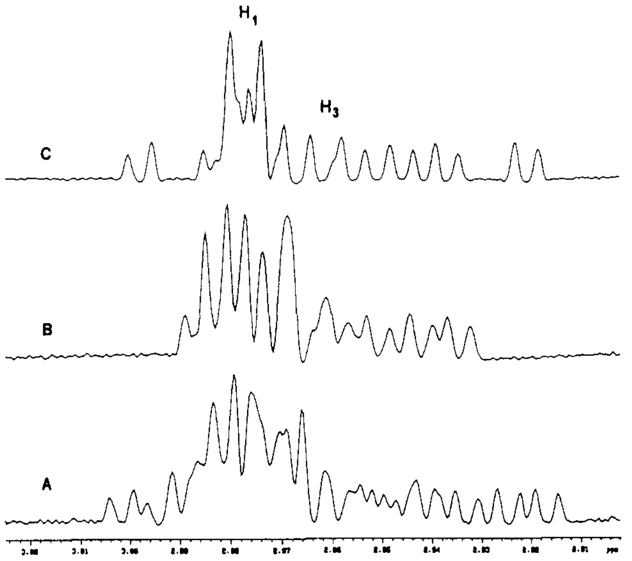


Figure 5. Resolution-enhanced 500-MHz $^{1}H\{^{31}P\}$ NMR spectra of **17** in $CDCl_3$ at 300 K: (A) normal ^{1}H spectrum of H_1 and H_3 multiplets; (B) spectrum with the 2-phosphino phosphorus decoupled; (C) spectrum with the 7-phospha phosphorus decoupled.

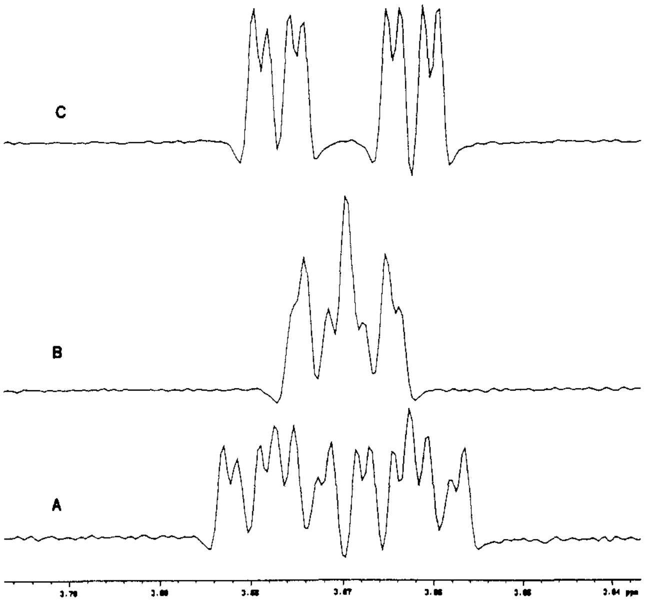


Figure 6. Resolution-enhanced 500-MHz $^{1}H\{^{31}P\}$ NMR spectra of **17** in $CDCl_3$ at 300 K: (A) normal ^{1}H spectrum of H_5 multiplet; (B) spectrum with the 2-phosphino phosphorus decoupled; (C) spectrum with the 7-phospha phosphorus decoupled.

resonances appear as doublets of doublets due to coupling to both phosphorus nuclei, and C_1 is downfield of C_2. All other carbon resonances are doublets. The C_5 and C_6 carbon resonances are the most downfield (~138 ppm) with the two methyl resonances being the most upfield (14–16 ppm) as expected. For **17**, $\delta(C_\alpha)$ is upfield of $\delta(C_\beta)$ and displays the largest J_{PC} value (72.5 Hz), with C_β exhibiting no coupling to phosphorus.

The NMR spectra obtained for the disulfides, which were formed with retention of configuration from the displaced ligands, were used as an aid in assigning the ^{1}H and ^{13}C spectra of the complexes. The ^{1}H NMR data are given in the Experimental Section and the ^{13}C NMR data in Tables II and III. For most of the complexes, selective $^{1}H\{^{31}P\}$ spectra at both 300 and 500 MHz were obtained to corroborate the assignments. The proton spectra of all the complexes are very similar to one another. The H_1 and H_5 resonances usually appear as broad singlets with the H_5 resonance being the most downfield of the ring proton resonances. When the H_2 resonance was not overlapped by other resonances, it appeared as a doublet of triplets with a large coupling to the 7-phospha phosphorus, a 6–10-Hz coupling to H_4, and a smaller coupling to the 2-phosphino phosphorus. The H_3 resonance usually appears as a doublet of doublets with the larger coupling arising from coupling to phosphorus and the smaller from coupling to H_4. The H_4 resonance occurs in the 1.6–2.0 ppm region and for some complexes could not be resolved due to overlap with the methyl resonances. When this resonance was resolved, four distinct couplings could be measured. The largest coupling is to the 7-phospha phosphorus, followed by a slightly smaller coupling to the 2-phosphino phosphorus and coupling to H_3 and H_2. The two methyl groups gave rise to chemical-shift-distinct singlets.

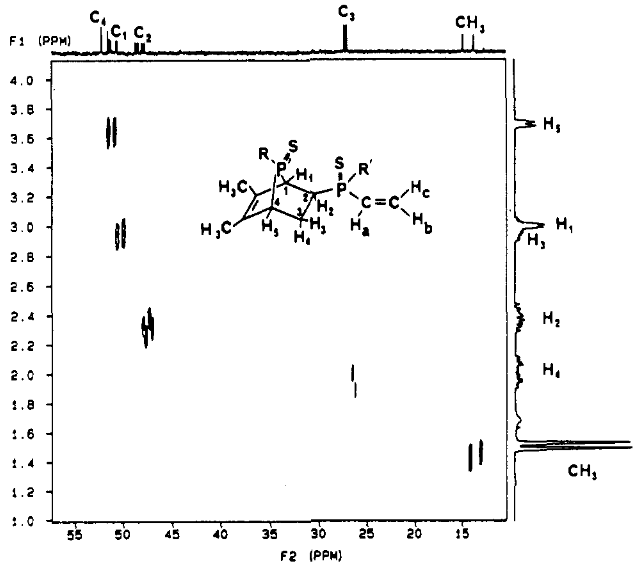


Figure 7. Heteronuclear 2-D $^{1}H/^{13}C$ chemical shift correlation for **17** in $CDCl_3$ at 75 MHz (^{13}C) and 300 K. This expansion shows the ring carbons (C_1–C_4) and the methyl carbons. Carbon 1-D and proton 1-D spectra are shown on the top and right side, respectively. P–C couplings are responsible for the splittings in the F2 domain, while P–H and H–H couplings are responsible for splittings in the F1 domain.

The vinyl proton resonances display the same splitting patterns as observed[14,15] for the palladium and platinum complexes of diphenylvinyl- and phenyldivinylphosphine.

The ^{13}C spectra for the complexes are very similar to those obtained for the two disulfides (Tables II and III). The C_1 and C_2 resonances appear as doublets of doublets due to coupling to both phosphorus nuclei, and for most complexes the C_3 resonance is also a doublet of doublets. Carbon-13 data for similar compounds[41,42] suggest that the larger coupling is to the 7-phospha phosphorus for carbons 1 and 3 and to the 2-phosphino phosphorus for carbon 2. The P–C coupling to C_4 is due to coupling to the 7-phospha phosphorus.

The ^{13}C NMR spectra for the complexes containing a vinyl group always show the C_α resonance upfield of the C_β resonance, and for C_α $^{1}J_{PC}$ is large. When phosphorus coupling to C_β is observed, it is in the range of 1–2 Hz.

The ^{13}C NMR spectra for complexes **7**, **14**, and **15** display additional resonances for their *tert*-butyl, benzyl, and ethyl groups, respectively.

The similarity of the ^{1}H and ^{13}C NMR data for the two sets of complexes suggests that the general structural features of all these complexes are the same. The complexes formed from diphenylvinylphosphine are racemic mixtures of a single diastereomer, and the major diastereomer formed from phenyldivinylphosphine is diastereomer A in each case. Thus, neither the metal nor the halide had a significant effect on the diastereoselectivity of these reactions. However, they both influenced the reaction rates. Generally, the palladium reactions are faster than

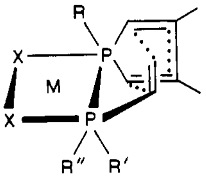
---

(41) Quin, L. D.; Kaster, D. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021.

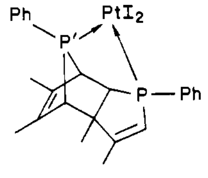
(42) Quin, L. D.; Nandakumar, S. R.; Topping, R. J.; McPhail, A. T. *J. Am. Chem. Soc.* **1986**, *108*, 4519.

the platinum reactions and for both metals the rates decreased in the sequence Cl > Br > I.

Reaction Mechanism. Diphenylvinylphosphine and 1-phenyl-3,4-dimethylphosphole were placed in a sealed tube and heated at 60 °C for 1 month without reaction. As reported earlier,[10] phosphole complexes of palladium and platinum undergo redistribution reactions with vinylphosphine complexes of palladium and platinum (reaction 1). Coordination of phospholes to palladium[17] or platinum[16] polarizes the ring, increasing the electron density on the α-carbon and decreasing the electron density on the β-carbon. Likewise, coordination of a vinylphosphine to palladium[14] or platinum[15] polarizes the vinyl group in the same sense. Thus, these reactions probably occur by a polar, stepwise, intramolecular[43] [4 + 2] cycloaddition between the vinylphosphine and the phosphole in mutually cis positions of the square-planar mixed-ligand complex with a transition state schematically represented as



The metal provides both electronic activation and molecular direction for a highly organized transition state. When R' and R'' are different, as in the case of phenyldivinylphosphine, the smaller of the R' and R'' groups will occupy the sterically more congested region near the halides, and this favors the formation of diastereomer A as experimentally observed. The reaction between dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) and dichlorobis(diethylvinylphosphine)platinum(II) to form compound **15** did not occur at room temperature in the same way. After several days only the two starting materials were present in solution. Upon addition of a trace of 1-phenyl-3,4-dimethylphosphole, compound **15** was formed at room temperature in 50% yield. This reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and no mixed-ligand complex could be detected. Instead, compound **18** was formed in about 20% yield after addition of NaI



18

to the reaction mixture. Details of the characterization of compound **18** and its preparation by other routes will be reported separately.

Thermal Analysis and Mass Spectrometry. The Diels–Alder reaction is often reversible,[44] and phosphanorbornadienes are known[45] to thermally eliminate arenes to produce transient phosphinidenes. There is intense current interest in the chemistry of phosphinidene complexes.[46] In order to probe the thermal stability and potential modes of decomposition of these new compounds, differential scanning calorimetry (DSC) and thermogravimetry (TG) experiments were carried out on complexes **1**, **4**, **8**, and **11** and the two disulfides **16** and **17**. The DSC curves for **1**, **8**, **16**, and **17** display a sharp endotherm immediately followed by an exotherm, representing melting and decomposition, respectively, as exemplified in Figure 8. The DSC curves for **4** and **11** only display the exotherm, showing that these two

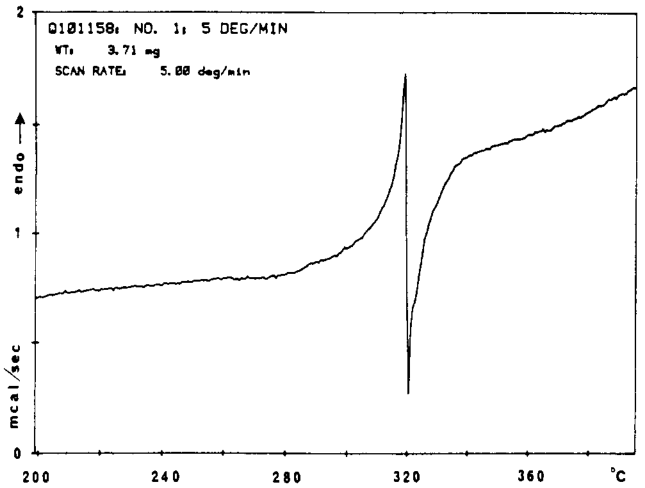


Figure 8. Differential scanning calorimetry curve for complex **1**. Heating rate is 5 °C min^{-1} under nitrogen.

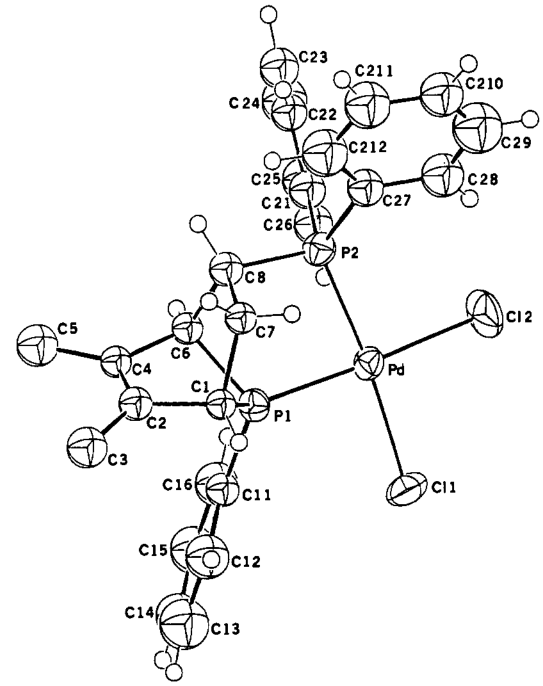


Figure 9. ORTEP plot of the structure of dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (**1**) showing the atom-labeling scheme (50% probability ellipsoids).

compounds decompose rather than melt. The TG curves indicate that for all compounds studied, the exotherms are accompanied by significant mass loss with M, MCl_2, or MO being the final product in the thermal decomposition of the metal complexes.

Mass spectrometry on these same compounds gives information regarding the nature of the thermal decompositions. The two disulfides differ from one another only in the nature of the substituents on the 2-phosphino phosphorus, with **16** having two phenyl substituents and **17** having a phenyl and a vinyl substituent. The mass spectra of both compounds show prominent peaks at *m/e* 91, 107, 108, and 140. The peaks at *m/e* 108 and 140 are due to the PPh^+ and $S{=}PPh^+$ fragments, respectively. Fragmentation of the 2-phosphino phosphorus groups Ph_2P (**16**) and PhVyP (**17**) is evidenced by the presence of major peaks at *m/e* 185 and 168, respectively. The ease of fragmentation of both the 7-phospha and the 2-phosphino groups aids in the explanation of the peaks at *m/e* 91 and 107. Fragmentation of both phosphorus groups would leave an *o*-xylyl fragment responsible for the peak at *m/e* 107. This fragment loses a CH_3 group to form a benzyl

---

(43) Ciganek, E. *Org. React.* **1984**, *32*, 1. Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. Saver, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(44) Kloetzel, M. C. *Org. React.* **1948**, *4*, 1. Holmes, H. L. *Org. React.* **1948**, *4*, 60.

(45) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

(46) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81.

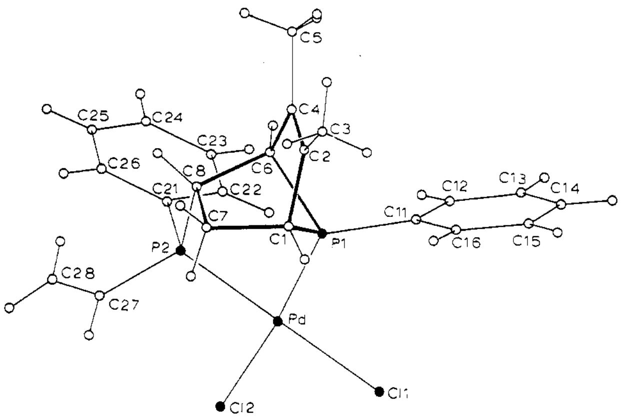


Figure 10. View of the structure of dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) (**4**) showing the atom-labeling scheme. This is drawn with arbitrary small atomic radii to emphasize the central norbornene skeleton and the diastereomer found.

carbonium ion, which rearranges to a tropylium ion.[47]

Complexes **1** and **8**, like disulfide **16**, contain a 2-diphenylphosphino group and behave similarly by displaying a significant *m/e* peak at 185 for the Ph_2P^+ fragment as well as prominent peaks at *m/e* 91, 107, and 108. Complexes **4** and **11** contain a 2-(phenylvinylphosphino) group and as expected exhibit a major peak at *m/e* 168 corresponding to this fragment and prominent peaks at *m/e* 91, 107, and 108. No evidence of retro Diels–Alder fragmentation was seen for any of these six compounds, suggesting that these [4 + 2] cycloadditions are not reversible processes.

Crystal Structure Analysis. In order to gain conclusive support for the diastereoselectivity discussed previously and to characterize the new ligand system, X-ray crystal structures of complexes **1** and **4** were obtained. The structures of these molecules are shown in Figures 9 and 10, respectively. Both complexes exist as discrete molecules with no abnormal intermolecular contacts. Neither complex contains any element of symmetry. As a result both complexes are chiral. As can be seen in Figures 9 and 10, the chelate rings are very rigid and the isolated compound **4** is the diastereomer A. The phosphanorbornene rings in these molecules are less strained than in complexes that contain similar polycyclic ring systems[4,28,48,49] not containing a heteroatom. This strain can best be examined by considering the angles made by the bridgehead carbons and the 7-phospha phosphorus, which are 82.5 and 82.3° for **1** and **4**, respectively. These CPC angles are larger than the analogous angles found for chromium[28] and molybdenum complexes, which have CPC angles of 79.0 and 79.4°, respectively. However, these bond angles 82.5 and 82.3° are slightly smaller than that found for the phosphole [4 + 2] Diels–Alder dimer[48] (86.9°) and considerably smaller than those within the phosphole ring in the platinum[16] and palladium[17] complexes of 1-phenyl-3,4-dimethylphosphole (91.2 and 92.3°, respectively). This increased angle strain in the [4 + 2] adducts manifests itself as an extreme downfield shift of the associated ^{31}P resonances for the 7-phospha phosphorus.

The coordination geometries of both **1** and **4** show a small amount of tetrahedral distortion as gauged by the dihedral angles formed between the P_2Pd and $PdCl_2$ planes. These angles, 7.6 (2) and 5.7 (1)° for **1** and **4**, respectively, compare with those of the palladium diphospholene[9] (5.2°) and Pd(DPPE)Cl_2[50] (3°) complexes.

The PdP bond lengths for **1** (2.213 (4), 2.251 (4) Å) and for **4** (2.244 (2) 2.236 (2) Å) are in the range found[9] in a similarly rigid palladium diphospholane complex (2.210 (1), 2.225 (1) Å) as well as for (DPPM)PdCl_2[50] (2.250 (1), 2.234 (1) Å), (DPPE)PdCl_2[50] (2.233 (2), 2.226 (2) Å), and (DPPP)PdCl_2[50] (2.249 (2), 2.244 (1) Å). Also, the PdCl bond lengths for **1** (2.344 (4) 2.351 (4) Å) and for **4** (2.356 (2), 2.366 (2) Å) are in the normal range.[15,17] The structural results show that the bonding of these new rigid chiral bidentate phosphine ligands to palladium(II) is typical of bidentate phosphines in five-membered chelate rings.

Acknowledgment. The financial assistance of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We wish to thank Dr. Karl Reimer for the thermal analyses.

Supplementary Material Available: For the two structure studies, listings of crystal and refinement data, H atom coordinates, thermal parameters (*U*), and bond distances and angles (7 pages); listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

---

(47) Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Spectroscopy*; Saunders: Philadelphia, 1979; pp 250–252.

(48) Chiu, Y. Y.; Lipscomb, W. *J. Am. Chem. Soc.* **1969**, *91*, 4150.

(49) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 3021.

(50) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.