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Cleavage Reactions of Halogen-Bridged Heterobimetallic Palladium-Platinum Complexes. Crystal and Molecular Structure of [(P-*n*-Bu$_3$)Cl$_2$Pd(*t*-BuN=CHCH=N-*t*-Bu)PtCl$_2$(P-*n*-Bu$_3$)]

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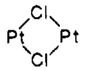
Cleavage reactions of dichloro-bridged species [(P-*n*-Bu$_3$)ClPd(μ-Cl)$_2$PtCl(P-*n*-Bu$_3$)] (I) with nitrogen-containing ligands (e.g. 4-cyanopyridine) and a variety of bis(phosphines) generally give mixtures of mononuclear products. However, reactions of I with bis(1-pyrazolyl)methane or with *N,N'*-dialkyl-1,2-diiminoethanes preserve the 1:1 Pd:Pt ratio and apparently give bridged heterobimetallic products. Crystals of the reaction product of I with *t*-BuN=CHCH=N-*t*-Bu, with a composition corresponding to [(P-*n*-Bu$_3$)ClPd(*t*-BuN=CHCH=N-*t*-Bu)PtCl(P-*n*-Bu$_3$)], are monoclinic, space group $P2_1/n$, with a = 11.454 (4) Å, b = 16.026 (4) Å, c = 12.909 (3) Å, and β = 99.91 (2)°. With Z = 2, the molecules must lie about inversion centers, 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 = 0.044 and R_w = 0.047 for 2707 reflections. The geometry around the metal atom is distorted square planar with M-P = 2.230 (2) Å, M-Cl = 2.295 (2) Å, and M-N = 2.135 (5) Å. The data are consistent with the preservation of a 1:1 Pd:Pt ratio in this product of a Pd(μ-Cl)$_2$Pt bridge cleavage reaction.

Introduction

Heterobimetallic compounds attract considerable interest at present, largely because of their relevance to catalysis. The possibility exists, at least theoretically, of developing model systems in which two adjacent but different metal centers can jointly catalyze a desired chemical transformation. Such a bimetallic combination of palladium and platinum would possess advantages. Although heterobimetallic complexes of palladium and platinum containing chelating ligands have been prepared,[1-3] few simple species having been fully characterized especially as discrete solid compounds. Recently, we investigated[4] the preparation of simple heterobimetallic complexes of the type [(PR$_3$)ClPd(μ-Cl)$_2$PtCl(PR$_3$)]; while we were able to show unambiguously that such species do exist in the solid state, a wide range of experimental evidence established that, in solution and perhaps also in the solid state, a temperature-independent equilibrium exists between such species and the Pd and Pt dimers [(PR$_3$)$_2$Pd$_2$Cl$_4$] and [(PR$_3$)$_2$Pt$_2$Cl$_4$]. Despite the occurrence of this equilibrium, the reaction of a solution of this mixture with bis(diphenylphosphino)acetylene gave a single product[5] containing disordered Pd and Pt but in an exactly 1:1 ratio. On the other hand, a similar reaction with bis(diphenylphosphino)ethane (diphos) produced only asymmetric cleavage products, notably *cis*-PtCl$_2$(diphos), *cis*-PtCl$_2$(PR$_3$)$_2$ and *trans*-PdCl$_2$(PR$_3$)$_2$. It is thus not at all clear as to which ligands will cleave asymmetrically the halo-bridged heterobimetallic species; more interestingly, the mechanism by which the halo-bridged heterobimetallic species is converted to a new heterobimetallic complex with a different bridging ligand(s), so as to preserve exactly the 1:1 Pd:Pt ratio, is by no means obvious. Accordingly, we have performed reactions with other symmetrical and unsymmetrical ligands, on which we now report, hoping to understand more fully some of the factors involved.

Results and Discussion

Two basically different types of reactions appear to occur when the solution mixture characterized as [(PR$_3$)ClPd(μ-Cl)$_2$PtCl(PR$_3$)] (I) is allowed to react with ligands capable of bridge cleavage. In the majority of cases, a mixture of mononuclear Pd and Pt complexes is obtained, but in the second type of reaction, bimetallic products are formed that preserve the 1:1 Pd:Pt ratio. Thus, reaction of I (PR$_3$ = P-*n*-Bu$_3$) with 4-cyanopyridine in 1:1 stoichiometry in dichloromethane solution gave quantitative yields of hexane-insoluble [P-*n*-Bu$_3$PdCl$_2$]$_2$ and hexane-soluble *trans*-[(P-*n*-Bu$_3$)(4-CN-py)PtCl$_2$] (^{31}P NMR: δ = −7.0, ^1J(Pt-P) = 3405 Hz). This suggests that reaction occurs preferentially at the



bridge and that consumption of this species causes further disproportionation of the heterobimetallic complex. Similarly, reaction with a variety of symmetrical and unsymmetrical bidentate ligands gave only mixtures of mononuclear Pd and Pt complexes. Thus, reaction of I (PR$_3$ = P-*n*-Bu$_3$) with bis(diphenylphosphino)methane (dppm, Ph$_2$PCH$_2$PPh$_2$) in benzene gave PtCl$_2$(dppm) (^{31}P NMR: δ = −71.1, ^1J(PPt) = 3100 Hz; lit.[6] δ = −69.7 (in CDCl$_3$ relative to trimethyl phosphate), ^1J(PPt) = 3088 Hz) and (P-*n*-Bu$_3$)$_2$PdCl$_2$. On the other hand, reaction of I (PR$_3$ = P-*n*-Bu$_3$) with bis(diphenylphosphino)ethane (Ph$_2$PCH$_2$CH$_2$PPh$_2$, dppe) in dichloromethane solution gave all four mononuclear products, *cis*-(dppe)PtCl$_2$ (^{31}P NMR: δ = 41.8, ^1J(PPt) = 3621 Hz; lit.[7] δ = 40.9, ^1J(PPt) = 3618 Hz), *trans*-(P-*n*-Bu$_3$)$_2$PtCl$_2$, *cis*-(dppe)PdCl$_2$ (^{31}P NMR: δ = 64.7), and *trans*-(P-*n*-Bu$_3$)$_2$PdCl$_2$. With unsymmetrical bidentate ligands, even more complex mixtures of products were apparently formed. The reaction of I (PR$_3$ = P-*n*-Bu$_3$) with Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (appe) gave a mixture containing probably six different products, of which, according to the ^{31}P NMR spectrum, (appe)PdCl$_2$, (appe)PtCl$_2$ and (P-*n*-Bu$_3$)$_2$MCl$_2$ (M = Pd, Pt) were probable components.

In contrast to the above rather complex reactions, only products containing Pd and Pt in a 1:1 ratio were obtained in reactions of I with bis(1-pyrazolyl)methane or with *N,N'*-dialkyl-1,2-diiminoethanes. Treatment of [(PPhMe$_2$)Cl$_2$Pd(μ-Cl$_2$)PtCl$_2$(PPhMe$_2$)] with bis(1-pyrazolyl)methane in dichloromethane solution gave a crystalline product of composition [(PPhMe$_2$)Cl$_2$Pd((pz)$_2$CH$_2$)PtCl$_2$(PPhMe$_2$)], in which the pyrazolyl rings provide the bridge between the two metal centers and for which the ^{31}P NMR spectrum shows three resonances, two of which display ^{195}Pt satellites. This might indicate that two forms of the product exist containing either a cis or a trans geometry at platinum, but with the same geometry at Pd in both forms. This would, however, require accidental degeneracy of two PdP resonances. Cleavage of the chloro-bridges of I with *N,N'*-dialkyl-1,2-diiminoethanes, (R'N=CHCH=NR', where R' = cyclohexyl

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Table I. Physical and Analytical Data for the Complexes $[(PR_3)Cl_2Pd(dim\text{-}R')PtCl_2(PR_3)]$[a]

complex	solvent of cryst	mp, °C	anal. found (calcd) % C	anal. found (calcd) % H	anal. found (calcd) % N
$[(PhMe_2P)Cl_2Pd(CH_2(pz)_2)PtCl_2(PPhMe_2)]$	benzene/hexane	125–130	31.97 (31.83)	3.54 (3.48)	7.14 (6.46)
$[(PEt_3)Cl_2Pt(dim\text{-}c\text{-}Hx)PtCl_2(PEt_3)]$	chloroform/hexane	195–200	31.43 (31.59)	5.42 (5.50)	3.04 (2.83)
$[(PEt_3)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PEt_3)]$	benzene/CH_2Cl_2/hexane	205–207	35.08 (34.70)	6.20 (6.05)	3.32 (3.11)
$[(PPr_3)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PPr_3)]$	benzene/hexane	184–185	39.65 (39.05)	6.40 (6.76)	2.88 (2.85)
$[(PhMe_2P)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PPhMe_2)]$	CH_2Cl_2/hexane	177–178	38.15 (38.33)	4.72 (4.65)	3.20 (2.98)
$[(PhMe_2P)Cl_2Pd(dim\text{-}t\text{-}Bu)PtCl_2(PhMe_2P)]$	CH_2Cl_2/$CHCl_3$/hexane	198–202	35.35 (35.17)	4.83 (4.77)	3.56 (3.15)
$[(PBu_3)Cl_2Pd(dim\text{-}t\text{-}Bu)PtCl_2(PBu_3)]$	benzene/hexane	129–130[b]	39.98 (40.18)	7.21 (7.34)	2.82 (2.76)

[a] dim-R′ = *N*,*N*′-dialkyl-1,2-diiminoethane. [b] With decomposition.

Table II. ^{31}P NMR Spectral Data for $[(PR_3)Cl_2M(NN)MCl_2(PR_3)]$ (M = Pd, Pt)

complex	solvent	δ(Pd–P)	δ(Pt–P)	$^1J(^{31}P\text{–}^{195}Pt)$, Hz
$[(PhMe_2P)Cl_2Pd(CH_2(pz)_2)PtCl_2(PPhMe_2)]$	$CDCl_3$	7.0	−19.7	3525
			−25.4	2569
$[(PEt_3)Cl_2Pt(dim\text{-}c\text{-}Hx)PtCl_2(PEt_3)]$	$CDCl_3$		−0.6	3391
$[(PEt_3)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PEt_3)]$	$CDCl_3$	34.2	−0.8	3401
$[(PPr_3)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PPr_3)]$	C_6D_6	25.0	−9.0	3423
$[(PhMe_2P)Cl_2Pd(dim\text{-}c\text{-}Hx)PtCl_2(PPhgMe_2)]$	$CDCl_3$	5.2	−25.6	3427
$[(PhMe_2P)Cl_2Pd(dim\text{-}t\text{-}Bu)PtCl_2(PPhMe_2)]$[a]	$CDCl_3$	5.1	−25.9	3496
$[(PBu_3)Cl_2Pd(dim\text{-}t\text{-}Bu)PtCl_2(PBu_3)]$[b]	C_6D_6	26.1	−8.0	3506

[a] Another small signal appears at 15.2 ppm. [b] Another small signal appears at 38.3 ppm.

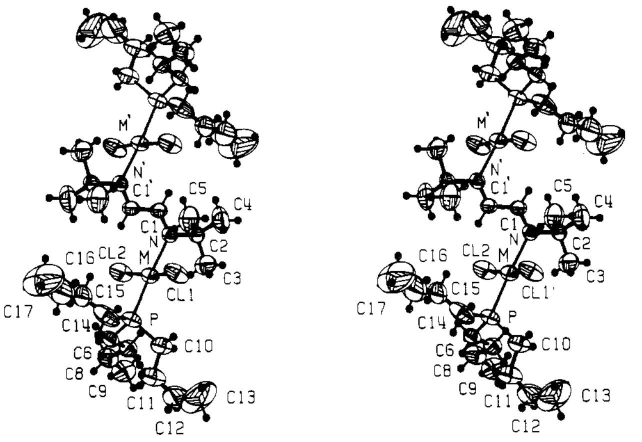


Figure 1. Stereoview of $C_{34}H_{74}Cl_4N_2P_2PdPt$ with ellipsoids at the 50% level.

(c-Hx) or *tert*-butyl (*t*-Bu); dim-R′)) gave products with the composition $[(PR_3)Cl_2Pd(dim\text{-}R')PtCl_2(PR_3)]$ as stable, yellow crystalline solids (Table I). Data for five such products are presented in Tables I and II; as Table II shows, each complex displayed two resonances of equal intensity in the ^{31}P NMR spectrum, only one of which showed coupling to ^{195}Pt. In the infrared spectra of both the ligands and the complexes, absorptions attributable to $\nu(C{=}N)$ appear in the region 1600–1625 cm^{-1}. In the free ligands, however, only one such band is observed, but in the complexes it is split into two distinct absorptions or is seen as an absorption with a noticeable shoulder. The absorption at higher frequency can be assigned to the Pd-bound N=C group and the lower frequency absorption to the Pt-bound N=C, although other explanations are also possible. These conclusions are supported by the observations that cleavage of the chloro-bridged diplatinum complex $[(PEt_3)_2Pt_2Cl_4]$ with dim-c-hx yields a similar yellow crystalline product whose ^{31}P NMR spectrum consisted of a single resonance with ^{195}Pt satellites and infrared spectrum consisted of a single $\nu(C{=}N)$ absorption at 1605 cm^{-1}. Nevertheless, all that the above results establish is that these products preserve the 1:1 Pd:Pt ratio of I; while the products might be pure heterobimetallic complexes, each might also be a 1:1 mixture of the Pt_2 and Pd_2 dimers, or mixtures of all three.

The single-crystal structure determination of $[P(n\text{-}Bu)_3Cl_2Pd(t\text{-}BuN{=}CHCH{=}N\text{-}t\text{-}Bu)PtCl_2(P\text{-}n\text{-}Bu_3)]$ is entirely consistent with the products maintaining the 1:1 Pd:Pt ratio of the starting material. The structure consists of discrete molecules apparently of the bimetallic complex separated by normal van der Waals distances. The molecule (Figure 1 and Table III) lies about an inversion center, which demands equal disorder of Pd and Pt atoms; the disordered Pd/Pt position is shown by M in Figure 1 and Table III.

Table III. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses[a]

(a) Distances

M–Cl(1)	2.298 (2)	P–C(10)	1.838 (9)
M–Cl(2)	2.292 (2)	P–C(14)	1.784 (9)
M–P	2.230 (2)	C(6)–C(7)	1.543 (11)
M–N	2.135 (5)	C(7)–C(8)	1.553 (11)
N–C(1)	1.254 (8)	C(8)–C(9)	1.472 (13)
N–C(2)	1.483 (8)	C(10)–C(11)	1.502 (12)
C(1)–C(1)^{I}	1.490 (14)	C(11)–C(12)	1.401 (18)
C(2)–C(3)	1.491 (12)	C(12)–C(13)	1.002 (26)
C(2)–C(4)	1.511 (13)	C(14)–C(15)	1.400 (15)
C(2)–C(5)	1.518 (13)	C(15)–C(16)	1.504 (17)
P–C(6)	1.812 (7)	C(16)–C(17)	0.967 (20)

(b) Angles

Cl(1)–M–Cl(2)	172.1 (1)	N–C(2)–C(3)	108.6 (6)
Cl(1)–M–P	88.5 (1)	N–C(2)–C(4)	108.7 (7)
Cl(1)–M–N	89.1 (2)	N–C(2)–C(5)	106.7 (7)
Cl(2)–M–P	94.1 (1)	C(3)–C(2)–C(4)	107.8 (9)
Cl(2)–M–N	88.6 (2)	C(3)–C(2)–C(5)	112.0 (8)
P–M–N	176.7 (2)	C(4)–C(2)–C(5)	113.0 (9)
M–P–C(6)	116.4 (3)	P–C(6)–C(7)	114.3 (5)
M–P–C(10)	111.7 (3)	C(6)–C(7)–C(8)	110.9 (7)
M–P–C(14)	110.0 (3)	C(7)–C(8)–C(9)	112.2 (9)
C(6)–P–C(10)	104.6 (4)	P–C(10)–C(11)	118.1 (7)
C(6)–P–C(14)	104.5 (4)	C(10)–C(11)–C(12)	116.7 (12)
C(10)–P–C(14)	109.0 (5)	C(11)–C(12)–C(13)	141.1 (26)
M–N–C(1)	121.7 (5)	P–C(14)–C(15)	119.4 (8)
M–N–C(2)	120.4 (4)	C(14)–C(15)–C(16)	119.0 (12)
C(1)–N–C(2)	117.8 (6)	C(15)–C(16)–C(17)	150.9 (30)
N–C(1)–C(1)^{I}	121.6 (8)		

(c) Deviations (Å) of Atoms from the Least-Squares Plane

atom	dev	atom	dev
M	0.044	Cl(2)	−0.104
P	0.080	N	0.088
Cl(1)	−0.108		

[a] Superscript I refers to equivalent position −*x*, −*y*, −*z*.

The geometry around the metal atom is distorted square planar (Table III). Because of the disorder of the Pd and Pt atoms, we cannot distinguish between Pd–X and Pt–X dimensions (where

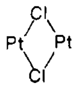
X = Cl, P, or N). The M–X dimensions in Table I (mean M–Cl = 2.295 (2), M–P = 2.230 (2), M–N = 2.135 (5) a) are close to values found in related molecules: M–Cl = 2.275–2.437 (1), M–P = 2.214 (1) Å in $[(PEt_3)ClPd(\mu\text{-}Cl)PtCl(PEt_3)]$[4]; M–Cl = 2.344 (2), M–P = 2.244 (2) Å in $[Cl_2Pd(Ph_2PC{\equiv}CPPh_2)PtCl_2]$[5]; Pt–Cl = 2.333 (2) and 2.356 (2) Å, Pt–P = 2.251 (2) and 2.265 (2) Å in $[PtCl_2(PPh_3)_2]$;[8] Pd–Cl = 2.290 (1), Pd–P = 2.337 (1) Å in $[PdCl_2(PPh_3)_2]$;[9] Pt–Cl = 2.297(3), Pt–N = 2.013 (6) Å in $[(C_7H_9N)(Me_2HCHO)PtCl_2]$;[10] Pt–Cl = 2.297 (2), Pt–P = 2.228 (3), Pt–N = 2.138 (7) Å in $[(PEt_3)Cl_2Pt(C_6H_{13}N)]$.[11]

The results of our analysis show that the metal atom disorder has no large effect on the central group of atoms linking the metal atoms. The bond lengths in this region are as anticipated (e.g. C=N = 1.254 (8), C(sp^2)—C(sp^2) = 1.490 (14), C—N = 1.483 (8) Å). The *n*-butyl side chains of the unique P-*n*-Bu$_3$ ligand show signs of considerable libration or disorder, and terminal methyl carbon atoms C(13) and C(17), which have the largest vibration parameters, have anomalously short bond lengths.

The interesting and surprising feature of this chemistry is the preservation of the 1:1 Pd:Pt ratio in the products of the reactions with the *N*,*N'*-dialkyl-1,2-diiminoethanes and bis(1-pyrazolyl)methane. We had previously shown[4] that the chloro-bridged species I, while certainly containing the heterobimetallic complex $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ in the solid state, exists in solution as the equilibrium

$$2(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3) \rightleftharpoons [(PR_3)PdCl_2]_2 + [(PR_3)PtCl_2]_2$$

Not only should there be subtle solubility differences between these three species and their respective reaction products depending on the solvent but there should also be differences in the ease of cleavage of the three different dichloro-bridged systems, II–IV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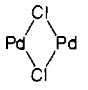
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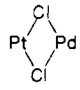
IV

It would, therefore, be reasonable to expect that, in cleavage reactions, the effect of the above factors would be to give a product richer in *either* Pd or Pt. This is obviously not the case for the reactions of I with 1,2-bis(diphenylphosphino)acetylene[5] or for the present reactions with $(pz)_2CH_2$ or dim-R' where the 1:1 Pd:Pt ratio is preserved. To understand why this is so, and also to understand why other bidentate ligands including different diphosphines give only mononuclear products, would require a detailed appreciation of the mechanism of the cleavage reactions. The complex nature of I would make such mechanistic investigations a formidable task.

Experimental Section

The preparation of the starting material, which we refer to as $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$, has been described previously.[4] The dinitrogen ligands R'N=CHCH=NR' (R' = cyclohexyl or *tert*-butyl)[12] and bis(1-pyrazolyl)methane[13] were prepared by literature methods. Phosphine and arsine ligands were obtained from Strem Chemical Co., and all manipulations involving them were performed under a nitrogen atmosphere. Spectrograde solvents were used throughout this work.

^{31}P NMR spectra were recorded on Bruker WP-60 and Bruker WH-200 spectrometers operating in the Fourier transform mode at 24.29 and 161.98 MHz, respectively. Spectra were recorded in $CDCl_3$ or C_6D_6 solutions unless otherwise stated, and ^{31}P chemical shifts were measured relative to external H_3PO_4, more positive values representing deshielding. Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer using Nujol mulls between KBr plates. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

Table IV. Final Fractional Coordinates (M, ×10^5; Remainder, ×10^4) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
M[a]	22397 (3)	9438 (2)	8208 (3)
P	3055 (2)	2048 (1)	1718 (2)
Cl(1)	1775 (3)	1788 (1)	−630 (2)
Cl(2)	2430 (3)	100 (1)	2274 (2)
N	1507 (5)	−91 (3)	−111 (5)
C(1)	419 (6)	−252 (5)	−254 (6)
C(2)	2274 (7)	−628 (5)	−647 (6)
C(3)	3512 (8)	−306 (6)	−403 (10)
C(4)	1866 (11)	−560 (9)	−1821 (8)
C(5)	2174 (10)	−1507 (6)	−233 (10)
C(6)	3839 (7)	1851 (5)	3038 (6)
C(7)	4975 (7)	1325 (5)	3086 (6)
C(8)	5425 (10)	1009 (6)	4222 (7)
C(9)	6607 (9)	625 (7)	4333 (9)
C(10)	4153 (8)	2561 (5)	1048 (7)
C(11)	4716 (11)	3354 (7)	1513 (9)
C(12)	5552 (25)	3727 (14)	986 (17)
C(13)	5824 (25)	3724 (13)	288 (25)
C(14)	1935 (10)	2784 (13)	1887 (9)
C(15)	982 (9)	2529 (7)	2359 (10)
C(16)	8 (15)	3141 (12)	2444 (16)
C(17)	−763 (20)	3271 (15)	2611 (24)

[a] M is the disordered Pt–Pd atom.

Preparation of the Complexes $[(PEt_3)Cl_2Pd(RN{=}CHCH{=}NR)PtCl_2(PEt_3)]$. Typically, to the chloro-bridged startingmaterial, $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)$ (83 mg) in dichloromethane (ca. 15 mL) was added a dichloromethane solution (ca. 8 mL) of *N*,*N'*-dialkyl-1,2-diiminoethane (in this example dim-c-Hz) (28 mg) was added dropwise with stirring over a period of 20 min. Stirring was continued for a further 1 h, and the solvent was then pumped off to leave a yellow residue. This was dissolved in a 1:1 (v/v) mixture of benzene/dichloromethane (ca. 5 mL) in a small beaker (20 mL). Hexane (ca. 5 mL) was added slowly, and the solution was set aside for crystallization to occur. After a few hours, the supernatant liquid was decanted off the resulting yellow crystals, which were washed with hexane and dried. Yield: 78 mg, 70%. The related complexes were all prepared similarly, and pertinent analytical data for the products are given in Table I. The reactions with bis(1-pyrazolyl)methane and with phosphine and arsine ligands were generally performed similarly, although for the latter, product characterization was based on NMR parameters as described in the text.

Crystal Data and Structure Determination. Crystal data: $C_{34}H_{74}Cl_4N_2P_2PdPt$, M_r = 1016.23, monoclinic, a = 11.454 (4) Å, b = 16.026 (4) Å, c = 12.909 (3) Å, β = 99.91 (2)°, V = 2334 (2) Å^3, D_c = 1.45 g cm^{-3}, Z = 2, $F(000)$ = 1028, Mo Kα radiation, γ = 0.710 69 Å, μ(Mo Kα) = 38.45 cm^{-1}. Space group $P2_1/n$ was uniquely determined from the systematic absences ($h0l$ if $h + l = 2n + 1$; $0k0$ if $k = 2n + 1$).

Data were collected to a maximum θ of 24° on an Enraf Nonias CAD4 diffractometer by the $\omega/2\theta$ scan technique using monochromatized Mo Kα radiation and a yellow crystal of dimension 0.35 × 0.40 × 0.60 mm, cut from a larger plate. After machine location and centering of 25 reflections with θ in the range $10° < \theta < 15°$, accurate cell constants and the orientation matrix were obtained by a least-square refinement. The intensities of three standard reflections monitored at regular intervals did not change significantly over the period of data collection. The data were corrected[14] for Lorentz and polarization factors, and for absorption.[15] Maximum and minimum values for the transmission coefficients are 0.361 and 0.186 respectively. A total of 4014 reflections were measured with $+h,+k,\pm l$. After equivalent reflections were averaged (R_{int} = 0.030), we were left with 3661 unique observations of which the 2707 with $I > 3\sigma(I)$ were used in structure selection and refinement.

The structure was solved by the heavy-atom method. With two molecules in the unit cell, space group $P2_1/n$ requires the molecules to be on inversion centers; consequently, there is equal disorder of the palladium and platinum atoms.

Initial refinement by full-matrix least-squares calculations with isotropic temperature factors for the non-hydrogen atoms lowered R to 0.109, which further dropped to 0.051 after six cycles of anisotropic refinement. A difference map calculated at this stage revealed maxima

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(1.0–0.4 e Å^{-3}) corresponding to the hydrogen atoms, which were included in the subsequent refinement in geometrically idealized positions (C–H = 0.95 Å), and in addition overall isotropic thermal parameters were refined for the various types of hydrogen atoms. In the final cycles of refinement, a weighting scheme of the form $w = 1/(\sigma^2F + pF^2)$ was employed where the final p parameter was 0.0032. Scattering factors used in the structure factor calculations were taken from ref 16 for non-hydrogen atoms and ref 17 for hydrogen atoms, and allowance was made for anomalous dispersion. A composite scattering factor curve with 0.5 occupancy for Pd and Pt was used for the disordered metal site. Refinement converged with $R = 0.044$ and $R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2} = 0.047$. A difference map calculated at the conclusion of the refinement showed electron density (~1.0 e Å^{-3}) in the vicinity of the metal atom and was insignificant.

The final fractional coordinates with estimated standard deviations are given in Table IV. Tables of hydrogen coordinates, anisotropic temperature factors and a structure factor listing have been deposited as supplementary material.

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Registry No. $(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)$, 95387-53-4; $(PhMe_2P)Cl_2Pd(CH_2(pz)_2)PtCl_2(PPhMe_2)$, 103835-56-9; $(PEt_3)Cl_2Pt(\text{dim-c-Hx})PtCl_2(PEt_3)$, 103835-57-0; $(PEt_3)Cl_2Pd(\text{dim-c-Hx})PtCl_2(PEt_3)$, 103835-58-1; $(PPr_3)Cl_2Pd(\text{dim-c-Hx})PtCl_2(PPr_3)$, 103835-59-2; $(PhMe_2P)Cl_2Pd(\text{dim-c-Hx})PtCl_2(PPhMe_2)$, 103835-60-5; $(PhMe_2P)Cl_2Pd(\text{dim-}t\text{-Bu})PtCl_2(PhMe_2P)$, 103835-61-6; $(PBu_3)Cl_2Pd(\text{dim-}t\text{-Bu})PtCl_2(PBu_3)$, 103835-62-7.

Supplementary Material Available: Listings of anisotropic thermal parameters and calculated hydrogen atom coordinates (3 pages). Ordering information is given on any current masthead page.

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Complexes with Phosphinomethanes and -methanides as Ligands. 10.[1] Formation, Structure, and Properties of $\{[(PMe_2CH_2PMe_2)(PMe_3)Co]_2PMe_2\}$, a Dinuclear, Odd-Electron Cobalt Complex of Formal Oxidation State Co_2^+. Electronic Structure of $[CoL_3]_2PR_2$ Radicals

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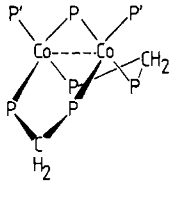
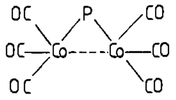
The paramagnetic, dinuclear complex $\{[(PMe_3)(Me_2PCH_2PMe_2)Co]_2PMe_2\}$ (**1**) is formed by P–C cleavage of a phosphine–Co(0) intermediate. Its solid-state structure was determined by X-ray diffraction methods (hexagonal, space group $P6_3/m$; $Z = 6$; $a = b = 16.285$ (7), $c = 19.296$ (6) Å; $R = 0.068$, $R_w = 0.062$, $w = 1/\sigma^2(F_o)$ for 130 refined parameters and 817 observables with $F_o \geq 4.0\sigma(F_o)$). Each cobalt atom binds four P atoms in a pseudotetrahedral environment. Two $Me_2PCH_2PMe_2$ groups and one PMe_2 group bridge the two cobalt atoms. The Co–Co distance is 2.603 (3) Å. The magnetic moment ($\mu_{\text{eff}} = 1.85$ (15) μ_B) is temperature-independent and corresponds to the presence of one unpaired electron. This is in accord with MO calculations (EHT), which show the delocalized electron to occupy a Co–Co antibonding (δ^*) and mainly metal centered SOMO. The results are compared with model calculations for the related complex $\{[(CO)_3Co]_2P[CH(SiMe_3)_2]_2\}$. In both cases actual geometries and ligand donor or acceptor properties of the Co_2L_6 skeleton have a pronounced effect upon energy and composition of the singly occupied molecular orbital. The molecular orbital results are in accord with cyclovoltammetric measurements, which reveal the existence of one reduction and three distinct oxidation steps for **1**, which are quasi-reversible. The diamagnetic monocation **1**$^+$ is obtained by chemical oxidation of **1** and isolated as the BF_4^- salt. This complex cation exhibits fluxional behavior in solution (NMR), analogous to so-called molecular "A-frames".

Introduction

Much of the research on dinuclear complexes is dominated by the interest in metal–metal interactions[2] and, most recently, in so-called molecular "A-frames",[3,4] where two nearly planar metal centers are triply bridged by two diphosphino- (or diarsino-) methane ligands and an "apex" ligand like Cl, S, CO, SO_2, SR, PR_2, or others. Most of the A-frames described so far contain $Ph_2PCH_2PPh_2$ ligands. As an attractive alternative we have introduced $Me_2PCH_2PMe_2$[5] as a sterically less demanding ligand in metal complexes, which in addition improves their solubility properties.[5b] Therefore, a rapidly growing number of complexes with $Me_2PCH_2PMe_2$ ligands has now been described.[6] Normally the A-frames so far reported are even-electron-numbered, closed-shell diamagnetic compounds. In a preliminary communication we have briefly reported the formation and X-ray structure of the triply bridged dicobalt complex $\{[(PMe_3)(Me_2PCH_2PMe_2)Co]_2PMe_2\}$ (**1**),[6a] which formally seems related



1 (P=PMe$_2$, P'=PMe$_3$)



2 (P=P[CH(SiMe$_3$)$_2$]$_2$)

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