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Synthesis of Heterobimetallic Bis(diphenylphosphino)acetylene-Bridged Palladium-Platinum Complexes. Crystal and Molecular Structure of [PdPtCl$_4$(Ph$_2$PC$\equiv$CPPh$_2$)$_2$]·2CHCl$_3$

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Reaction of [(PMe$_2$Ph)PdCl(μ-Cl)$_2$PtCl(PMe$_2$Ph)] (I) with 1,2-bis(diphenylphosphino)acetylene yields the heterobimetallic complex [Cl$_2$Pd(Ph$_2$PC$\equiv$CPPh$_2$)$_2$PtCl$_2$] (II). Solution studies using ^{31}P and ^{195}Pt NMR spectra reveal that II exists in an equilibrium of the type 2[Cl$_2$Pd(Ph$_2$PC$\equiv$CPPh$_2$)$_2$PtCl$_2$] $\rightleftharpoons$ [Cl$_2$Pd(Ph$_2$PC$\equiv$CPPh$_2$)$_2$PdCl$_2$] + [Cl$_2$Pt(Ph$_2$PC$\equiv$CPPh$_2$)$_2$PtCl$_2$]. Crystals of II [as the bis(chloroform) solvate] are monoclinic, space group $P2_1/n$ with two formula units in a cell of dimensions a = 14.415 (3) Å, b = 12.149 (3) Å, c = 15.949 (3) Å, and β = 91.33 (2)°. The bimetallic complex lies about a crystallographic inversion center, and the Pd and Pt atoms are mutually disordered. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters; R = 0.033 and $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0.044 for 2407 observed reflections. The unique metal atom has slightly distorted square-planar geometry with mean M-Cl = 2.344 (2) Å and mean M-P = 2.244 (2) Å. The strained 10-membered PtPdP$_4$C$_4$ ring system is nonplanar; there is significant bowing of the P—C$\equiv$C—P moiety [mean P—C$\equiv$C = 172.2 (3)°] and enlargement of the M-P-C(acetylene) angles from tetrahedral [mean value 121.3 (2)°].

Introduction

The bridge-cleavage reactions of [PtCl$_2$L]$_2$ (L = PEt$_3$) with mono(tertiary phosphines) have been used to prepare mixed-ligand complexes of low symmetry,[2,3] of the type [PtCl$_2$LL′] (L′ = PPh$_3$, PMe$_2$Ph, P-*i*-Pr$_3$, P(cy)$_3$). Recently, we have described[4] the synthesis of heterobimetallic halogen-bridged complexes of the type [(PR$_3$)ClPd(μ-Cl)$_2$PtCl(PR$_3$)] and their cleavage reactions with neutral donor ligands, which occur symmetrically and uninfluenced by the heterobimetallic nature of the complexes. We now report our study of similar bridge-cleavage reactions of [(PMe$_2$Ph)ClPd(μ-Cl)$_2$PtCl(PMe$_2$Ph)] with various bis(tertiary phosphines) in an attempt to prepare heterobimetallic complexes containing bridging bis(tertiary phosphine) ligands. Recently, a number of heterobimetallic complexes containing the bridging 1,2-bis(diphenylphosphino)methane ligand have been reported for platinum with rhodium(I), iridium(I), iridium(III), tungsten(0), mercury, and silver[5-7] and for palladium with manganese.[8]

Results and Discussion

The reaction of Ph$_2$PCH$_2$CH$_2$PPh$_2$ (diphos) with [(PMe$_2$Ph)ClPd(μ-Cl)$_2$PtCl(PMe$_2$Ph)] (I) gave the mononuclear *cis*-[PtCl$_2$(diphos)], *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] [δ = −15.5, $J(^{195}\text{Pt}-^{31}\text{P})$ = 3547.35 Hz (lit.[9] δ = −15.2, $J(^{195}\text{Pt}-^{31}\text{P})$ = 3549.0 Hz)], and *trans*-[PdCl$_2$(PMe$_2$Ph)$_2$] [δ = 5.72 (lit.[10] δ = 5.20)]. Although PdCl$_2$(diphos) must also have been formed, it was not observed in the ^{31}P NMR spectrum. The nonformation of a heterobimetallic complex with diphos may be ascribed to the greater stability of the chelate complex[11] compared with that of the bridging diphosphine complex.[12] Next, the reactions of I with the diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 5 and 6), which are known to give cis as well as trans monomeric and dimeric complexes with platinum,[13] were studied. Both diphosphines on reaction with I gave yellow crystalline products. The ^{31}P NMR spectra were very complicated and appeared to suggest the formation of a mixture of products, perhaps including heterobimetallic Pt-Pd complexes. Separation of these mixtures could not be achieved.

Table I. Important Molecular Dimensions[a]

	(a) Bond Distances (Å)		
M-P(1)	2.242 (2)	P(1)-C(21)	1.804 (7)
M-P(2)	2.245 (2)	P(2)-C(2)	1.780 (8)
M-Cl(1)	2.346 (2)	P(2)-C(31)	1.810 (7)
M-Cl(2)	2.341 (2)	P(2)-C(41)	1.808 (7)
P(1)-C(1)	1.773 (8)	C(1)-C(2)′	1.195 (9)
P(1)-C(11)	1.816 (7)		
	(b) Bond Angles (deg)		
P(1)-M-P(2)	103.4 (1)	M-P(2)-C(41)	113.5 (2)
P(1)-M-Cl(1)	85.7 (1)	C(2)-P(2)-C(31)	100.2 (3)
P(1)-M-Cl(2)	170.6 (1)	C(31)-P(2)-C(41)	110.2 (3)
P(2)-M-Cl(1)	170.6 (1)	C(2)-P(2)-C(41)	99.8 (3)
P(2)-M-Cl(2)	83.2 (1)	P(1)-C(1)-C(2)′	171.9 (7)
Cl(1)-M-Cl(2)	88.0 (1)	P(2)-C(2)-C(1)′	172.4 (7)
M-P(1)-C(1)	120.5 (2)	P(1)-C(11)-C(12)	123.2 (6)
M-P(1)-C(11)	119.5 (2)	P(1)-C(11)-C(16)	119.2 (5)
M-P(1)-C(21)	106.3 (2)	P(1)-C(21)-C(22)	119.7 (5)
C(1)-P(1)-C(11)	100.3 (3)	P(1)-C(21)-C(26)	120.1 (6)
C(1)-P(1)-C(21)	102.2 (3)	P(2)-C(31)-C(32)	123.0 (5)
C(11)-P(1)-C(21)	106.2 (3)	P(2)-C(31)-C(36)	117.8 (6)
M-P(2)-C(2)	122.0 (2)	P(2)-C(41)-C(42)	120.3 (5)
M-P(2)-C(31)	110.1 (2)	P(2)-C(41)-C(46)	121.1 (6)

[a] Primed atoms are related to the unprimed atoms by the transformations $-x$, $-y$, $-z$. The phenyl ring dimensions are in the range C-C = 1.31 (1)-1.42 (1) Å and C-C-C = 117.3 (7)-123.0 (9)°. Full details are given with the supplementary material.

trans-1,2-Bis(diphenylphosphino)ethylene and 1,2-bis(diphenylphosphino)acetylene ligands, in which the rigidity of the unsaturated carbon backbone forces two phosphorus atoms to remain too far apart for them both to bond to a single metal atom, were then allowed to react with I in an attempt to prepare heterobimetallic Pd-Pt complexes by bridge-cleavage reactions. The reaction of I with *trans*-Ph$_2$PCh=CHPPh$_2$ gave a product whose ^{31}P NMR spectrum was complicated and again indicated that a mixture of products was present, perhaps including a heterobimetallic Pd-Pt complex; attempted separation on a Florisil column was unsuccessful. However, the bridge-cleavage reaction of I with Ph$_2$PC$\equiv$CPPh$_2$ gave a yellow crystalline product (II) whose crystal structure was determined.

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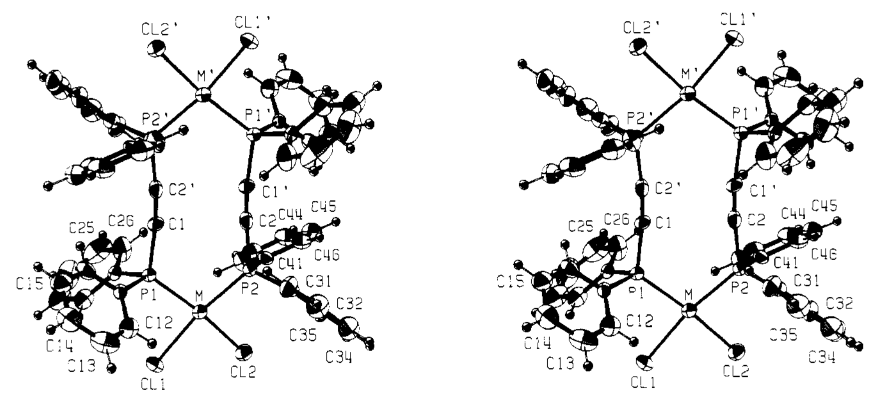


Figure 1. Stereoview of II with the crystallographic numbering scheme. The ellipsoids are shown at the 50% probability level; the hydrogen atoms are shown as spheres with an arbitrary radius.

The material crystallizes as the bis(chloroform) solvate in space group $P2_1/n$, and with only two molecules in the unit cell, the molecules are required by space group symmetry to lie about inversion centers. A view of the dimer is shown in Figure 1; there are only van der Waals contacts between the dimers and the solvate molecules (Figure 2, supplementary material). The disorder required by the space group and the results of our refinement (see Experimental Section) yield metal atom population parameters consistent with there being equal amounts of both Pd and Pt atoms in the centrosymmetric dimer. Thus, the results of the crystal structure analysis can be interpreted in three distinct ways. (a) The heterobimetallic molecule was formed and is disordered in the crystals. (b) No heterobimetallic molecules were formed, and the crystal contains *equal* amounts of disordered Pd–Pd and Pt–Pt dimers. (c) Some heterobimetallic molecules were formed and both Pd–Pd and Pt–Pt dimers (in *equal* amounts) are present but disordered to scramble Pd and Pt equally in the solid state. Spectral data, presented below, lead us to believe that case c is the more likely situation in solution, but in the solid state, no unambiguous distinction can be drawn among cases a–c.

The results of our crystal structure analysis show that the disorder of the Pd and Pt atoms has little effect on the remaining atoms of the complex. The phenyl rings have normal dimensions (Table I) and vibration parameters.

The geometry around the unique metal atom is slightly distorted square planar. Because of the disorder we cannot distinguish between Pd–Cl and Pt–Cl dimensions nor between Pd–P and Pt–P dimensions. The M–Cl distances [mean 2.344 (2) Å] and M–P distances [mean 2.244 (2) Å] are intermediate between values found in *cis*-dichlorobis(phosphine)palladium[14] and -platinum complexes[15] with *cis*-Cl–M–Cl less than 90° [88.0 (1)°] and P–M–P greater than 90° [103.4 (1)°].

The 10-membered $PdPtP_4C_4$ ring is puckered, with C(1) being 0.097 Å and C(2)′ being 0.114 Å from the P_4 plane, and there is considerable concave bowing of the P—C≡C—P moiety [P—C≡C = 171.9 and 172.4 (7)°] to accommodate the strain of ring formation. There are concomitant increases from tetrahedral values in M–P–C angles to 120.5 and 122.0 (2)°. The Cl atoms lie 0.19 Å above and below the P_4 plane.

The remaining bond lengths, mean P–C = 1.777 (8) Å, mean P–C(phenyl) = 1.810 (7) Å, mean C–C(aromatic) = 1.374 (11) Å and C≡C = 1.195 (9) Å are in accord with accepted values. The ^{31}P NMR spectrum of II, obtained in CH_2Cl_2 solution, shows four phosphorus resonances, in a 1:1:1:1 intensity ratio, at δ = 4.24, 5.20, −10.14, and −10.94 (Table II), only two of which (δ = −10.14 and −10.94) show coupling to ^{195}Pt. The remaining two signals are sharp singlets (Figure 4A). An identical ^{31}P NMR spectrum was also obtained when equimolar amounts of $[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$[16] and $[Pd_2Cl_4(PPh_2PC{\equiv}CPPh_2)_2]$[16] were mixed at room temperature in CH_2Cl_2, indicating that this synthetic route leads to the same products in solution.

Table II. ^{31}P NMR Spectral Data for Platinum and Palladium Complexes[a]

complex	Pd δ	Pt δ	$J(^{195}Pt-^{31}P)$
$[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$		−10.93	3668.3
$[Pt_2Br_4(Ph_2PC{\equiv}CPPh_2)_2]$		−12.05	3606.8
$[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$	5.22		
$[PtPdCl_4(Ph_2PC{\equiv}CPPh_2)_2]$	4.24	−10.14	3665.5
$[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ + $[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$			
1:1 mixture	5.22	−10.91	3667.5
	4.25	−10.11	3662.9
1:5 mixture	5.17		
	4.22	−10.20	3667.1

[a] Spectra were run in CH_2Cl_2 solution, with δ relative to the high frequency of external H_3PO_4 and J in Hz.

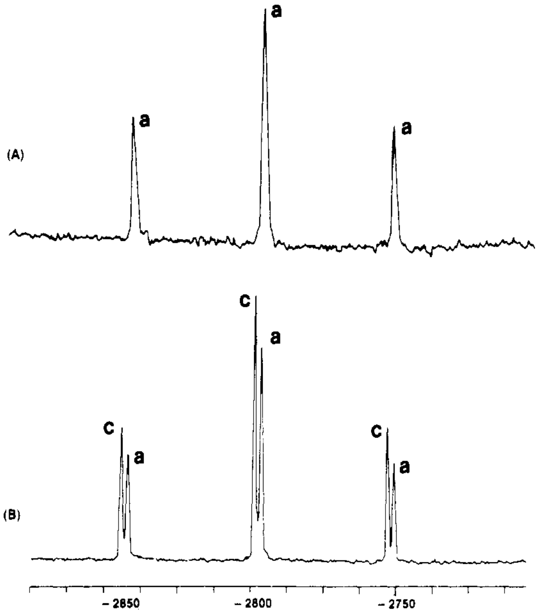
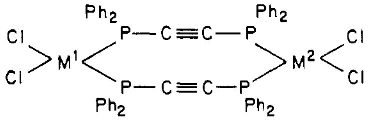


Figure 3. ^{195}Pt NMR spectra in CH_2Cl_2 solution: (A) spectrum of $[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$; (B) spectrum of II, $[PdPtCl_4(Ph_2PC{\equiv}CPPh_2)_2]$. Peaks labeled a are attributed to the Pt–Pt dimer and those labeled c are attributed to the Pd–Pt dimer.

The reaction solutions, then, may contain any or all of the three complexes with the structure



IIa: $M^1 = M^2 = Pt$
IIb: $M^1 = M^2 = Pd$
IIc: $M^1 = Pd$; $M^2 = Pt$

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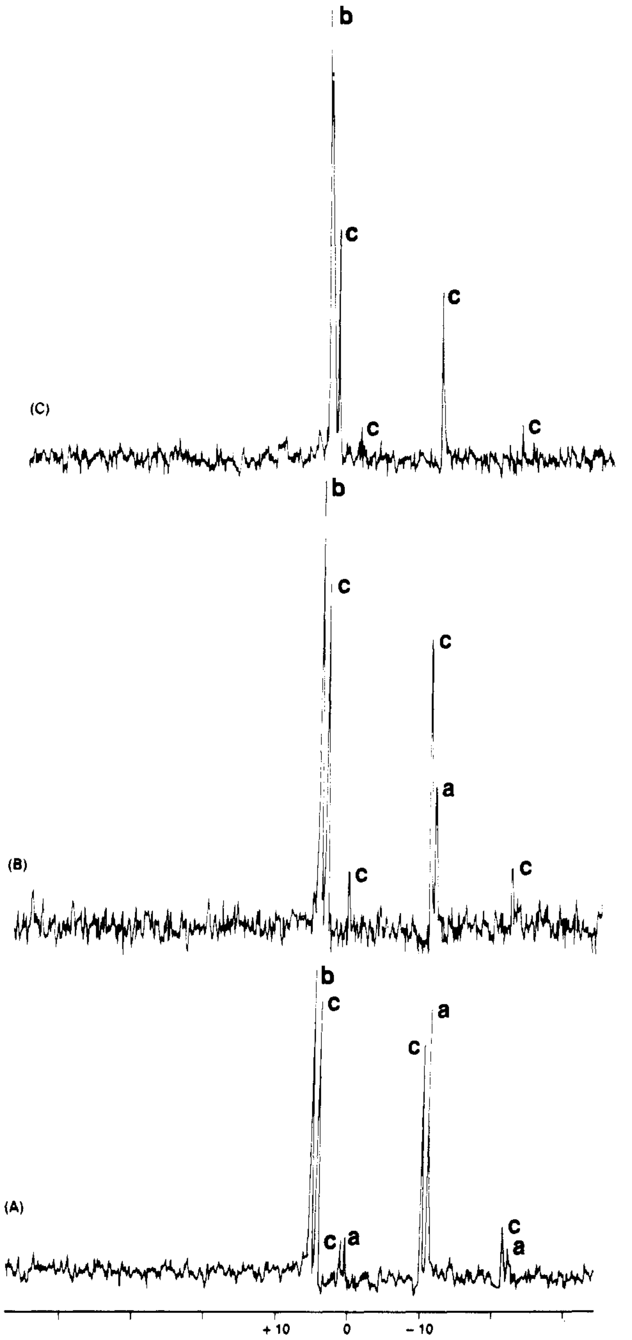

Figure 4. ^{31}P NMR spectra of mixtures of $[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ and $[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ in CH_2Cl_2 solution. Spectra labeled A, B, and C are for 1:1, 1:2, and 1:5 molar ratios, respectively. Peaks labeled a, b and c are attributed to Pt–Pt, Pd–Pd, and Pd–Pt dimers respectively.

The ^{31}P NMR spectrum of IIa consists of a singlet at $\delta = -10.93$ with satellites due to the direct $^{195}Pt-^{31}P$ coupling [$J(^{195}Pt-^{31}P) = 3668.3$ Hz], whereas that of IIb shows simply a singlet at $\delta = 5.22$ (see Table II). In the ^{31}P NMR spectrum of the mixture, two new phosphorus resonances are present, of which one has platinum satellites and is assigned to the phosphorus nucleus bound to platinum in IIc. The remaining signal is assigned to the phosphorus nucleus bound to palladium in IIc. Thus, the ^{31}P NMR spectra obtained from either reaction of I with $Ph_2PC{\equiv}CPPh_2$ or from mixing equimolar amounts of $[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ and $[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ suggest that all three species IIa, IIb, and IIc are present in solution and are in equilibrium, e.g. eq 1.

$$\underset{\text{IIa}}{[Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]} + \underset{\text{IIb}}{[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]} \rightleftharpoons \underset{\text{IIc}}{2[PtPdCl_4(Ph_2PC{\equiv}CPPh_2)_2]} \quad (1)$$

We have considered also the possibility that, even in solution, *only* the mixed heterobimetallic complex, IIc, is present. The crystal structure of II shows that the orientations of the phenyl rings are different at each phosphorus and together with the distortion of the 10-membered ring would make all four phosphorus atoms in a Pd–Pt dimer nonequivalent. Such nonequivalence would produce the observed ^{31}P NMR spectrum, two resonances for the two nonequivalent P nuclei bound to Pd and two resonances showing the expected coupling for P bound to Pt. However, the distortion in the crystal structure is small and might well be insufficient to produce the differences in chemical shift that we observe. Moreover, fuller evidence that an equilibrium exists in solution, rather than the presence of only IIc, comes from the ^{195}Pt NMR spectrum (see Figure 3).

The ^{195}Pt NMR spectrum of IIa shows a triplet at $\delta = -2797.18$ [$J(^{195}Pt-^{31}P) = 3657.5$ Hz], whereas the ^{195}Pt NMR spectrum of the complex obtained from the reaction of I with $Ph_2PC{\equiv}CPPh_2$ shows two sets of triplets at $\delta = -2795.97$ [$J(^{195}Pt-^{31}P) = 3656.7$ Hz] and $\delta = -2797.86$ [$J(^{195}Pt-^{31}P) = 3660.6$ Hz]. We thus assign the triplet at $\delta = -2797.8$ to species IIa and the triplet at $\delta = 2795.97$ to species IIc.

Since the ^{31}P and ^{195}Pt NMR spectra show no change with time over a period of days, it is reasonable to conclude that equilibrium is indeed attained. However, such an equilibrium should be reversible and should also show temperature and concentration dependence. The temperature dependence of the ^{31}P NMR spectrum of the solution mixtures was investigated in tetrachloroethylene over the temperature range +20 to +120 °C. Surprisingly, the relative intensitities of the resonances of all three species present in solution did not change, although the chemical shifts showed some solvent dependence. However, the equilibrium can be shifted if the concentration of one of the species is increased, as can be seen from the ^{31}P NMR spectra (Figure 4). When the ratio of IIb:IIa is increased from 1:1 to 5:1, only maxima consistent with IIc and excess IIb could be seen in the ^{31}P NMR spectra and there is no evidence for IIa present in solution.

The solid-state ^{31}P NMR spectra of IIa, IIb, and the product (II) obtained from the reaction of $Ph_2PC{\equiv}CPPh_2$ with I were also obtained in the hope that it would be possible to determine the nature of the product in the solid state. The spectrum of IIa shows a single peak at $\delta = -10.7$ (line width $\nu_{1/2} = 273.4$ Hz) with platinum satellites [$J(^{195}Pt-^{31}P) = 3668.0$ Hz]. That of IIb shows a peak at $\delta = 1.3$ with a shoulder at $\delta = 5.4$ (line width $\nu_{1/2} = 400.4$ Hz) due to the inequivalence of the phosphorus atoms attached to each palladium in the solid state. The spectrum of II shows two peaks at $\delta = -12.1$ [$J(^{195}Pt-^{31}P) = 3662.0$ Hz] and $\delta = 5.3$. Although this spectrum is consistent with the presence of IIc in the solid state, the line width of the peaks and the small chemical shift differences do not make this characterization unambiguous.

An attempt was also made to prepare analogous heterobimetallic mixed-halogen complexes by mixing $[Pt_2Br_4(Ph_2PC{\equiv}CPPh_2)_2]$ and $[Pd_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2]$ in equimolar ratio in CH_2Cl_2. The ^{31}P NMR spectrum gave a broad peak, which could not be resolved, thus suggesting that scrambling of halogen also occurs, giving rise to a substantial number of species in solution.

That the equilibrium described by eq 1 occurs in solution thus seems clearly established. Such an equilibrium requires transfer of a $PtCl_2$ or $PdCl_2$ unit during the reaction. Transfer reactions of this type are not common although they obviously also must occur in the following previously reported studies: (i) reaction of equimolar amounts of $[Pt_2Cl_4(P\text{-}n\text{-}Bu_3)_2]$ and $[Pd_2Cl_4(P\text{-}n\text{-}Bu_3)_2]$,[17] (ii) reaction of equimolar amounts of $[M_2Cl_4(Pr_3)_2]$ (M = Pd or Pt) and $RhHCl_2(PR_3)_2$,[18] and (iii) reaction of equimolar amounts of $[PtR(MeOH)(PR_3)_2]^+$ and $[IrH_5(PR_3)_2]$.[19] However, the above examples must all entail exchange through cleavage of halogen or halogen-hydrido bridges; what is remarkable in the

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present study is the apparently facile exchange of $PtCl_2$ for $PdCl_2$ when both are bonded to two diphosphines.

It should be noted, however, that zerovalent platinum and palladium complexes of $Ph_2PC\equiv CPPh_2$ have been shown[19] to dissociate in solution and that ligand exchange between $(R_3P)_2PdX_2$ and $(R_3P)_2PtX_2$ has been shown to occur.[20]

The nature of the solid is less clear. While it may consist only of IIc, it is possible that it also consists of equimolar amounts of IIa and IIb, together with some IIc. However, this latter possibility has the additional other curious requirements that (i) IIa and IIb will randomly cocrystallize and (ii) that they will do so at the same rate. This latter point is necessary to account for the observed perfect randomness of occupation of the two metal sites by either Pd or Pt. Since these are very demanding requirements, it may be that the solid consists only of IIc, but absolute proof is obviously lacking.

Experimental Section

All bis(tertiary phosphine) ligands were obtained from Strem Chemical Co., and all manipulations involving them were performed under a nitrogen atmosphere. Spectrograde solvents were used in all experiments.

^{31}P NMR spectra were obtained on a Bruker WH-400 spectrometer operating in the Fourier transform mode at 161.98 MHz. Spectra were recorded in CH_2Cl_2 solutions, and ^{31}P NMR chemical shifts were measured relative to external H_3PO_4, more positive values representing deshielding. ^{195}Pt NMR spectra were recorded on a Bruker WH-400 spectrometer operating in the Fourier transform mode at 85.88 MHz. Spectra were recorded in CH_2Cl_2 solutions, and chemical shifts are relative to that of Na_2PtCl_4. Elemental analyses were performed by Guelph Chemical Laboratories. $[Pt_2Cl_4(Ph_2PC\equiv CPPh_2)_2]$ and $[Pd_2Cl_4(ph_2PC\equiv CPPh_2)_2]$ were prepared by the literature method.[16]

Preparation of $[(PMe_2Ph)ClPd(\mu\text{-}Cl)_2PtCl(PMe_2Ph)]$. *cis*-$PtCl_2(PMe_2Ph)_2$ (1.0 g) and $PdCl_2$ (0.3 g) were ground together in a mortar and transferred to a 20-mL flask, and then a small volume (5 mL) of xylene was added. The mixture was heated under reflux with stirring under N_2 atmosphere until all the $PdCl_2$ was dissolved. After the mixture had cooled, solvent was pumped off under vacuum and all residues were washed well with hexane and extracted with $CHCl_3$. The extract was passed over a small Florisil column to remove any unreacted $PdCl_2$ and decomposition products, after which the volume was reduced to about 10 mL by evaporation. Hexane (10 mL) was added, and slow evaporation of the solvent gave a deep orange crystalline solid (I) (0.56 g). Mp: 214–217 °C dec. Anal. Calcd for $C_{16}H_{22}P_2Cl_4PtPd$: C, 26.70; H, 3.08. Found: C, 27.04; H, 3.00. ^{31}P NMR spectrum: $\delta = 17.58, 15.94$; $\delta = -17.16, -18.46$ with $J(^{195}Pt-^{31}P) = 3914.69, 3935.54$ Hz, respectively.[4]

Reaction of I with $Ph_2PC\equiv CPPh_2$. The complex $[(PMe_2Ph)ClPd(\mu\text{-}Cl)_2PtCl(PMe_2Ph)]$ (0.20 g) was dissolved in 20 mL of benzene, and to it was added slowly a benzene (10 mL) solution of $Ph_2PC\equiv CPPh_2$ (0.10 g). Immediately the color of the solution changed from deep orange to pale yellow, and a yellow solid separated. The solution was stirred for 2 h and then filtered. The residue was dissolved in $CHCl_3$ and the solvent allowed to evaporate slowly to yield a 0.15 g of a yellow crystalline solid (mp 268–272 °C dec) $II\cdot 2CHCl_3$ on which we performed the crystal structure analysis. Anal. Calcd for $C_{54}H_{42}P_4Cl_{10}PtPd$: C, 44.10; H, 2.88; Cl, 24.10. Found: C, 44.39; H, 2.94; Cl, 25.00.

The filtrate from the above preparation on evaporation of solvent gave a yellow crystalline solid, the ^{31}P NMR spectrum of which indicates that it contains *cis*-$[PtCl_2(PMe_2Ph)_2]$ [$\delta = -14.38$, $J(^{195}Pt-^{31}P) = 3548.9$ Hz] and *trans*-$[PdCl_2(PMe_2Ph)_2]$ ($\delta = 5.52$).

Crystal Data for $[PtPdCl_4(Ph_2PC\equiv CPPh_2)_2]\cdot 2CHCl_3$: $C_{54}H_{42}Cl_{10}P_4PdPt$, $II\cdot 2CHCl_3$, $M_r = 1470.9$, monoclinic, $a = 14.415$ (3) Å, $b = 12.149$ (3) Å, $c = 15.949$ (3) Å, $\beta = 91.33$ (2)°, $V = 2792.4$ Å^3, $Z = 2$, $D_c = 1.75$ g cm^{-3}, $F(000) = 1440$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo kα) = 32.5 cm^{-1}. Space group P_{21}/n was uniquely determined from the systematic absences ($h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$).

Structure Determination. Accurate unit cell constants and crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer by a least-squares treatment of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected in the range $2 < \theta < 20°$ by the $\omega-2\theta$ scan method using monochromatized Mo kα radiation. The intensities of three reflections, chosen as standards, were monitored at regular intervals and showed no reduction in intensity. Intensities of 2625 unique reflections were measured, of which 2407 had $I > 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz and polarization factors and for absorption. Maximum and minimum values of the transmission coefficients are 0.4280 and 0.2833, respectively.

Table III. Final Fractional Coordinates ($\times 10^4$; $\times 10^5$ for M) with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*
M	4552 (2)	21695 (3)	16282 (2)
P(1)	−586 (1)	799 (1)	1658 (1)
P(2)	1173 (1)	1901 (2)	411 (1)
Cl(1)	−183 (1)	2737 (2)	2897 (1)
Cl(2)	1598 (1)	3520 (2)	1827 (1)
Cl(3)	1308 (3)	2657 (4)	4823 (2)
Cl(4)	3023 (2)	3313 (3)	4256 (3)
Cl(5)	2219 (4)	1242 (3)	3695 (2)
C	2052 (6)	2558 (8)	3949 (6)
C(1)	−649 (5)	−184 (6)	837 (5)
C(2)	796 (5)	881 (6)	−322 (5)
C(11)	−1808 (5)	1122 (6)	1759 (4)
C(12)	−2144 (7)	2192 (6)	1821 (5)
C(13)	−3017 (7)	2406 (8)	1958 (6)
C(14)	−3664 (6)	1545 (9)	2024 (5)
C(15)	−3344 (6)	500 (8)	1952 (5)
C(16)	−2430 (5)	285 (7)	1844 (4)
C(21)	−271 (4)	−41 (5)	2553 (4)
C(22)	−700 (6)	127 (6)	3306 (5)
C(23)	−424 (7)	−488 (8)	4015 (6)
C(24)	287 (8)	−1168 (11)	3960 (7)
C(25)	741 (7)	−1337 (8)	3243 (8)
C(26)	459 (6)	−750 (7)	2513 (6)
C(31)	1076 (5)	3120 (6)	−237 (4)
C(32)	1745 (5)	3938 (6)	−239 (5)
C(33)	1588 (6)	4917 (7)	−655 (5)
C(34)	778 (7)	5079 (7)	−1065 (5)
C(35)	77 (6)	4290 (8)	−1065 (6)
C(36)	234 (6)	3315 (6)	−651 (5)
C(41)	2377 (4)	1506 (5)	543 (4)
C(42)	2684 (5)	1012 (6)	1272 (5)
C(43)	3583 (6)	663 (6)	1371 (5)
C(44)	4195 (6)	759 (7)	721 (6)
C(45)	3888 (5)	1248 (6)	−36 (6)
C(46)	3000 (6)	1593 (6)	−126 (5)

[a] M is the disordered Pt/Pd atom. Atoms C and Cl(3)–Cl(5) are in the chloroform solvate.

The structure was solved by the heavy-atom method. A chloroform molecule of solvation was also located in the asymmetric unit. With two molecules of II in the unit cell, space group $P2_1/n$ requires the molecules to lie on inversion centers; consequently there is disorder, which only appears to affect the metal atoms. In the initial isotropic refinement[22] of the structure by full-matrix least-squares calculations, the scattering factor data for the unique metal atom were obtained by assigning refinable occupancy factors of 0.5 to both Pd and Pt atoms, constrained to lie in the same position. In subsequent refinement the occupancy parameters did not move significantly from 0.5, and in the final anisotropic refinement cycles their occupancies were fixed at 0.5. At an intermediate stage in the refinement a difference map revealed all hydrogen atoms in positions close to those expected; these atoms were then positioned geometrically (C–H = 0.95 Å), and in subsequent cycles, although they were included, only an overall isotropic thermal parameter was refined for them. Refinement converged with $R = 0.033$ and $R_w = (\sum w\Delta^2/\sum wF_o^2) = 0.044$. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2F + 0.00083F^2)$. Scattering factors were taken from ref 23 and 24, and allowance was made for anomalous dispersion.[25] A difference map calculated at the conclusion of the refinement showed some residual density between 0.5 and 1.0 e Å^{-3} around the Cl atoms of the $CHCl_3$ solvate molecule but no other significant features.

The final fractional coordinates with estimated standard deviations are given in Table III. Additional information regarding the structure determination is offered as supplementary material, see paragraph below.

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Registry No. I, 95387-54-5; IIa, 21108-38-3; IIb, 21108-42-9; IIc, 98087-77-5; *cis*-$\mathrm{PtCl_2(PMe_2Ph)_2}$, 15393-14-3; $[\mathrm{Pt_2Br_4(Ph_2PC{\equiv}CPPh_2)_2}]$, 21108-37-2.

Supplementary Material Available: Listings of calculated and observed structure factors, thermal parameters, calculated hydrogen atom coordinates, molecular dimensions, and mean plane data and Figure 2, showing a stereoview of the unit cell contents (18 pages). Ordering information is given on any current masthead page.

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Steric Effects and the Behavior of $\mathrm{Cu(NN)(PPh_3)_2^+}$ Systems in Fluid Solution. Crystal and Molecular Structures of $\mathrm{[Cu(dmp)(PPh_3)_2]NO_3}$ and $\mathrm{[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH}$

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The contrasting behavior of $\mathrm{Cu(phen)(PPh_3)_2^+}$ and $\mathrm{Cu(dmp)(PPh_3)_2^+}$ (phen = 1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline) in acetonitrile solution is analyzed and related to significant interligand steric repulsions that occur in the dmp complex. Both complexes undergo solvolysis with the dissociation of $\mathrm{PPh_3}$, but the dissociation is more extensive for the dmp complex. At 25 °C the measured binding constants are $K^{\mathrm{Cu(dmp)}}{}_{\mathrm{Cu(dmp)(L)}} = 10\ (5) \times 10^4\ \mathrm{M^{-1}}$, $K^{\mathrm{Cu(dmp)(L)}}{}_{\mathrm{Cu(dmp)(L)_2}} = 4\ (2) \times 10^2\ \mathrm{M^{-1}}$, and $K^{\mathrm{Cu(phen)(L)}}{}_{\mathrm{Cu(phen)(L)_2}} = 2\ (1) \times 10^4\ \mathrm{M^{-1}}$, where L stands for $\mathrm{PPh_3}$. Of the various species present in solution, $\mathrm{Cu(dmp)(PPh_3)_2^+}$ is unique in that it exhibits appreciable charge-transfer emission. Steric crowding in the coordination sphere of $\mathrm{Cu(dmp)(PPh_3)_2^+}$ apparently inhibits solvent-induced quenching by exciplex formation, a quenching phenomenon well established in related systems. Crystal structures of the nitrate salts of each complex confirm that steric repulsions arise in the dmp complex as a result of the presence of the 2- and 9-methyl substituents. The Cu–N and Cu–P bond distances are elongated in the dmp complex relative to those in the phen derivative, and several atom–atom contacts occur at distances less than the summed van der Waals radii. For $\mathrm{[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH}$, the crystal data are space group $P\bar{1}$, $Z = 2$, $a = 12.232$ (2) Å, $b = 12.496$ (2) Å, $c = 16.608$ (3) Å, $\alpha = 107.95$ (1)°, $\beta = 90.23$ (1)°, $\gamma = 113.62$ (1)°, $V = 2189$ (2) Å^3, and $R_w = 5.3\%$ for 5805 reflections. For $\mathrm{[Cu(dmp)(PPh_3)_2]NO_3}$, the crystal data are space group $P\bar{1}$, $Z = 2$, $a = 15.43$ (1) Å, $b = 13.20$ (1) Å, $c = 10.660$ (5) Å, $\alpha = 80.88$ (5)°, $\beta = 88.98$ (4)°, $\gamma = 94.65$ (6)°, $V = 2136$ (2) Å^3, and $R_w = 6.4\%$ for 4196 reflections.

Introduction

The mixed-ligand complexes $\mathrm{Cu(phen)(PPh_3)_2^+}$ and $\mathrm{Cu(dmp)(PPh_3)_2^+}$, where phen and dmp denote 1,10-phenanthroline and its 2,9-dimethyl derivative, respectively, both exhibit simultaneous emissions from thermally nonequilibrated $^3\pi$–π^* and ^{3}d–π^* states in an alcohol glass.[1,2] This emissive behavior is unusual,[3] and it presumably occurs because the intraligand and charge-transfer states have different geometries and do not readily interconvert in rigid matrices.[2] The properties of the complexes are no less intriguing in fluid solution. Whereas the dmp complex is a good emitter in methanol ($\phi \approx 10^{-3}$) at room temperature, the phen complex exhibits almost no charge-transfer emission ($\phi \leqslant 10^{-5}$) under the same conditions. In the same solvent the dmp complex is prone to dissociate phosphine, while there is minimal dissociation from the phen analogue.[2]

Steric interactions are often important in complexes involving bulky phosphine ligands,[4-8] and we have suggested that steric effects could explain the differences in solution behavior of these copper systems.[2,9] In particular, steric repulsions among the 2- and 9-methyl substituents of dmp and the neighboring phosphines would promote phosphine dissociation. At the same time, steric crowding in the coordination shell would hinder the approach of a fifth ligand to the excited state. Hence solvent-induced quenching by an exciplex mechanism[9-11] would be impeded. Here we report the crystal and molecular structures of the nitrate salts of the dmp and phen complexes, and we identify the important interligand steric interactions in $\mathrm{Cu(dmp)(PPh_3)_2^+}$. In addition, we have carried out equilibrium analyses for both complexes in acetonitrile, and we find that the ligand binding constants also reflect the steric forces.

Experimental Section

Materials and Methods. The ligands dmp (99%) and $\mathrm{PPh_3}$ were purchased from Aldrich, phen was purchased from Fisher, and reagent grade $\mathrm{Cu(NO_3)_2{\cdot}3H_2O}$ was purchased from Baker. The chemicals were of adequate purity for synthetic purposes, but the $\mathrm{PPh_3}$ used in the equilibrium studies was recrystallized four times from ethanol. Yellow $\mathrm{[Cu(dmp)(PPh_3)_2]NO_3}$ and $\mathrm{[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH}$ were prepared as reported.[2] Crystals suitable for structure determination were obtained by slow evaporation of ethanol solutions. For the absorption measurements, reagent grade acetonitrile (Mallinckrodt) sufficed; however, for the luminescence work the solvent was distilled over $\mathrm{P_4O_{10}}$ in order to reduce blank emission.

The absorbance measurements were taken at 25 °C for the dmp and phen complexes with copper concentrations of 1.360×10^{-4} and 1.464×10^{-4} M, respectively. Spectra were obtained as a function of added $\mathrm{PPh_3}$. *Excess* $\mathrm{PPh_3}$ concentrations of up to 40 times the total copper concentration were employed for the dmp complex, whereas 10 times less phosphine was used for the phen complex. The equilibrium analyses were carried out with the program SPECDEC.[12] Luminescence studies were conducted on samples of the $\mathrm{BF_4^-}$ salts, which had been deoxygenated

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