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Coupling of Acetylenes Held Proximate to a Metal: Alkyne–Alkyne Interactions in *cis*-Phosphinoacetylene Complexes, Including Structural Characterization of the Unsymmetrical Diphosphine 1-Phenyl-2,3-bis(diphenylphosphino)naphthalene and Three Platinum(II) Complexes of $Ph_2PC\equiv CPh$

David K. Johnson, Thitima Rukachaisirikul, Yan Sun, Nicholas J. Taylor, Allan J. Canty,[†] and Arthur J. Carty*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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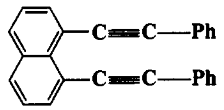
The diphenyl(phenylethynyl)phosphine complexes *cis*-$PtX(Y)(Ph_2PC\equiv CPh)_2$ [X = Y = Cl, I, CF_3, C_6F_5, Me; X (Y) = *o*-$C_6H_4O_2$, Me(Cl)] have been synthesized, and for all of the complexes except the dimethyl complex, intramolecular coupling of the phosphinoacetylene ligands occurs on heating to form *cis*-$PtX(Y)\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$. A mixture of the two possible structural isomers is formed for *cis*-$PtMe(Cl)\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$. The complex *cis*-$PtMe_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ has been obtained by reaction of the dichloro analogue with methyllithium. The unsymmetrical diphosphine 1-phenyl-2,3-bis(diphenylphosphino)naphthalene [*o*-$C_{16}H_{10}(PPh_2)_2$], produced as a coordinated ligand via these intramolecular coupling reactions, has been isolated in moderate yield from the dichloro complex and its structure determined by X-ray diffraction. Crystals of *o*-$C_{16}H_{10}(PPh_2)_2$ are triclinic, space group $P\bar{1}$, with a = 11.437(13) Å, b = 9.628(12) Å, c = 16.712(21) Å, α = 82.31(9)°, β = 119.08(3)°, γ = 110.03(5)°, and Z = 2. The structure was solved and refined to R = 0.058, R_w = 0.070. Structure determinations of *cis*-$PtCl_2(Ph_2PC\equiv CPh)_2\cdot 2MeCN$, *cis*-$PtMe(Cl)(Ph_2PC\equiv CPh)_2\cdot 0.5CH_2Cl_2$, and *cis*-$PtMe_2(Ph_2PC\equiv CPh)_2$ have been carried out to evaluate interligand interactions in the complexes. Crystallographic data: *cis*-$PtCl_2(Ph_2PC\equiv CPh)_2\cdot 2MeCN$, monoclinic, space group $P2_1/c$, a = 11.604(2) Å, b = 18.416(5) Å, c = 19.344(3) Å, β = 98.63°, Z = 4, R = 0.031, R_w = 0.035; *cis*-$PtMe(Cl)(Ph_2PC\equiv CPh)_2\cdot 0.5CH_2Cl_2$, orthorhombic, space group *Pbca*, a = 16.910(2) Å, b = 17.207(1) Å, c = 25.300(2) Å, Z = 8, R = 0.039, R_w = 0.044; *cis*-$PtMe_2(Ph_2PC\equiv CPh)_2$, orthorhombic, space group *Pbca*, a = 11.934(2) Å, b = 16.885(3) Å, c = 34.098(8) Å, Z = 8, R = 0.037, R_w = 0.042. Factors affecting the occurrence of intramolecular coupling are assessed, together with a comparison of this reaction with related reactions of organic diacetylenes. The complex *cis*-$PtMe(Cl)(Ph_2PC\equiv CPh)_2$ reacts with diphenylphosphine to form a mixture of the two structural isomers of *cis*-$PtMe(Cl)\{Ph_2PCH{=}C(Ph)PPh_2\}$.

Introduction

Intra- and intermolecular cycloaddition and cycloisomerization reactions of alkynes, diynes, and enynes are among the most powerful strategies for the assembly of complex polycyclic ring systems.[1] Examples include the intramolecular Diels–Alder reaction[2] and transition metal mediated[3,4] or catalyzed[5] carbon–carbon bond forming processes. Intramolecular coupling of alkynes in the absence of metal atom interaction also occurs with aromatic diacetylenes where the two alkynyl groups are held rigidly adjacent to one another, as in the formation of the benzofluoranthene (**2**) from 1,8-bis(phenylethynyl)naphthalene (**1**),[6–8] or where the alkynyl groups are in close proximity to one another but have more conformational flexibility, as in the thermal or photochemical conversion of **3** to **4**.[9–12] Coupling of alkyne unitsexhibiting intramolecular interactions can also be effected chemically as illustrated by the conversion of *o*-bis(phenylethynyl)benzene to benzofulvenes via electrophilic, nucleophilic, or radical reagents.[13]



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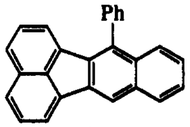

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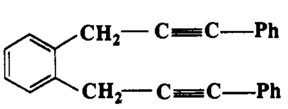

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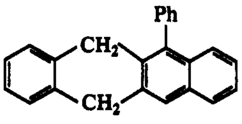

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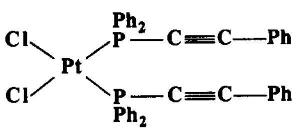

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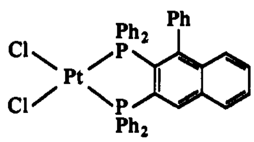

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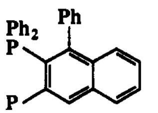

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[†] On sabbatical leave from the Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia.

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During our studies on the synthetic utility of coordinated heteroatom-functionalized acetylenes,[14] we discovered a novel method to achieve the proximity of uncoordinated alkyne triple bonds necessary to promote coupling. In this method, involving *cis* transition metal complexes of phosphorus-coordinated alkynylphosphines, e.g. *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$ (**5**), the sterically less demanding $-C{\equiv}CPh$ groups are forced into a configuration facilitating alkyne–alkyne interaction. Thermally induced coupling leads to the formation of complexes containing the new unsymmetrical diphosphine ligand 1-phenyl-2,3-bis(diphenylphosphino)naphthalene [o-$C_{16}H_{10}(PPh_2)_2$] (**6**).[15] The concept of promoting alkyne–alkyne interactions via heteroatom coordination to a metal has potential not only for the synthesis of unsymmetrical diphosphines with an aromatic backbone[16] and their complexes but also as a general strategy for acetylene elaboration. In this paper we report the synthesis of a range of platinum(II) diphenyl(phenylethynyl)phosphine complexes, together with studies of their tendency to undergo intramolecular coupling. Structural studies of the free ligand o-$C_{16}H_{10}(PPh_2)_2$ (**7**), generated from **5** via intramolecular coupling and decomplexation, and the complexes *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2{\cdot}2MeCN$, *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2{\cdot}0.5CH_2Cl_2$, and *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ have been carried out to gain insights into factors influencing the intramolecular cycloaddition reactions.

Experimental Section

Physical Measurements. IR spectra were recorded with Perkin-Elmer 180 and 983 spectrophotometers using Nujol mulls on CsI plates. Data are reported in cm^{-1}. ^1H and ^{31}P NMR spectra were obtained at 250.0 and 110.9 MHz, respectively, on a Bruker AM-250 spectrometer, or at 400.0 and 161.5 MHz, on a Bruker WH-400 spectrometer. ^1H chemical shifts for $CDCl_3$ solutions are in parts per million with respect to internal Me_4Si; ^{31}P chemical shifts are in parts per million relative to an external 85% H_3PO_4 standard, shifts to low field of this being shown as positive. ^{31}P NMR spectra were normally recorded under conditions of broad-band proton decoupling. Elemental analyses were performed by Canadian Analytical Services (Vancouver, BC), Guelph Chemical Laboratories (Guelph, Ontario), and the Department of Chemical Engineering (University of Waterloo).

Reagents. Diphenyl(phenylethynyl)phosphine and the 1,5-cyclooctadiene (COD) complexes $PtX_2(COD)$ (X = Cl, I, Me, CF_3) and PtMe(Cl)(COD) were prepared as described previously;[17,18] $Pt(C_6F_5)_2(COD)$ was prepared by a Grignard method, although an alternative organolithium method was reported recently.[19] All solvents were dried and deoxygenated, and reactions were carried out in a dry nitrogen atmosphere. Halide-free methyllithium (Aldrich, 1.2 M in diethyl ether) was used without standardization.

Bis(pentafluorophenyl)(1,5-cyclooctadiene)platinum(II) was prepared by addition of $PtI_2(COD)$ (2.0 g, 3.6 mmol) to a filtered solution of C_6F_5MgBr [from Mg turnings (3.0 g, 120 mmol) and C_6F_5Br (5.33 g, 20 mmol) under reflux for 2 h in diethyl ether (80 mL)] at ambient temperature. The mixture was stirred for 10 h and hydrolyzed at 0 °C with an ice-cold saturated aqueous solution of NH_4Cl. The ether layer was separated from the mixture and the aqueous layer extracted with diethyl ether (3 × 60 mL). The combined ether solution was dried over anhydrous $MgSO_4$ containing a small amount of activated charcoal, the solution filtered, and the solvent removed by rotary evaporation to give a white solid (1.26 g, 55%). Colorless crystals from benzene–heptane were obtained for microanalysis; mp 264 °C (lit.[19] 254–256 °C dec). Anal. Calcd for $C_{20}H_{12}F_{10}Pt$: C, 37.68; H, 1.90. Found: C, 37.36; H, 1.80.

Table I. $^{31}P\{^1H\}$ NMR Data for the Complexes[a]

complex	δ	$^1J_{P-Pt}$, Hz
cis-$PtCl_2(Ph_2PC{\equiv}CPh)_2$	-10.8	3765
cis-$PtMe_2(Ph_2PC{\equiv}CPh)_2$	3.9	1841
cis-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2$	-3.9^b	4516^c
	3.9^d	1734^c
cis-$PtI_2(Ph_2PC{\equiv}CPh)_2$	-13.5	3508
cis-$Pt(CF_3)_2(Ph_2PC{\equiv}CPh)_2$	-5.2	2052^e
cis-$Pt(C_6F_5)_2(Ph_2PC{\equiv}CPh)_2$	-6.8	2388^e
cis-$Pt(o\text{-}C_6H_4O_2)(Ph_2PC{\equiv}CPh)_2$	-15.2	3583
cis-$PtCl_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	35.8	3570^f
	44.2	3499^f
cis-$PtMe_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	47.1	1814
	56.2	1714
cis-$PtMe(Cl)\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$		
(**A** or **B**)	38.7^b	4209^g
	56.8^d	1653^g
(**B** or **A**)	46.2^d	1732^h
	42.7^b	4103^h
cis-$PtI_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	35.9	3308
	44.7	3260
cis-$Pt(CF_3)_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	38.0	1989
	45.8	1924
cis-$Pt(C_6F_5)_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	40.3	2302
	45.5	2276
cis-$Pt(o\text{-}C_6H_4O_2)_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$	26.0	3405^i
	35.8	3291^i
cis-$PtCl_2\{Ph_2PCH{=}C(Ph)PPh_2\}$	$30.5^{j,k}$	3552
	$53.1^{j,l}$	3640
cis-$PtMe_2\{Ph_2PCH{=}C(Ph)PPh_2\}$	42.0^k	1774
	66.4^l	1766
cis-$PtMe(Cl)\{Ph_2PCH{=}C(Ph)PPh_2\}$		
A′ [m]	$34.3^{b,k}$	4207
	$66.3^{d,l}$	1714
B′ [m]	$41.9^{d,k}$	1721
	$54.3^{b,l}$	4275

[a] In $CDCl_3$. [b] *Trans* to chloro group. [c] J_{P-P} = 13.2 Hz. [d] *Trans* to methyl group. [e] Unresolved multiplet due to coupling to ^{19}F. [f] J_{P-P} = 7.8 Hz. [g] J_{P-P} = 5.9 Hz. [h] J_{P-P} = 6.2 Hz. [i] J_{P-P} = 14.8 Hz. [j] From ref 20, with assignment of δ 30.5 as $Ph_2P{=}$ and δ 53.1 as $Ph_2C(Ph){=}$. [k] $Ph_2PCH{=}$. [l] $Ph_2PC(Ph){=}$. [m] Isomers **A′** and **B′** are in ~2:5 ratio from ^1H NMR integration, assuming that ^{31}P resonances from **A′** result from the most abundant isomer, as ^{31}P resonances of **A′** and **B′** occur in the ratio ~3:11.

Complexes of Diphenyl(phenylethynyl)phosphine. (a) *Cis*-$PtX_2(Ph_2PC{\equiv}CPh)_2$ (X=Cl, I, CF_3, C_6F_5, Me). The preparation of the dichloro complex has been reported,[20] but it may be more conveniently obtained as described here. The reagents $PtX_2(COD)$ (~1–3 mmol) and $Ph_2PC{\equiv}CPh$ in 1:2 mole ratio were stirred for ~12 h in benzene (30 mL). The resulting mixture was concentrated to ~5 mL, and a small amount of heptane was added to precipitate the desired product. In some cases the product precipitated after stirring at ambient temperature for 5–10 min, and for these reactions (after ~12 h) the product was removed by filtration, washed with a small amount of benzene, and dried under vacuum. The complexes prepared by this method were obtained in 90–98% yields and were used for subsequent reactions. Suitable recrystallization solvents, color, melting point data, microanalysis data (except for X = Cl[20]), and IR and ^1H NMR data are given for each complex; ^{31}P NMR data are given in Table I.

X = Cl: dichloromethane–diethyl ether, colorless, darkens above ~185°C. IR: ν(Ph—P) 1100 s. ^1H NMR: δ 8.0–6.9 m. Other characterization data are given elsewhere.[20]

X = I: dichloromethane–petroleum ether, pale yellow, 243–245 °C. Anal. Calcd for $C_{40}H_{30}I_2P_2Pt$: C, 47.03, H, 2.97. Found: C, 46.28; H, 3.42. IR: ν(C≡C) 2170 m, 2159 m; ν(Ph—P) 1098 s. ^1H NMR: δ 8.0–6.8 m.

X = CF_3: dichloromethane–petroleum ether, pale yellow, 218 °C. Anal. Calcd for $C_{42}H_{30}F_6P_2Pt$: C, 55.69, H, 3.34. Found: C, 55.77; H, 3.36.

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IR: ν(C≡C) 2185 s; ν(Ph—P) 1105 m; $\nu(\mathrm{C—F})_{\mathrm{sym}}$ 1127 s, 1080 s; $\nu(\mathrm{C—F})_{\mathrm{def}}$ 1038 m, 1020 m. ^{1}H NMR: 7.9–6.8 m.

X = C_6F_5: dichloromethane–petroleum ether, colorless, 263–265 °C. Anal. Calcd for $C_{52}H_{30}F_{10}P_2Pt$: C, 56.68, H, 2.75. Found: C, 56.61; H, 2.60. IR: ν(C≡C) 2174 s; ν(Ph—P) 1100 s; $\nu(C_6F_5)$ 1500 s, 1055 m, 957 s, 793 m, 783 m. ^{1}H NMR: 7.8–6.8 m.

X = Me: benzene–heptane, white, 177–178 °C. Anal. Calcd for $C_{42}H_{36}P_2Pt$: C, 63.22, H, 4.56. Found: C, 63.22; H, 4.86. IR: ν(C≡C) 2171 s; ν(Ph—P) 1097 s; δ (CH_3) 1212 w, 1190 w. ^{1}H NMR: 8.10–6.50 m (Ph); 0.54 m with complex ^{1}H–^{31}P coupling and $^2J_{\mathrm{H-Pt}}$ satellites, $^2J_{\mathrm{H-Pt}}$ = 70.5 Hz.

(b) *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$·0.5CH_2Cl_2. This complex was prepared in a similar manner, in darkness to avoid contamination of the product with the *trans* isomer. Addition of heptane was not required, and the pure complex formed as a white powder in 86% yield. The complex forms colorless crystals from dichloromethane–hexane; mp 145–150 °C. Anal. Calcd for $C_{41}H_{33}P_2ClPt{\cdot}0.5CH_2Cl_2$: C, 57.91; H, 3.98. Found: C, 58.12; H, 4.23. IR: ν(C≡C) 2175 s; ν(Ph—P) 1101 s; ν(Pt—P) 296 w. ^{1}H NMR: 7.90–6.80 m (Ph); 0.69 dd with $^2J_{\mathrm{H-Pt}}$ satellites, $^3J_{\mathrm{H-P}}$ = 7.67 and 5.50 Hz, $^2J_{\mathrm{H-Pt}}$ = 58.7 Hz.

(c) *cis*-Pt(*o*-$C_6H_4O_2$)($Ph_2PC{\equiv}CPh$)$_2$. A solution of *cis*-$PtCl_2$($Ph_2PC{\equiv}CPh$)$_2$ (1.13 g, 1.3 mmol) in chloroform (80 mL) was treated dropwise with a dark green solution of excess catechol (0.29 g, 2.6 mmol) and sodium hydroxide (1.32 g, 33 mmol) in methanol (40 mL) at ambient temperature. The solution became yellow-brown immediately and was refluxed for 1 h, with a brown-gray precipitate forming and the solution becoming brown. The precipitate was removed and the filtrate evaporated to give a green-brown oil. A chloroform solution of the oil was washed with water (3 × 100 mL) and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was eluted with diethyl ether from a Florisil column. On evaporation of the eluate, bright orange crystals were collected and washed with diethyl ether (0.77 g, 67%); mp 233–235 °C. The sample for microanalysis was obtained by recrystallization from petroleum ether–chloroform. Anal. Calcd for $C_{46}H_{34}O_2P_2Pt$: C, 63.08; H, 3.92. Found: C, 63.11; H, 3.97. IR: ν(C≡C) 2178 m; ν(CO) 1258 m, 1248 m; ν(Ph—P) 1095 m. ^{1}H NMR: 8.2–6.3 m.

Complexes of 1-Phenyl-2,3-bis(diphenylphosphino)naphthalene. (a) *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$}. A solution of *cis*-$PtCl_2$($Ph_2PC{\equiv}CPh$)$_2$ (0.41 g) in dry toluene (60 mL) was refluxed under nitrogen for 1 day. On cooling, a white powder (0.3 g, 73%) was collected; darkens above ~185 °C. Anal. Calcd for $C_{40}H_{30}Cl_2P_2Pt$: C, 57.29; H, 3.61. Found: C, 57.37; H, 3.62. IR: ν(Pt—Cl) 317 m, 274 m. ^{1}H NMR: 8.3–6.3 m.

(b) *cis*-PtI_2{*o*-$C_{16}H_{10}(PPh_2)_2$}. A similar procedure gave a yellow solid, which formed yellow crystals (71%) from benzene–dichloromethane; mp > 270 °C. Anal. Calcd for $C_{40}H_{30}I_2P_2Pt$: C, 47.03; H, 2.97. Found: C, 47.79; H, 3.22. ^{1}H NMR: 8.3–6.3 m.

(c) *cis*-Pt(CF_3)$_2${*o*-$C_{16}H_{10}(PPh_2)_2$}. A sealed tube containing *cis*-Pt(CF_3)$_2$($Ph_2PC{\equiv}CPh$)$_2$ (0.5 g) in benzene (5 mL) was heated at 100 °C for 12 h. The resulting orange-yellow solution was eluted with dichloromethane on a Florisil column, to give a yellow oil (on removal of solvent) which crystallized from dichloromethane–petroleum ether as a white solid (18%); mp > 270 °C. Anal. Calcd for $C_{42}H_{30}F_6P_2Pt$: C, 55.69; H, 3.34. Found: C, 55.17; H, 3.65. IR: ν(CF_3) 1128 s (br), 1080 s, 990 s (br), 979 s (br). ^{1}H NMR: 8.2–6.2 m.

(d) *cis*-Pt(C_6F_5)$_2${*o*-$C_{16}H_{10}(PPh_2)_2$}. A sealed tube containing *cis*-Pt(C_6F_5)$_2$($Ph_2PC{\equiv}CPh$)$_2$ (0.4 g) in decalin (3 mL) was heated at 210 °C for 2.5 h. A dark-brown solid in a brown-yellow solution was obtained, solvent removed at 100 °C under vacuum, and the residue dissolved in a small amount of benzene and eluted from a Florisil column with a mixture of benzene and acetone. On concentration of the eluate to ~10 mL, addition of heptane gave a yellow solid (34%); mp > 270 °C. Anal. Calcd for $C_{52}H_{30}F_{10}P_2Pt$: C, 56.68; H, 2.75. Found: C, 56.57; H, 2.91. IR: ν(C_6F_5) 1500 s, 1060 m, 961 s, 796 sh, 787 s. ^{1}H NMR: 8.5–6.3 m.

(e) *cis*-Pt(*o*-$C_6H_4O_2$){*o*-$C_{16}H_{10}(PPh_2)_2$}. A similar procedure, with *cis*-Pt(*o*-$C_6H_4O_2$)($Ph_2PC{\equiv}CPh$)$_2$ (0.4 g) in a mixture of xylene (1.5 mL) and decalin (1.5 mL) at 150 °C for 2 days, gave an orange precipitate (38%), which was collected, washed with acetone, and recrystallized from dichloromethane–petroleum ether; mp > 270 °C. Anal. Calcd for $C_{46}H_{34}O_2P_2Pt$: C, 63.08; H, 3.92. Found: C, 62.89; H, 4.06. IR: ν(CO) 1254 s. ^{1}H NMR: 8.2–6.3 m.

(f) *cis*-$PtMe_2${*o*-$C_{16}H_{10}(PPh_2)_2$}. A solution of halide-free methyllithium (1.5 mL, 1.2 M, 1.8 mmol) in diethyl ether (10 mL) was added over 10 min to a stirred solution of *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$} (0.519 g, 0.6 mmol) in benzene (15 mL) at ambient temperature under nitrogen. After being stirred for a further 30 min, the solution was hydrolyzed with an ice-cold saturated aqueous solution of NH_4Cl, and hexane (10 mL) added. The organic layer was separated from the mixture, and the aqueous layer was washed with diethyl ether (3 × 20 mL). The extracts were dried over anhydrous $MgSO_4$ and charcoal and filtered, and the combined extract was evaporated to ~5 mL. On addition of hexane (~20 mL), a buff precipitate formed, which was collected and washed with hexane (0.287 g, 58%); mp > 270 °C. Anal. Calcd for $C_{42}H_{36}P_2Pt$: C, 63.29; H, 4.55. Found: C, 63.01; H, 4.83. IR: δ(CH_3) 1180 w, 1158 w; ν(Ph—P) 1098 m. ^{1}H NMR: 8.30–6.40 m; 0.66 "t" with $^2J_{\mathrm{H-Pt}}$ satellites, $^3J_{\mathrm{H-P}}$ ~ 7.36 Hz, $^2J_{\mathrm{H-Pt}}$ = 53.9 Hz; 0.45 "t" with $^3J_{\mathrm{H-P}}$ ~ 7.35 Hz, $^2J_{\mathrm{H-Pt}}$ = 53.7Hz.

Thermolysis Reactions of *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$. (a) Solid *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$ (0.33 g) was heated in a sealed tube at 150–155 °C for 1 day and the brown-black solid dissolved in dichloromethane to give a deep red solution. On evaporation to dryness, an oily solid was obtained. On dissolution in benzene (2 mL) and addition of heptane (10 mL), a buff powder was formed and collected (0.29 g, ~87%). IR: ν(Pt—Cl) 296 m. ^{1}H NMR: 8.3–6.3 m; 0.63 dd with $^2J_{\mathrm{H-Pt}}$ satellites, $^3J_{\mathrm{H-P}}$ = 7.5 and 3.3 Hz, $^2J_{\mathrm{H-Pt}}$ = 55.9 Hz; 0.44 dd with $^3J_{\mathrm{H-P}}$ = 7.7 and 3.3 Hz, $^2J_{\mathrm{H-Pt}}$ = 57.0 Hz, with resonances at 0.63 and 0.44 ppm in ~3:1 ratio. ^{31}P NMR spectra showed the presence of two isomers of *cis*-PtMe(Cl){*o*-$C_{16}H_{10}(PPh_2)_2$} and of *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$} in ~3:1:1 ratio.

(b) A similar experiment, with the complex dissolved in toluene at 150–155 °C for 2 days, gave an orange-brown powder (59%) exhibiting only broad ^{1}H NMR resonances at δ 8.3–6.2. Washing with cold benzene gave a small quantity of *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$} (~2%, NMR identification); reduction of filtrate volume to ~2 mL and addition of heptane gave a pale brown powder with only broad resonances at δ 8.3–6.2.

(c) A similar experiment, with the complex dissolved in toluene at 120–125 °C for 11 days, gave crystals of *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$ (26%, NMR identification) on reduction of the volume to ~1 mL. The filtrate was treated as in procedure a to give a brown powder (~40%), identified as a mixture of *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$} and isomers of *cis*-PtMe(Cl){*o*-$C_{16}H_{10}(PPh_2)_2$} with the latter in ~5:1 ratio (from $MePt^{II}$ multiplets at 0.63 and 0.44 ppm).

Thermolysis Reactions of *cis*-$PtMe_2$($Ph_2PC{\equiv}CPh$)$_2$. (a) *cis*-$PtMe_2$($Ph_2PC{\equiv}CPh$)$_2$ was unchanged when heated at its melting point (180 °C) for 5 min (NMR identification), but upon 2 h of heating, the brown solid obtained exhibited only broad resonances at δ 9–6.

(b) Similarly, the complex was unchanged on refluxing in toluene for 2 days; but in decalin in a sealed tube at 160 °C, a reddish-brown liquid was obtained after 1 h. Attempts to purify the liquid were unsuccessful.

Isolation of 1-Phenyl-2,3-bis(diphenylphosphino)naphthalene. *cis*-$PtCl_2${*o*-$C_{16}H_{10}(PPh_2)_2$} (0.5 g) and KCN (5 g) were refluxed for ~12 h in benzonitrile (70 mL) under nitrogen. Following evaporation of solvent, extraction with diethyl ether, dry chromatography on Florisil, and recrystallization from dichloromethane–ethanol, a mixture of needles (2,4,6-triphenyl-*s*-triazine from trimerization of PhCN, identified by mass spectrometry, microanalysis, and comparison with an identical sample) and prisms of *o*-$C_{16}H_{10}(PPh_2)_2$ (~30% yield) was obtained.

***cis*-$PtMe_2${$Ph_2PCH{=}C(Ph)PPh_2$}.** According to a procedure identical to that for the synthesis of *cis*-$PtMe_2${*o*-$C_{16}H_{10}(PPh_2)_2$}, $PtCl_2${$Ph_2PCH{=}C(Ph)PPh_2$} (prepared as reported[21]) was reacted with excess MeLi to give pale brown crystals of the product (23%); mp > 270 °C. Anal. Calcd for $C_{34}H_{32}P_2Pt$: C, 58.53; H, 4.62. Found: C, 58.69; H, 4.74. IR: ν(C=C) 1601 vw, 1591 vw, 1572 vw; δ(CH_3) 1179 m, 1159 w; ν(Ph—P) 1102 s. ^{1}H NMR: 7.7–6.7 m; 0.73 "t" with $^2J_{\mathrm{H-Pt}}$ satellites, $^3J_{\mathrm{H-P}}$ = 7.4 Hz, $^2J_{\mathrm{H-Pt}}$ = 71.1 Hz; 0.47 "t" with satellites, $^3J_{\mathrm{H-P}}$ = 7.6 Hz, $^2J_{\mathrm{H-Pt}}$ = 70.8 Hz.

Reactions Involving Diphenylphosphine. (a) *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$. According to the procedure described earlier,[20] *cis*-PtMe(Cl)($Ph_2PC{\equiv}CPh$)$_2$ (1.00 g) gave a white powder (0.547 g, 65%), identified by ^{1}H and ^{31}P NMR spectroscopy as a mixture of isomers of *cis*-PtMe(Cl){$Ph_2PCH{=}C(Ph)PPh_2$}. IR: ν(C=C) 1599 vw, 1589 vw, 1571 vw; δ(CH_3) 1183 m, 1159 w; ν(Ph—P) 1100 s; ν(Pt—Cl) 297 m. ^{1}H NMR: 8.0–6.7 m; 0.75 dd with $^2J_{\mathrm{H-Pt}}$ satellites, $^3J_{\mathrm{H-P}}$ = 7.7, 3.3 Hz, $^2J_{\mathrm{H-Pt}}$ = 55 Hz; 0.55 dd with satellites, $^3J_{\mathrm{H-P}}$ = 7.7, 3.3 Hz, $^2J_{\mathrm{H-Pt}}$ = 56 Hz; with resonances at 0.75 and 0.55 ppm in ~2:5 ratio.

(b) *cis*-$PtMe_2$($Ph_2PC{\equiv}CPh$)$_2$. According to the procedure described earlier,[20] *cis*-$PtMe_2$($Ph_2PC{\equiv}CPh$)$_2$ gave a cream-yellow powder (~2%) that did not exhibit $MePt^{II}$ resonances and which had a broad resonance

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[21] Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

Table II. Crystallographic Data for *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2{\cdot}2MeCN$, *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2{\cdot}0.5CH_2Cl_2$, *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$, and *o*-$C_{16}H_{10}(PPh_2)_2$

chem formula	$C_{40}H_{30}P_2Cl_2Pt{\cdot}2MeCN$	$C_{41}H_{33}P_2ClPt{\cdot}0.5CH_2Cl_2$	$C_{42}H_{36}P_2Pt$	$C_{40}H_{30}P_2$
crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/c$	*Pbca*	*Pbca*	$P\bar{1}$
a, Å	11.604(2)	16.910(2)	11.934(2)	11.437(13)
b, Å	18.416(5)	17.207(1)	16.885(3)	9.628(12)
c, Å	19.344(3)	25.300(2)	34.098(8)	16.712(21)
α, deg				82.31(9)
β, deg	98.63(1)			119.08(9)
γ, deg				110.03(5)
V, Å^3	4087.0(5)	7362(1)	6871(2)	1510.3(5)
Z	4	8	8	2
fw	920.73	862.18	797.79	572.63
T, K	295	295	295	295
λ, Å	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)	1.5418 (Cu Kα)
ρ_{calcd}, g·cm^{-3}	1.496	1.556	1.542	1.259
μ, cm^{-1}	38.53	42.70	44.20	14.98
R^a	0.031	0.039	0.037	0.058
$R_w{}^b$	0.035	0.044	0.042	0.070

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

at 8.5–6.0 ppm. Attempted isolation of products under conditions known to precipitate *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ and *cis*-$PtMe_2\{Ph_2PCH{=}C(Ph)PPh_2\}$ (benzene–hexane) gave a dark red oil.

X-ray Crystal Structure Analyses. Collection, Reduction, and Refinement of X-ray Data. (a) *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$. Crystals of *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2{\cdot}2MeCN$ from acetonitrile are colorless, monoclinic prisms. Preliminary photography established the cell constants which were refined by least-squares methods from the 2θ values of 15 reflections well dispersed in reciprocal space. Crystal data are listed in Table II. Intensity data were measured at 295 K on a crystal of dimensions 0.25 mm^3 sealed in a glass capillary using Mo Kα (λ = 0.710 69 Å) radiation on a Syntex P2$_1$ diffractometer operating in a θ–2θ scan mode. The structure analysis and refinement were based on 3716 observed ($I > 3\sigma(I)$) reflections from 5382 independent measurements. No significant variations in the intensities of 3 standard reflections monitored every 100 reflections occurred over the course of the collection. Lorentz and polarization corrections were applied to the derivation of structure amplitudes, and no absorption correction was applied. The structure was solved by Patterson and Fourier techniques and refined by least-squares methods using the full matrix. All non-hydrogen atoms were refined anisotropically. Scattering factors used were taken from ref 22. All calculations were performed on an IBM 4341 or 370 system in the University of Waterloo computing Centre using computer programs described elsewhere.[23] Atomic coordinates are listed in Table III, with a comparison of bond lengths and angles for all three structures *cis*-$PtX(Y)(Ph_2PC{\equiv}CPh)_2$ (X = Y = Cl; X = Cl, Y = Me; X = Y = Me) given in Table IV. Anisotropic thermal parameters (Table S1) and remaining bond lengths (Table S2) are available as supplementary data material.

(b) *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2{\cdot}0.5CH_2Cl_2$ and *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$. Both of these molecules crystallize in the orthorhombic space group *Pbca*, the former as a hemisolvate. Refined unit cell parameters and information on intensity data collection are given in Table II. Both structures were solved via the heavy-atom method and subsequent Fourier syntheses. With anisotropic thermal parameters for all non-hydrogen atoms, full-matrix least-squares refinement led to final *R* values of 0.039 and 0.037 for the chloro methyl and dimethyl complexes, respectively. Scattering factors and computer programs used were the same as those described for the dichloro complex. Table IV includes a comparison of relevant bond lengths and angles. Atomic coordinates are listed in Table V for *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2$ and in Table VI for *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$. Anisotropic thermal parameters for these two compounds are contained in Tables S3 and S4 with additional bond lengths and angles in Tables S5 and S6 (supplementary material).

(c) 1-Phenyl-2,3-bis(diphenylphosphino)naphthalene. Colorless prisms of $[o\text{-}C_{16}H_{10}(PPh_2)_2]$ from CH_2Cl_2–C_2H_5OH were found to be triclinic by preliminary Weissenberg and precession photography. The cell was refined using 2θ values for 15 strong reflections well dispersed in reciprocal space. Confirmation of the space group followed the successful refinement of the structure to convergence. Crystal data and parameters used in data collection, reduction, and refinement are given in Table II. Intensities were collected on a GE-XRD-6 diffractometer operating in a 2θ–θ scan mode with Cu Kα radiation (λ = 1.5418 Å) out to 2θ = 90°. Background measurements were made at the beginning and end of each scan with a 10-s stationary count. No significant change in the intensities of two standard reflections was observed. No absorption corrections were deemed necessary. All carbon atoms were refined with anisotropic thermal parameters, and the refinement converged at *R* = 0.058. Atomic positional parameters are listed in Table VII, and pertinent bond lengths and angles are given in Table VIII. Anisotropic thermal parameters are included in Table S7 (supplementary material).

Results and Discussion

A series of complexes *cis*-$PtX_2(Ph_2PC{\equiv}CPh)_2$ (X = Cl, I, CF_3, C_6F_5, Me), *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2$, and the *o*-catecholato complex *cis*-$Pt(o\text{-}C_6H_4O_2)(Ph_2PC{\equiv}CPh)_2$ were synthesized in order to study the steric and electronic effects on the scope of the phosphinoacetylene coupling reaction noted initially[15] for *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$. The complexes were obtained either directly from the cyclooctadiene reagents $PtX_2(COD)$ (X = Cl, I, CF_3, C_6F_5, Me) and PtMe(Cl)(COD) or on reaction of *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$ with deprotonated *o*-catechol. ^1H NMR spectra of the complexes appear as complex multiplets, with similar resonances for the $Ph_2PC{\equiv}CPh$ groups in all of the complexes, and the $MePt^{II}$ and Me_2Pt^{II} complexes exhibit characteristic multiplets that may be readily assigned. The chloro complexes have ν(Pt—Cl) bands characteristic of Cl ligands *trans* to phosphines, and $^{31}P\{^1H\}$ NMR spectra clearly allow structural assignment as *cis* Pt^{II} complexes. Spectroscopic data are given in the Experimental Section, with the exception of the ^{31}P data, which are collected in Table I. The availability of two series of *cis* complexes with a variety of halo, oxygen, and carbon anionic ligands, one series with two monodentate alkynylphosphines and the other with a chelating *o*-phenylenediphosphine, allows some interesting comparisons of $^1J_{Pt-P}$ coupling constants and *trans* influences. The one-bond ^{195}Pt–^{31}P coupling constants in the series of *cis*-$PtX_2(Ph_2PC{\equiv}CPh)_2$ complexes changes dramatically from a high of 3765 Hz for X = Cl to 1841 Hz for X = Me. The ordering of the anionic ligands, which presumably reflects their relative *trans* bond weakening influence is Me > CF_3 > C_6F_5 > I > *o*-$C_6H_4O_2$ > Cl. Complexes of the chelating diphosphine $[o\text{-}C_{16}H_{10}(PPh_2)_2]$ exhibit two separate $^{31}P\{^1H\}$ NMR resonances with ^1J (^{195}Pt–^{31}P) values for the two nonequivalent ^{31}P sites differing by up to 100 Hz. Values of ^1J (^{195}Pt–^{31}P) are systematically smaller for complexes of *o*-$C_{16}H_{10}(PPh_2)_2$ than for the phosphinoalkyne $Ph_2PC{\equiv}CPh$, with differences varying from 77 Hz for X = Me up to 235 Hz for X = *o*-$C_6H_4O_2$. If the usual correlation between Pt–P bond strength and ^1J (^{195}Pt–^{31}P) holds, these results imply somewhat weaker Pt–P interactions in

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[22] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

[23] Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

Table III. Atomic Coordinates (Fractional × 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2 \cdot 2MeCN$

	x	y	z	U_{eq}[a]
Pt(1)	465.6(3)	2378.3(1)	1827.2(1)	41.2
Cl(1)	639(2)	1902(1)	2958(1)	57
Cl(2)	−1299(2)	2904(1)	2029(1)	61
P(1)	203(2)	2932(1)	787(1)	43
P(2)	2064(2)	1784(1)	1627(1)	45
C(1)	1483(7)	3057(4)	420(4)	51
C(2)	2390(6)	3194(4)	229(4)	53
C(3)	3498(6)	3331(4)	19(4)	54
C(4)	4201(8)	3883(5)	340(5)	77
C(5)	5304(9)	4003(6)	143(6)	95
C(6)	5666(9)	3580(7)	−368(6)	101
C(7)	4949(10)	3016(7)	−689(6)	102
C(8)	3847(9)	2897(6)	−509(5)	91
C(9)	1921(7)	1425(4)	779(4)	57
C(10)	1767(8)	1132(4)	223(4)	63
C(11)	1574(8)	759(5)	−434(4)	64
C(12)	1426(10)	17(5)	−465(5)	88
C(13)	1243(13)	−335(6)	−1114(6)	111
C(14)	1199(12)	89(8)	−1730(6)	115
C(15)	1334(12)	830(7)	−1706(6)	107
C(16)	1495(10)	1182(6)	−1052(5)	84
C(17)	−775(6)	2453(4)	121(3)	45
C(18)	−563(8)	2406(5)	−562(4)	71
C(19)	−1336(9)	2031(6)	−1063(5)	83
C(20)	−2339(9)	1718(5)	−873(5)	81
C(21)	−2572(9)	1782(5)	−185(5)	82
C(22)	−1771(7)	2139(5)	316(5)	67
C(23)	−320(6)	3861(4)	793(3)	47
C(24)	−1180(7)	4117(4)	274(5)	63
C(25)	−1521(8)	4848(5)	285(5)	77
C(26)	−1005(9)	5314(5)	801(5)	70
C(27)	−134(10)	5061(5)	1297(5)	78
C(28)	224(9)	4334(5)	1302(5)	74
C(29)	2434(7)	974(4)	2159(4)	52
C(30)	3262(8)	1011(5)	2754(5)	71
C(31)	3500(9)	386(6)	3179(6)	92
C(32)	2897(10)	−253(5)	2985(6)	85
C(33)	2057(10)	−284(5)	2397(5)	86
C(34)	1820(9)	335(4)	1966(5)	72
C(35)	3392(6)	2310(4)	1755(4)	58
C(36)	4292(7)	2114(6)	1375(6)	87
C(37)	5382(9)	2486(7)	1563(7)	110
C(38)	5527(13)	3005(7)	2040(9)	131
C(39)	4622(12)	3210(6)	2407(8)	125
C(40)	3499(9)	2844(5)	2258(6)	90
N(1S)	6789(12)	130(8)	3247(8)	176
C(1S)	7041(12)	711(9)	3080(7)	126
C(2S)	7429(16)	1416(8)	2922(9)	161
N(2S)	5271(15)	−903(9)	448(11)	248
C(3S)	5174(13)	−427(12)	948(13)	217
C(4S)	5161(22)	161(11)	1277(13)	286

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

the complexes of the asymmetric chelating diphosphine, perhaps due to strain in forming a five-membered PtP_2C_2 ring and the steric effect of the 1-phenyl substituent.

Studies of Intramolecular Alkyne Coupling in the Complexes *cis*-$PtX(Y)(Ph_2PC{\equiv}CPh)_2$. The dichloro and diiodo complexes are converted cleanly in ~72% yield to *cis*-$PtX_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ (X = Cl, I) on refluxing for 24 h in toluene (eq 1).

$$cis\text{-}PtX(Y)(Ph_2PC{\equiv}CPh)_2 \xrightarrow{\Delta} cis\text{-}PtX(Y)\{o\text{-}C_{16}H_{10}(PPh_2)_2\} \quad (1)$$

$$X = Y = Cl, I, CF_3, C_6F_5$$

$$X\ (Y) = o\text{-}C_6H_4O_2,\ Me\ (Cl)$$

Table IV. Comparison of Selected Bond Lengths (Å) and Angles (deg) for *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2 \cdot 2MeCN$, *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2 \cdot 0.5CH_2Cl_2$, and *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$

	X(1) = X(2) = Cl	X(1) = Cl, X(2) = Me	X(1) = X(2) = Me
Pt–X(1)	2.335(2)	2.349(3)	2.124(11)
Pt–X(2)	2.350(2)	2.150(8)	2.102(11)
Pt–P(1)	2.235(2)	2.208(2)	2.275(3)
Pt–P(2)	2.237(2)	2.309(2)	2.276(3)
P(1)–C(1)	1.756(8)	1.764(9)	1.783(11)
P(1)–C(17)	1.814(7)	1.815(9)	1.839(10)
P(1)–C(23)	1.816(7)	1.831(10)	1.842(9)
P(2)–C(9)	1.753(8)	1.762(10)	1.769(11)
P(2)–C(29)	1.826(7)	1.804(10)	1.818(10)
P(2)–C(35)	1.806(8)	1.818(9)	1.829(10)
C(1)–C(2)	1.193(11)	1.168(13)	1.185(15)
C(2)–C(3)	1.427(11)	1.464(13)	1.422(15)
C(9)–C(10)	1.193(11)	1.199(13)	1.188(14)
C(10)–C(11)	1.432(12)	1.431(14)	1.442(14)
C(1)···C(9)	3.110(10)	3.213(14)	5.599(14)
X(1)–Pt–X(2)	88.64(7)	86.72(2)	88.5(4)
X(1)–Pt–P(1)	174.63(7)	175.52(9)	168.7(8)
X(1)–Pt–P(2)	89.98(7)	88.23(8)	89.0(3)
X(2)–Pt–P(1)	87.52(7)	89.6(2)	89.0(3)
X(2)–Pt–P(2)	174.95(7)	174.4(2)	170.9(3)
P(1)–Pt–P(2)	94.16(6)	95.63(8)	99.76(9)
Pt–P(1)–C(1)	114.5(2)	115.5(3)	110.7(3)
Pt–P(1)–C(17)	113.8(2)	117.5(3)	118.3(3)
Pt–P(1)–C(23)	115.2(2)	114.3(3)	117.7(2)
C(1)–P(1)–C(17)	104.6(3)	98.7(4)	102.0(4)
C(1)–P(1)–C(23)	100.5(3)	103.7(4)	99.4(4)
C(17)–P(1)–C(23)	106.8(3)	105.0(4)	106.1(4)
Pt–P(2)–C(9)	112.4(2)	116.9(3)	111.5(3)
Pt–P(2)–C(29)	115.7(2)	115.3(3)	116.1(3)
Pt–P(2)–C(35)	115.2(2)	113.7(3)	122.5(2)
C(9)–P(2)–C(29)	101.6(3)	98.6(4)	102.1(4)
C(9)–P(2)–C(35)	106.8(3)	104.6(4)	102.6(4)
C(29)–P(2)–C(35)	103.8(3)	106.3(4)	99.3(4)
P(1)–C(1)–C(2)	172.7(3)	178.8(5)	172.4(5)
C(1)–C(2)–C(3)	177.4(4)	179.4(6)	174.9(6)
P(2)–C(9)–C(10)	174.1(4)	169.3(5)	170.5(4)
C(9)–C(10)–C(11)	178.2(5)	178.2(6)	177.4(6)

The remaining complexes give lower yields of the product complexes *cis*-$PtX(Y)\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ (~18% for X = Y = CF_3, in benzene at 100 °C in a sealed tube), require higher temperatures [150 °C for ~38% yield when X (Y) = $o\text{-}C_6H_4O_2$; 210 °C for ~34% yield when X = Y = C_6F_5], or require melting of the solid sample for isolation of the product in moderate yield [~87%, 150–155 °C, is optimal for X (Y) = Me(Cl) (see below)]. In sharp contrast however, coupling could not be achieved for *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ at temperatures up to its decomposition point. Although *cis*-$PtMe_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ could not be obtained by cyclization, it was readily synthesized from the dichloro complex on reaction with methyllithium (eq 2).

$$cis\text{-}PtCl_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\} + 2MeLi \rightarrow cis\text{-}PtMe_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\} + 2LiCl \quad (2)$$

The complex *cis*-$PtMe_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ is stable up to >270 °C, and thus the observed decomposition of samples of *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ on heating (reflux in toluene or decalin or melting at 180 °C) does not result from coupling followed by decomposition.

Complexes of the unsymmetrical diphosphine ligand exhibit complex and characteristic ^1H NMR resonances for the ligand protons, and Me_2Pt^{II} and $MePt^{II}$ resonances are consistent with *cis* stereochemistry; ^{31}P NMR spectra exhibit two resonances separated by 3–10 ppm (Table I), with $^1J_{P-Pt}$ as expected for the group (X, Y) *trans* to P, e.g. on comparison with the related complexes *cis*-$PtX(Y)(Ph_2PC{\equiv}CPh)_2$ (Table I). The ^{31}P resonances occur in the range 26.0–56.2 ppm, similar to that for complexes of related unsymmetrical diphosphines *cis*-$PtX_2\{Ph_2PCH{=}C(Ph)PPh_2\}$.

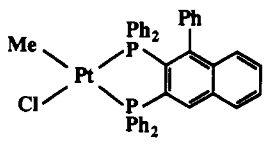
The complex *cis*-$PtMe(Cl)\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$ was obtained as a mixture of isomers together with *cis*-$PtCl_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}$,

Table V. Atomic Coordinates (Fractional × 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for *cis*-$\mathrm{PtMe(Cl)(Ph_2PC{\equiv}CPh)_2 \cdot 0.5CH_2Cl_2}$

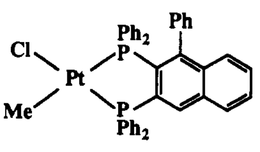
	x	y	z	$U_{eq}{}^a$
Pt(1)	1610.4(2)	2402.5(2)	1459.3(1)	36.5
Cl(1)	2649(2)	1749(1)	1887(1)	56
C(42)	1096(5)	1276(4)	1328(3)	40
P(1)	572(1)	2945(1)	1081(1)	39
P(2)	2281(1)	3552(1)	1605(1)	39
C(1)	280(6)	3848(5)	1345(4)	45
C(2)	92(6)	4443(5)	1529(4)	50
C(3)	−144(6)	5185(5)	1764(3)	42
C(4)	395(7)	5801(6)	1767(4)	57
C(5)	167(8)	6503(6)	2012(4)	65
C(6)	−594(7)	6575(7)	2230(4)	66
C(7)	−1133(8)	5957(7)	2216(5)	72
C(8)	−910(7)	5264(6)	1974(4)	59
C(9)	2097(6)	4317(5)	1160(4)	49
C(10)	2053(6)	4773(6)	802(4)	50
C(11)	1992(6)	5298(6)	365(4)	47
C(12)	1978(7)	6098(5)	445(4)	55
C(13)	1916(8)	6572(7)	2(5)	75
C(14)	1863(6)	6266(7)	−512(4)	66
C(15)	1875(6)	5467(7)	−581(4)	64
C(16)	1940(7)	4964(7)	−140(4)	63
C(17)	−367(5)	2438(6)	1131(3)	50
C(18)	−650(7)	1988(6)	698(5)	66
C(19)	−1383(7)	1591(7)	753(6)	79
C(20)	−1790(7)	1622(7)	1218(6)	72
C(21)	−1498(8)	2041(7)	1644(5)	80
C(22)	−782(6)	2450(6)	1600(4)	66
C(23)	696(6)	3144(5)	375(4)	47
C(24)	1238(6)	2701(6)	98(4)	52
C(25)	1322(7)	2826(6)	−447(4)	57
C(26)	864(7)	3383(7)	−708(4)	66
C(27)	330(7)	3821(7)	−415(4)	64
C(28)	218(6)	3702(6)	126(4)	57
C(29)	3340(6)	3497(5)	1533(4)	48
C(30)	3864(7)	3823(8)	1899(6)	79
C(31)	4686(8)	3794(10)	1785(7)	97
C(32)	4970(8)	3411(8)	1337(6)	91
C(33)	4449(8)	3085(8)	998(5)	79
C(34)	3633(7)	3113(7)	1088(5)	69
C(35)	2099(5)	3971(5)	2254(4)	44
C(36)	1973(7)	4760(6)	2326(4)	58
C(37)	1813(8)	5038(7)	2839(5)	75
C(38)	1799(7)	4546(7)	3262(5)	67
C(39)	1958(8)	3772(8)	3198(4)	69
C(40)	2097(7)	3474(6)	2699(4)	61
Cl(1S)	−723(5)	5411(5)	5142(3)	219
C(1S)	−193(31)	4901(19)	4616(15)	140

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

in a 3:1 ratio on melting *cis*-$\mathrm{PtMe(Cl)(Ph_2PC{\equiv}CPh)_2}$ in a sealed tube at 150–155 °C for 24 h. A solution in toluene at this temperature led to decomposition, and reaction in toluene at 120–125 °C for 11 days gave a lower yield of the isomers and *cis*-$\mathrm{PtCl_2\{}$*o*-$\mathrm{C_{16}H_{10}(PPh_2)_2\}}$. Although the ^{1}H and ^{31}P NMR spectra (Figure 1) are consistent with the presence of the isomers **A** and **B** shown here, comparison of spectra with those of *cis*-$\mathrm{PtX_2\{}$*o*-$\mathrm{C_{16}H_{10}(PPh_2)_2\}}$ (X = Cl, Me) does not allow an unequivocal assignment of resonances to the individual isomers.



(A)



(B)

X-ray Structural Studies. Single crystal X-ray analyses were undertaken to establish the identity of the decomplexed diphosphine ligand and to attempt to gain insights into solid-state interactions which might be responsible for the observed alkyne coupling. In particular, the relative orientation of the two $\mathrm{Ph_2PC{\equiv}CPh}$ ligands in three closely related structures that show a range of reactivity toward coupling, namely *cis*-$\mathrm{PtX(Y)(Ph_2PC{\equiv}CPh)_2}$ (X = Y = Cl or Me; X (Y) = Me (Cl)] was of interest. The dichloro complex undergoes alkyne coupling under relatively mild conditions (reflux in benzene), the methyl chloro species requires a higher temperature (150-155 °C) or more ideally melting, and the dimethyl complex shows no evidence of coupling below its decomposition temperature.

Table VI. Atomic Coordinates (Fractional × 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for *cis*-$\mathrm{PtMe_2(Ph_2PC{\equiv}CPh)_2}$

	x	y	z	$U_{eq}{}^a$
Pt(1)	1660.0(3)	1206.8(2)	1001.7(1)	34.6
C(41)	329(10)	380(6)	1060(3)	57
C(42)	2118(10)	486(7)	525(3)	55
P(1)	3303(2)	1876(1)	932.8(7)	37
P(2)	886(2)	1907(1)	1503.3(8)	35
C(1)	4410(9)	1210(7)	823(3)	46
C(2)	5075(9)	700(6)	758(3)	47
C(3)	5781(10)	47(6)	666(3)	51
C(4)	6911(11)	26(7)	800(4)	63
C(5)	7577(12)	−614(9)	690(4)	77
C(6)	7123(12)	−1221(9)	474(4)	82
C(7)	6085(14)	−1224(9)	347(4)	80
C(8)	5348(12)	−579(8)	442(4)	69
C(9)	1036(8)	1408(5)	1956(3)	41
C(10)	1246(9)	1005(6)	2233(3)	40
C(11)	1553(10)	528(6)	2567(3)	44
C(12)	773(12)	−27(7)	2717(4)	69
C(13)	1112(15)	−500(9)	3028(4)	83
C(14)	2186(15)	−428(9)	3193(4)	83
C(15)	2930(14)	117(8)	3041(4)	79
C(16)	2621(11)	599(7)	2725(4)	61
C(17)	3421(10)	2600(5)	536(3)	42
C(18)	2451(11)	2841(7)	361(3)	44
C(19)	2511(12)	3402(8)	50(3)	64
C(20)	3554(14)	3703(7)	−65(3)	67
C(21)	4533(13)	3439(9)	114(4)	83
C(22)	4488(12)	2888(8)	427(4)	67
C(23)	3892(8)	2357(6)	1372(2)	37
C(24)	4102(9)	3160(6)	1390(3)	44
C(25)	4559(9)	3498(7)	1736(4)	54
C(26)	4780(10)	3009(8)	2059(3)	59
C(27)	4559(10)	2203(8)	2033(4)	59
C(28)	4129(10)	1859(7)	1690(3)	49
C(29)	−620(8)	2062(6)	1478(3)	40
C(30)	−1226(9)	2271(7)	1807(3)	54
C(31)	−2380(11)	2411(9)	1774(4)	65
C(32)	−2917(10)	2335(7)	1425(4)	63
C(33)	−2326(10)	2137(7)	1080(4)	56
C(34)	−1161(10)	1989(7)	1111(4)	58
C(35)	1327(7)	2916(6)	1624(3)	37
C(36)	1722(10)	3128(6)	1999(3)	46
C(37)	2034(9)	3924(7)	2073(4)	56
C(38)	1950(10)	4467(7)	1772(3)	57
C(39)	1541(10)	4270(6)	1401(4)	53
C(40)	1223(9)	3491(6)	1319(3)	49

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

Crystals of the free diphosphine were obtained in moderate yield on treatment of *cis*-$\mathrm{PtCl_2\{}$*o*-$\mathrm{C_{16}H_{10}(PPh_2)_2\}}$ with excess KCN at reflux in benzonitrile followed by chromatography and recrystallization. The molecular structure of the free ligand is shown in Figure 3, and the structures of the three phosphine complexes *cis*-$\mathrm{PtX(Y)(Ph_2PC{\equiv}CPh)_2}$ are shown in Figure 2. Bond lengths and angles for [*o*-$\mathrm{C_{16}H_{10}(PPh_2)_2}$] are listed in Table VIII, and structural parameters for *cis*-$\mathrm{PtX(Y)(PPh_2PC{\equiv}CPh)_2}$ are compared in Table IV.

Although the naphthalene ring in *o*-$\mathrm{C_{16}H_{10}(PPh_2)_2}$ is planar with the maximum deviation from the least-squares plane containing C(1)–C(10) being −0.084 Å for C(11) (Table S8, supplementary material), the two phosphorus atoms P(1) and P(2) lie significantly out of this plane by −0.409 and 0.142 Å, respectively. In addition, it is notable that in the free ligand the $\mathrm{Ph_2P}$ groups adopt a configuration which minimizes lone pair–

Table VII. Atomic Coordinates (Fractional × 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for o-$C_{16}H_{10}(PPh_2)_2$

	x	y	z	U_{eq}[a]
P(1)	572(2)	–772(2)	3597(1)	27
P(2)	1479(2)	2209(2)	2376(1)	33
C(1)	1456(7)	–813(7)	2926(4)	26
C(2)	1799(8)	–2038(8)	2920(5)	32
C(3)	2256(7)	–2202(8)	2299(5)	32
C(4)	2423(8)	–1064(7)	1682(5)	30
C(5)	2771(8)	–1346(8)	1030(5)	44
C(6)	3014(10)	–2629(9)	1020(6)	60
C(7)	2899(10)	–3747(9)	1646(6)	58
C(8)	2550(8)	–3521(8)	2274(5)	45
C(9)	1673(7)	383(7)	2338(5)	26
C(10)	2124(7)	247(7)	1724(4)	24
C(11)	2332(8)	1456(8)	1094(4)	29
C(12)	1164(8)	1817(8)	390(5)	33
C(13)	1349(9)	2901(9)	–204(5)	50
C(14)	2678(10)	3636(9)	–129(6)	57
C(15)	3837(9)	3285(8)	575(5)	52
C(16)	3659(8)	2197(8)	1170(5)	40
C(17)	–636(8)	–2696(8)	3423(5)	34
C(18)	–266(8)	–3893(8)	3867(5)	35
C(19)	–1274(10)	–5301(8)	3732(6)	49
C(20)	–2704(10)	–5443(9)	3130(6)	54
C(21)	–3089(10)	–4269(9)	2674(6)	58
C(22)	–2064(9)	–2858(8)	2815(5)	37
C(23)	1871(7)	–774(7)	4800(5)	28
C(24)	1423(8)	–802(8)	5443(5)	42
C(25)	2371(9)	–582(8)	6374(5)	40
C(26)	3771(8)	–383(8)	6673(5)	40
C(27)	4247(8)	–410(9)	6069(5)	45
C(28)	3273(8)	–630(8)	5121(5)	43
C(29)	–422(8)	1784(8)	1930(5)	47
C(30)	–949(9)	2859(9)	1913(5)	54
C(31)	–2384(10)	2629(10)	1535(6)	66
C(32)	–3356(9)	1229(10)	1131(6)	58
C(33)	–2855(9)	146(10)	1115(5)	48
C(34)	–1416(8)	368(8)	1490(5)	43
C(35)	2284(8)	2619(7)	3606(5)	26
C(36)	1635(8)	2890(8)	4069(5)	45
C(37)	2425(10)	3279(9)	5001(5)	52
C(38)	3822(10)	3371(10)	5479(5)	51
C(39)	4484(9)	3145(9)	5029(6)	55
C(40)	3718(9)	2760(9)	4104(6)	47

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

Table VIII. Pertinent Bond Lengths (Å) and Angles (deg) for o-$C_{16}H_{10}(PPh_2)_2$

P(1)–C(1)	1.851(9)	C(13)–C(14)	1.389(16)
P(1)–C(17)	1.850(8)	C(15)–C(16)	1.378(11)
P(1)–C(23)	1.829(8)	C(17)–C(18)	1.364(11)
P(2)–C(9)	1.859(8)	C(19)–C(20)	1.410(16)
P(2)–C(29)	1.829(10)	C(21)–C(22)	1.415(12)
P(2)–C(35)	1.833(8)	C(23)–C(24)	1.392(12)
C(1)–C(2)	1.367(11)	C(25)–C(26)	1.374(15)
C(1)–C(9)	1.447(9)	C(27)–C(28)	1.417(11)
C(2)–C(3)	1.415(12)	C(29)–C(30)	1.355(13)
C(3)–C(8)	1.431(12)	C(31)–C(32)	1.413(13)
C(4)–C(10)	1.434(11)	C(33)–C(34)	1.393(15)
C(6)–C(7)	1.419(12)	C(35)–C(36)	1.400(14)
C(9)–C(10)	1.391(12)	C(37)–C(38)	1.371(16)
C(11)–C(12)	1.401(12)	C(39)–C(40)	1.382(12)
C(1)–P(1)–C(17)	101.8(3)	C(9)–P(2)–C(29)	103.6(3)
C(17)–P(1)–C(23)	100.8(3)	C(29)–P(2)–C(35)	105.9(3)
C(9)–P(2)–C(35)	103.1(3)	P(1)–C(1)–C(9)	120.6(3)
P(1)–C(1)–C(2)	120.0(3)	P(2)–C(9)–C(1)	124.2(3)
C(1)–P(1)–C(23)	105.7(3)	P(2)–C(9)–C(10)	115.2(3)

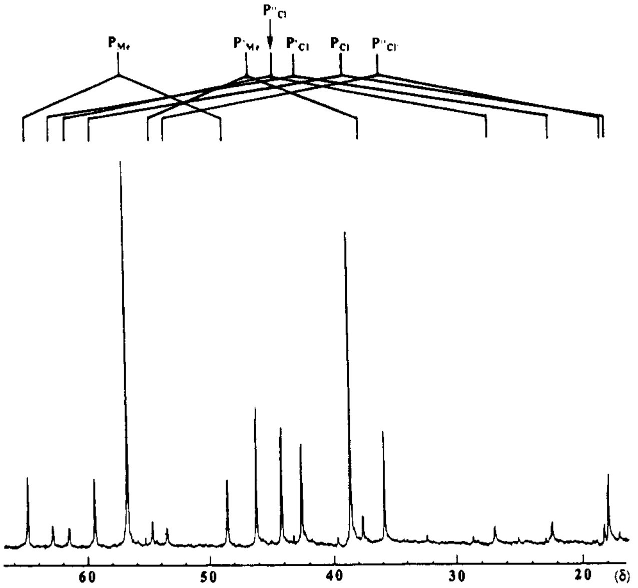


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a sample of *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2$ melted at 150–155 °C for 1 day showing resonances of isomer A or B of *cis*-$PtMe(Cl)\{o$-$C_{16}H_{10}(PPh_2)_2\}$ (labeled P_{Cl} and P_{Me} where the subscript denotes the *trans* atom), isomer B or A (labeled P'_{Cl} and P'_{Me}), and *cis*-$PtCl_2\{o$-$C_{16}H_{10}(PPh_2)_2\}$ (labeled P''_{Cl} and $P''_{Cl'}$).

lone pair repulsions and steric interactions between phenyl substituents. Nevertheless, nonbonded repulsions between Ph_2P groups may account for some distortion of angles subtended at the phenyl substituents: P(1)–C(17)–C(18), 125.8(3); P(1)–C(23)–C(28), 125.7(3), P(2)–C(35)–C(36), 126.8(3)°.

The complexes *cis*-$PtX(Y)(Ph_2PC{\equiv}CPh)_2$ all have square planar geometry at the metal center, with the maximum deviation from the $PtXYP_2$ mean planes observed for C(1) (–0.116 Å) in the $PtMe_2$ complex. The Pt–C and Pt–Cl distances [2.102(11)–2.150(8) and 2.355(2)–2.350(2) Å, respectively] are within the normal ranges found for these ligands *trans* to phosphines.[24] Platinum–phosphorus bond lengths *trans* to methyl groups [2.275(3)–2.309(2) Å] are in all cases significantly longer than those *trans* to chlorine [2.208(2)–2.237(2) Å], reflecting the stronger *trans* influence of the methyl group and consistent with the values of $^1J_{Pt-P}$ obtained from ^{31}P NMR spectra (vide supra).

Figure 2 illustrates the nature of the interaction between the alkyne units. In *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$, the phenyl groups on phosphorus are directed away from the polyhedral edge defined by the two phosphorus atoms, while the linear alkynyl moieties "cross" one another. The close approach of the α-carbon atoms of the phenethynyl groups is shown by the C(1)–C(9) distance [3.110(10) Å], which is considerably less than twice the van der Waals radius of carbon (1.65–1.70 Å). For comparison, the corresponding distance in the rigid organic diacetylene **1** is 2.86 Å,[25] and for a related rigid diacetylene which is also activated toward alkynyl coupling,[8] *o*-bis(phenylethynyl)benzene, we estimate a distance of ~2.82 Å.

Muller[4] has suggested that, for organic diynes containing near-rigid acetylene groups held adjacent to one another, coupling can occur in the presence of transition metal reagents whenever the distances between the α-carbon atoms of the proximate alkyne units is <3.4 Å.

Comparison of Figure 2b,c with Figure 2a shows that the phosphinoalkynes in the methyl chloro and dimethyl complexes have undergone a significant reorientation of their substituents with respect to the ligand conformation in the dichloride. The change in conformation from *cis*-$PtCl_2(Ph_2PC{\equiv}CPh)_2$ to *cis*-$PtMe(Cl)(Ph_2PC{\equiv}CPh)_2$ (Figure 2ab) can be viewed simplistically as a clockwise rotation of the ligand about the Pt–P(1) bond, which increases the separation between the C(1) and C(9) atoms of the alkynes in the latter to 3.213(14) Å. The

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(24) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Pregosin, P. S.; Kunz, R. W. In *Phosphorus-31 and Carbon-13 Nuclear Magnetic Resonance of Transition Metal Phosphine Complexes;* Diel, D., Fluck, E., Kosfield, R., Eds.; *NMR: Basic Principles and Progress Series*; Springer-Verlag; Berlin, 1979. Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 346.

(25) Jungk, A. E.; Schmidt, G. M. J. *Chem. Ber.* **1971**, *104*, 3272.

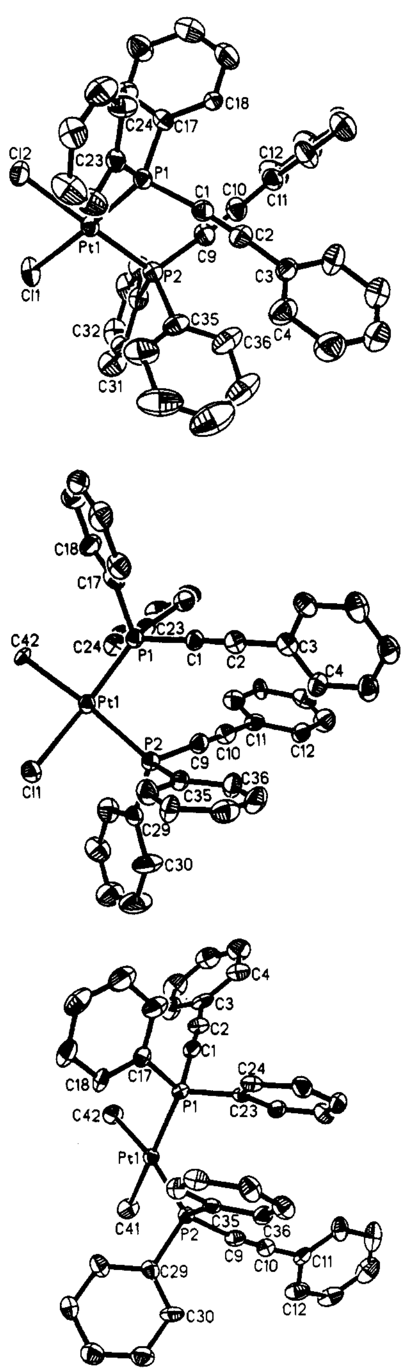


Figure 2. Molecular structures of (a, top) *cis*-$PtCl_2(PPh_2C{\equiv}CPh)_2{\cdot}2MeCN$, (b, middle) *cis*-$PtMe(Cl)(PPh_2C{\equiv}CPh)_2{\cdot}0.5CH_2Cl_2$, and (c, bottom) *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ drawn to illustrate the disposition of the alkyne groups in each molecule. The atom numbering scheme corresponds to the expected position of $-C{\equiv}CPh$ groups of $Ph_2PC{\equiv}CPh$ ligands in (a) and (b) incorporated into the *o*-$C_{16}H_{10}(PPh_2)_2$ ligand upon coupling. Solvent of crystallization is not shown.

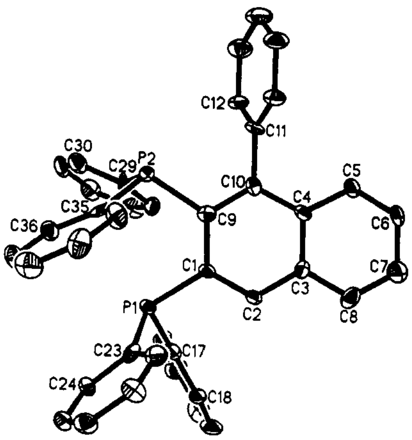
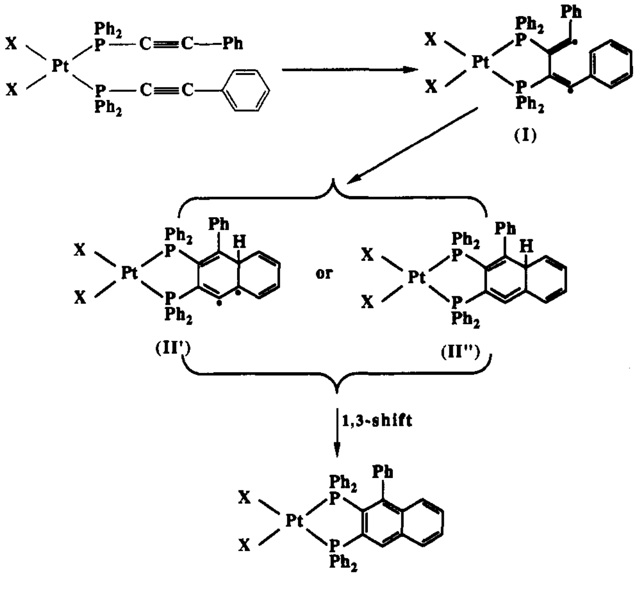


Figure 3. Perspective view of the molecular structure of 1-phenyl-2,3-bis(diphenylphosphino)naphthalene [*o*-$C_{16}H_{10}(PPh_2)_2$].

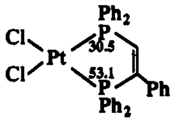
Scheme I

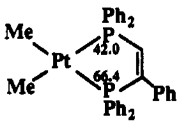


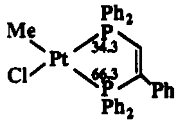
change is even more notable in *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$, where the triple bonds have rotated away from one another to the point where they are no longer proximate [C(11)···C(9) = 5.599(14) Å]. We attribute these structural changes in the solid state to diminished steric pressure between the anionic groups and the phosphine substituents in the dimethyl complex. Conversely, in the dichloro compound, increased nonbonded repulsion between the bulky phenyl substituents on the phosphines and lone pairs on the halide ligands forces the *cis* phosphines to adopt a configuration which places the least bulky substituents (the alkynyl units) in proximity. This hypothesis gains support from the increase in P(1)–Pt–P(2) angles across the series from 94.16(6)° in the dichloro compound to 95.63(8)° in the methyl chloro to 99.76(9)° in the dimethyl complex. That the relative orientation found in the solid state may account for the *ease* of coupling (i.e., higher barriers to conformational change are required for coupling) receives some support from the observation that while the $PtMe_2$ complex does not undergo cycloaddition, the corresponding $Pt(CF_3)_2$ compound does couple, albeit in low yield. Although CH_3 and CF_3 are similar in size, nonbonded repulsions between lone pairs on CF_3 groups and Ph_2P groups are likely to be more severe, increasing proximate triple-bond interaction.

Mechanism of the Coupling Reaction. Two closely related mechanisms have been suggested for coupling in aromatic diynes: coupling via a biradical intermediate or a concerted [2+2+2] cycloaddition, to form a common intermediate, followed by a 1,3-hydrogen shift.[8] The similarity between the products of coupling in these aromatic diacetylenes and the *o*-$C_{16}H_{10}(PPh_2)_2$ ligand generated from *cis*-$PtX(Y)(Ph_2PC{\equiv}CPh)_2$ is striking, and entirely analogous pathways can be postulated for coupling in the phosphinoalkyne complexes (Scheme I). The intermediate **I** formed in the biradical mechanism may undergo ring closure to the biradical **II′** or to the enallene **II″**. A 1,3-hydrogen shift then completes the formation of the naphthalene ring system.

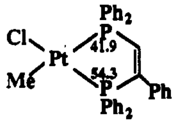
Reactivity of $Ph_2PC{\equiv}CPh$ Complexes Toward Diphenylphosphine. In view of the different reactivity of $Ph_2PC{\equiv}CPh$ toward cyclization in *cis*-$PtMe_2(Ph_2PC{\equiv}CPh)_2$ compared with the other complexes studied, we have investigated the reactivity of this complex, and *cis*-PtMe(Cl)(Ph$_2$PC≡CPh)$_2$, toward diphenylphosphine, since diphosphines RR'PH react with a range of *cis*-dihalogenometal(II) complexes of Ph$_2$PC≡CR to form chelating diphosphine complexes,[21] e.g. with *cis*-MCl$_2$(Ph$_2$PC≡CPh)$_2$ (M = Ni, Pd, Pt) to form *cis*-MCl$_2${Ph$_2$PCH=C(Ph)PPh$_2$}. Reaction of *cis*-PtMe$_2$(Ph$_2$PC≡CPh)$_2$ with Ph$_2$PH using the reported procedure[21] for *cis*-PtCl$_2$(Ph$_2$PC≡CPh)$_2$ gave a cream-yellow powder (2% yield) that exhibited only a broad resonance at 8.5–6.0 ppm and no MePt^{II} resonances. However, *cis*-PtMe(Cl)(Ph$_2$PC≡CPh)$_2$ reacted in the usual way to form a mixture of isomers of *cis*-PtMe(Cl)(Ph$_2$PCH=C(Ph)PPh$_2$} in ~2:5 ratio (^{1}H NMR integration of MePt^{II} resonances). The complex *cis*-PtMe$_2${Ph$_2$PCH=C(Ph)PPh$_2$} was synthesized by reaction of MeLi with *cis*-PtCl$_2${Ph$_2$PCH=C(Ph)PPh$_2$}. The ^{31}P NMR spectrum of *cis*-PtCl$_2${Ph$_2$PCH=C(Ph)PPh$_2$} has been assigned earlier,[21] with the resonance for Ph$_2$PC(Ph)= occurring 12.6 ppm downfield from that of Ph$_2$PCH= (Table I). With this assignment as a guide, the spectrum of *cis*-PtMe$_2${Ph$_2$PCH=C(Ph)PPh$_2$} may be similarly assigned, with methylation resulting in a downfield shift of ~12 ppm and a lowering of $^1J_{\text{Pt-P}}$ by ~1800 Hz. Thus, resonances for isomers A'and B' of *cis*-PtMe(Cl){Ph$_2$PCH=C(Ph)PPh$_2$} are assigned as shown in Table I and as follows:







(A')



(B')

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Supplementary Material Available: Anisotropic thermal parameters for non-hydrogen atoms (Tables S1, S3, S4, and S7), remaining bond lengths and angles (Tables S2, S5, S6 and S13), deviations from mean planes (Table S8), and structure determination summaries (Tables S9, S10, S11, S12) for *o*-C$_{16}$H$_{10}$(PPh$_2$)$_2$ and for *cis*-PtX(Y)(Ph$_2$PC≡CPh)$_2$ (X = Y = Cl; X = Me, Y = Cl; X = Y = Me) (16 pages). Ordering information is given on any current masthead page.