Table IV. X-ray Diffraction Powder Pattern of H_3OSbF_6 at about 370 K[a]

d_{obsd}, Å	d_{calcd}, Å	intens	*hkl*
5.12	5.12	vs	100
3.62	3.62	s	110
2.957	2.960	vw	111
2.560	2.563	w	200
2.293	2.292	vw	210
2.096	2.093	vw	211
1.813	1.813	vw	220
1.711	1.709	w	300, 221
1.621	1.621	w	310
1.371	1.370	w	321
1.281	1.282	vw	400
1.242	1.243	vw	410, 322
1.209	1.208	vw	411, 330

[a] Cubic, a = 5.126 (1) Å, V = 134.7 (1) Å^3, Z = 1, ρ_{calcd} = 3.14 g cm^{-3}, monochromatized Cu Kα_1 radiation (λ = 1.540 562 Å), Guinier-Simon camera, diameter 114.6 mm.

at low temperatures: $KAsF_6$ with one formula unit in a rhombohedral cell[12] and H_3OSbF_6 (as well as D_3OSbF_6) with eight formula units in a cubic, but large, body-centered cell.[4] In comparison, the high-temperature form of $KAsF_6$[13] is isotypic to that of H_3OAsF_6. For the structure of a high-temperature form of H_3OSbF_6 see the Appendix.

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Appendix: Unit Cell of H_3OSbF_6 at about 370 K

H_3OSbF_6 was prepared and studied by DTA and X-ray powder analysis between 103 and 423 K in a similar way as described in the Experimental Section for H_3OAsF_6. The phase transition in this temperature range, reported to occur at 361 ± 12 K,[4] was found at 368 K. Also, the reported X-ray powder pattern and crystal structure of the low-temperature form[4] was confirmed. In addition, the powder pattern of the high-temperature form was obtained and indexed for a cubic primitive unit cell with Z = 1 and a = 5.126 (1) Å (Table IV). From this the ions appear to be centered on the atomic positions of the small unit cell of the CsCl structure type.

Registry No. H_3OAsF_6, 21501-81-5; H_3OSbF_6, 55649-03-1.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

(12) Gafner, G.; Kruger, G. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 250.
(13) Heyns, A. M.; Pistorius, C. W. F. T. *Spectrochim. Acta, Part A* **1975**, *31A*, 1293.

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Binuclear Complexes of Platinum(II) and Palladium(II) with Bis(isopropylphosphino)methane and Related Ligands

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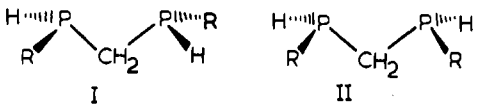
Bidentate phosphines $R_2PCH_2PR_2$ are often used as bridging ligands and are useful for reducing the tendency toward fragmentation of dimers to monomeric complexes during chemical reactions.[2,3] The chemistry of the secondary phosphine analogues such as R_2PCH_2PHR or $RHPCH_2PHR$ has hardly been studied.[4,5] through the presence of the PH group could lead to significantly different reactivity. Thus both the low steric hindrance of the PH substituent[6,7] and the ability of the PH group to undergo deprotonation and form a second potential bridging group, based on the resultant phosphido functionality,[8] could have major effects on the coordination chemistry. Earlier papers have been concerned with the effects of steric hindrance of ligands $R_2PCH_2PR_2$ on the coordination chemistry and organometallic reactivity of platinum complexes.[3,6,7,9] In this paper, the synthesis and some coordination complexes of the ligand *i*-PrHPCH$_2$PH-*i*-Pr are described.

Results and Discussion

Synthesis and Characterization of the Ligand. The ligand *i*-PrHPCH$_2$PH-*i*-Pr was prepared by reaction of $Cl_2PCH_2PCl_2$ with 2 molar equiv of *i*-PrMgBr followed by reduction of this reaction mixture with excess Li[AlH$_4$]. Analysis of the crude product by $^{31}P\{^1H\}$ and ^{31}P NMR indicated the presence of $H_2PCH_2PH_2$, *i*-PrHPCH$_2$PH$_2$ and *i*-Pr$_2$PCH$_2$PH-*i*-Pr as well as the desired compound. However, vacuum distillation gave a good separation of pure *i*-PrHPCH$_2$PH-*i*-Pr as a colorless, air-sensitive liquid. An independent synthesis of the ligand was reported while this research was in progress.[5] The ligand exists either as a mixture of isomers or in a configuration in which the two phosphorus atoms are nonequivalent but do not couple to each other, as shown by the $^{31}P\{^1H\}$ NMR spectrum, which contained two sharp singlets, of approximately equal intensity, at δ −46.20 and −47.61, each of which split into a doublet [^1J(PH) = 205 Hz] in the proton-coupled ^{31}P spectrum. Similarly, the ^1H NMR spectrum contained two C*H*Me$_2$ and two CH_2P$_2$ multiplets, tentatively attributed to the two isomeric forms, though the P*H* and CH_3C resonances of the two isomers were not resolved. The two isomers could be the racemic and meso isomers I and II, but it is also possible that they



are conformers that cannot readily interconvert due to restricted rotation about the P–C bonds.

Synthesis and Characterization of $[M_2X_4(\mu\text{-PP})_2]$ Complexes. Reaction of $[PtCl_2(SMe_2)_2]$ with PP in a 1:1 molar ratio gave the binuclear *cis,cis*-$[Pt_2Cl_4(\mu\text{-PP})_2]$ in two isomeric forms, **1a** and **1b**, which were easily separated by taking advantage of the much greater solubility of **1b** in organic solvents. Isomer **1a** gave a singlet, with apparent doublet satellites due to coupling to ^{195}Pt [^1J(PtP) = 3360, ^3J(PtP) = 80, $^2J + {}^4J$(PP) = 36 Hz], characteristic of the cis,cis stereochemistry with phosphorus trans to Cl.[7] These data are very similar to those for *cis,cis*-[Pt$_2$Cl$_4$(μ-*t*-BuHPCH$_2$PH-*t*-Bu)$_2$], and **1a** therefore has the symmetrical structure III with M = Pt, X = Cl, and R = *i*-Pr, in which all bulky isopropyl groups are equatorial and in which both diphosphine ligands are in the racemic form (I).

In contrast, the isomer **1b** gave four multiplets of equal intensity in the $^{31}P\{^1H\}$ NMR spectrum, each with ^1J(PtP) = 3300–3360

(1) On leave from Department of Chemistry, A. Mickiewicz University, Poznan, Poland.
(2) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L., Ed.; Plenum: New York, 1983.
(3) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.
(4) Brauer, D. J.; Hietkamp, S.; Sommer, H.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 734.
(5) Hietkamp, S.; Sommer, H.; Stelzer, O. *Chem. Ber.* **1984**, *117*, 3400.
(6) Steric effects on the chemistry of $R_2PCH_2PR_2$ ligands have been discussed previously: (a) Manojlović-Muir, Lj.; Muir, K. W.; Frew, A. A.; Ling, S. S. M.; Thomson, M. A.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 1637. (b) McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 485. (c) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (d) Lee, K.-W.; Brown, T. L. *Organometallics* **1985**, *4*, 1025.
(7) Azam, K. A.; Ferguson, G.; Ling, S. S. M.; Parvez, M.; Puddephatt, R. J.; Srokowski, D. *Inorg. Chem.* **1985**, *24*, 2799.
(8) Chen, L.; Kountz, D. J.; Meek, D. W. *Organometallics* **1985**, *4*, 598.
(9) Manojlović-Muir, Lj.; Jobe, I. R.; Ling, S. S. M.; McLennan, A. J.; Puddephatta, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1725.

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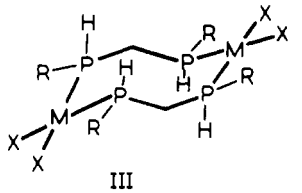
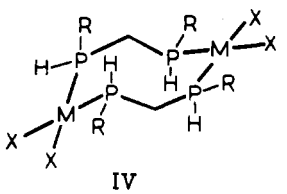


III

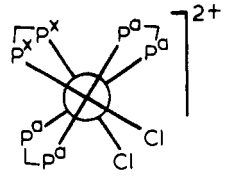


IV

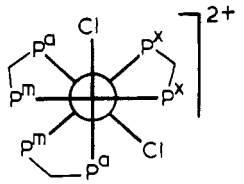
Hz, as expected for phosphorus atoms trans to chloride, and each gave a further doublet splitting with $^1J(PH) \sim 400$ Hz in the proton coupled ^{31}P NMR spectrum. This complex is therefore proposed to have structure IV, which contains one racemic (I) and one meso (II) diphosphine. In IV, all phosphorus atoms are nonequivalent as observed and one bulky isopropyl substituent must be in an axial position where steric hindrance is greater.[7] With the bulkier *t*-Bu substituents only isomer III (M = Pt, X = Cl, R = *t*-Bu) was formed.[7]

Very similar behavior was observed on reaction of the diphosphine ligands with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. With *i*-PrHPCH$_2$PH-*i*-Pr, the complex *cis,cis*-$[Pt_2Me_4(\mu\text{-}PP)_2]$ was formed as a mixture of isomers **2a** and **2b** of structures III and IV, respectively, but with *t*-BuHPCH$_2$PH-*t*-Bu, only *cis,cis*-$[Pt_2Me_4(\mu\text{-}t\text{-}BuHPCH_2PHt\text{-}Bu)]$ (**3a**) of structure III was formed. In this case, **2a** and **2b** could not be separated and were characterized spectroscopically as a mixture. Similarly, *i*-PrHPCH$_2$PH-*i*-Pr with $[PdCl_2(PhCN)_2]$ gave *cis,cis*-$[Pd_2Cl_4(\mu\text{-}PP)_2]$ as a mixture of isomers **4a** and **4b**, which are assigned structures III and IV, respectively, on the basis of the similarity of the NMR data to those of the platinum analogues **1a** and **1b**. Again **4b** gave four resonances in the $^{31}P\{^1H\}$ NMR spectrum, each resonance giving a further doublet splitting with $^1J(PH) \sim 400$ Hz in the proton-coupled ^{31}P NMR spectrum, and could be separated from **4a** by the great difference in solubility.

Synthesis and Characterization of Complex Cations of $[M_2Cl_2(\mu\text{-}PP)_3]^{2+}$. Reaction of $[PtCl_2(SMe_2)_2]$ with 1.5 or 2 molar equiv of *i*-PrHPCH$_2$PH-*i*-Pr gave $[Pt_2Cl_2(\mu\text{-}PP)_3]Cl_2$ (**5a**), and the chloride anions were readily exchanged to give $[Pt_2Cl_2(\mu\text{-}PP)_3][PF_6]_2$ (**5b**) by using $NH_4[PF_6]$. The structure of the cation is deduced to be VI, drawn as a Newman projection along the



V



VI

PtPt axis, largely on the basis of the $^{31}P\{^1H\}$ and ^{31}P NMR spectra (Figure 1).

The spectra contain three complex resonances, each having satellites due to coupling to ^{195}Pt, and can be interpreted in terms of an $[AMX]_2$ spin system (see structure VI). The combination of coupling constants gives a spectrum that can be analyzed by first-order methods, and a good simulation of the observed spectrum was obtained. There are three resonances, each with chemical shifts expected for μ-PP ligands and with characteristic $^1J(PtP)$ values of 3100 (P^a, trans to Cl), 2240 (P^x, trans to P^m), and 2200 Hz (P^m, trans to P^x). The presence of P^m trans to P^x is confirmed by the large coupling $^2J(P^xP^m) = 370$ Hz. These parameters are only consistent with structures V and VI. Both structures V and VI are derived from $[Pt_2Cl_4(\mu\text{-}PP)_2]$ by displacement of one chloride ligand on each platinum by a third μ-PP ligand, but differ in the orientation of the third μ-PP ligand. Thus VI is locked rigidly in a staggered conformation while V could have an eclipsed configuration or could also be staggered but fluxional. Structure VI necessarily has three phosphorus environments whereas V, in its most symmetrical form, could have only two. Structure VI has been established crystallographically for the hydride $[Pt_2H_2(\mu\text{-}Et_2PCH_2PEt_2)_3]^{2+}$, and from the similarities in the ^{31}P NMR data, this structure is considered most probable for **5a** and **5b**.[9]

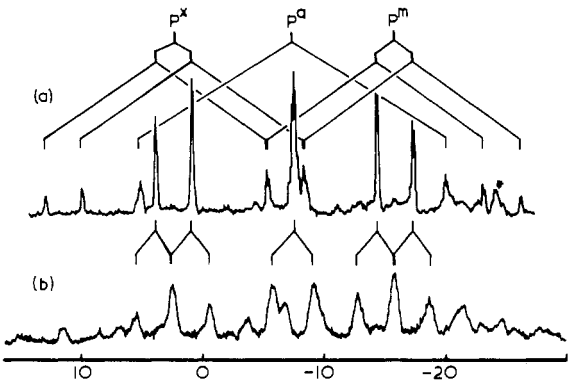


Figure 1. ^{31}P NMR spectra (121 MHz) of complex **5b**: (a) ^1H decoupled; (b) ^1H coupled. Assignments and ^{195}Pt satellite positions are given above and doublet splittings due to $^1J(PH)$ are given below spectrum a.

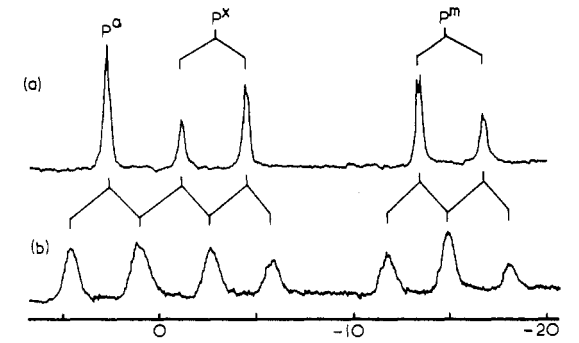
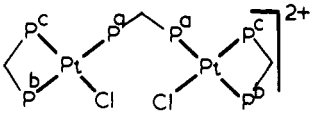


Figure 2. ^{31}P NMR spectra (121 MHz) of complex **6a**: (a) ^1H decoupled; (b) ^1H coupled.

Similarly, $[PdCl_2(PhCN)_2]$ reacted with excess ligand PP to give $[Pd_2Cl_2(\mu\text{-}PP)_3]Cl_2$ (**6a**) and, by anion exchange, $[Pd_2Cl_2(\mu\text{-}PP)_3][PF_6]_2$ (**6b**). The ^{31}P and $^{31}P\{^1H\}$ NMR parameters were very similar to those of the platinum analogues and indicate that they have the same structure (Figure 2). There were significant differences in ^{31}P chemical shifts betwween the chloride and hexafluorophosphate salts, which are attributed to the effects of ion pairing in the chloride derivative.

In contrast, the complex of formula $[Pt_2Cl_2(PP)_3]^{2+}$, where PP = $Et_2PCH_2PEt_2$ (depm) was characterized as having structure VII, $[Pt_2Cl_2(depm)_2(\mu\text{-}depm)]^{2+}$. The ^{31}P NMR spectrum again contained three signals, but two were in the region expected for chelate ligands ($\delta = -45.5$ and -50.8) and one was in the region typical of a bridging ligand ($\delta = +10.7$). A large coupling between the mutually trans phosphorus atoms P^a and P^b of structure VII was observed.



VII

Discussion

There are a number of unusual aspects of the coordination chemistry of the ligand *i*-PrHPCH$_2$PH-*i*-Pr with square-planar platinum(II) and palladium(II) complexes. These can be understood in terms of the low steric demands of the PH groups and the presence of two chiral phosphorus centers in the ligand.

The low steric demand of the PH substituents is thought to be the major factor in favoring binuclear complex formation. This has been discussed previously for derivatives $[M_2X_4(\mu\text{-}R_2PCH_2PR_2)_2]$ and $[MX_2(R_2PCH_2PR_2)]$.[6,7] It is also considered to be an important factor in formation of $[M_2Cl_2(\mu\text{-}PP)_3]^{2+}$ complexes, which appear to be the first examples of complexes with this general formula. In this case the ability of the very small PH substituents to mesh with the bulky isopropyl groups allows the presence of three μ-PP ligands. The related ligand

$Et_2PCH_2PEt_2$ (depm) is the only other diphosphine, of the many we have studied, which gives a complex with an analogous formula, but this has the structure $[\{PtCl(depm)\}_2(\mu\text{-depm})]^{2+}$ (VII), having only one bridging diphosphine ligand. Ligands with larger substituents, such as $Ph_2PCH_2PPh_2$ or $i\text{-}Pr_2PCH_2P\text{-}i\text{-}Pr_2$, give only $[PtCl_2(PP)]$ or $[Pt(PP)_2]^{2+}$ having only chelate ligands.[7] In these cases, binuclear complexes with square-planar metal centers and three $\mu\text{-}R_2PCH_2PR_2$ ligands are unfavorable due to steric hindrance between PR substituents on neighboring phosphorus centers. Although it is still not possible to predict in advance the stable product in all such reactions, this and the immediately preceeding papers[6,7] provide a framework that does allow planned synthesis from many ligands of the type $RR'PCH_2PRR'$.

The presence of chiral phosphorus centers leads to a new form of isomerism in the binuclear complexes *cis,cis*-$[M_2X_4(\mu\text{-PP})_2]$. The less soluble form has a symmetrical structure (III) with all *i*-Pr groups equatorial, while the more soluble form is assigned structure IV with one axial *i*-Pr group. There are many possible isomers of $[M_2Cl_2(\mu\text{-PP})_3]^{2+}$. With phosphines $R_2PCH_2PR_2$, forms V and VI can be distinguished by the number of ^{31}P resonances, two and three respectively, and both are found in the hydride derivatives $[Pt_2H_2(\mu\text{-depm})_3]^{2+}$ (VI) and $[Pt_2H_2(\mu\text{-deopm})_3]^{2+}$ (V) (deopm = $(EtO)_2PCH_2P(OEt_2)_2$) formed by double protonation of $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3]$.[9] Because of the chiral phosphorus centers, the most symmetrical form of V also has three nonequivalent phosphorus environments and so structures V and VI cannot be distinguished unambiguously by using this criterion. We have been unable to grow single crystals suitable for X-ray structure determination, and the preference for VI is based on the pattern of PP coupling constants.

Experimental Section

NMR spectra were recorded by using Varian XL100, XL200 and XL300 spectrometers. Chemical shifts were quoted with respect to Me_4Si (^1H) or trimethyl phosphate (^{31}P). Analyses were performed by Guelph Chemical Laboratories Ltd. $[PtCl_2(SMe_2)_2]$, $[Pt_2Me_4(SMe_2)_2]$, $[PdCl_2(C_6H_5CN)_2]$, and $Cl_2PCH_2PCl_2$ were prepared by the literature methods. All syntheses and reactions involving phosphine ligands were carried out under an atmosphere of dry nitrogen.

***i*-PrHPCH$_2$PH-*i*-Pr.** A solution of *i*-PrMgBr prepared from Mg turnings (3.28 g, 0.135 mol) and 2-bromopropane (16.60 g, 0.135 mol) in diethyl ether (120 mL) was added dropwise to a solution of $Cl_2PCH_2PCl_2$ (13 g, 0.06 mol) in diethyl ether (100 mL) over a period of 1 h at −78 °C. After 2 h of stirring, a suspension of $LiAlH_4$ (4.55 g, 0.12 mol) in ether (200 mL) was added dropwise at −10 °C over a period of 30 min. The stirring was continued overnight. The mixture was hydrolyzed with cold deoxygenated water (50 mL). The ether layer was separated, and the residue was extracted twice with ether. The combined ether extracts were dried with anhydrous Na_2SO_4, and the ether was distilled off. The ^{31}P NMR of the crude mixing in $CDCl_3$ showed signals at δ 2.65 and −48.6 for *i*-Pr_2PCH_2PH-*i*-Pr; δ = −31.5 and −140.50 for *i*-$PrHPCH_2PH_2$; δ = −122.80 for $H_2PCH_2PH_2$; and δ = 46.11 and −47.62 for *i*-$PrHPCH_2PH$-*i*-Pr. This was distilled under vacuum to give pure *i*-$PrHPCH_2PH$-*i*-Pr (3.4 g), bp 46 °C (1 mm). ^1H NMR (CD_2Cl_2): δ 1.08 (m, 6 H, CH_3); 1.44, 1.73 (m, 2 H, CH_2P_2); 1.64, 2.0 (m, 2 H, CH); 3.10 [m, 2 H, J(PH) = 204 Hz, PH]. ^{31}P NMR: −46.20 (s), −47.61 (s); each with ^1J(PH) = 205 Hz in the ^1H-coupled spectrum. in the distillation at 1 mm Hg pressure, $H_2PCH_2PH_2$ evaporated below room temperature, *i*-$PrPHCH_2PH_2$ (yield 0.9 g) distilled at 25 °C, and *i*-Pr_2PCH_2PH-*i*-Pr (yield 1.4 g) distilled at 60 °C.

$[Pt_2Cl_4(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_2]$ (1). To $[PtCl_2(SMe_2)_2]$ (0.21 g, 0.53 mmol) dissolved in CH_2Cl_2 (10 mL) was added diphosphine (0.09 g, 0.53 mmol) in CH_2Cl_2 (5 mL) dropwise with stirring. After 2 h the resultant white precipitate of isomer **1a** was filtered off and dried under vacuum; yield 0.13 g. ^{31}P NMR: δ 5.83 [m; ^1J(PtP) = 3360, ^3J(PtP) = 80, ^1J(PH) = 410 Hz]. The solvent was then removed from the filtrate and the yellow solid of isomer **1b** was washed with ether and dried under vacuum. A sample was recrystallized from CH_2Cl_2–pentane by slow diffusion; yield 0.29 g. Anal. Calcd for $C_{14}H_{36}Cl_4P_4Pt_2$: C, 19.54, H; 4.22. Found for **1a**: C, 19.27; H, 4.03. Found for **1b**: C, 19.0; H, 4.1. Mp: >320 °C (**1a**); 210–215 °C (**1b**). ^1H NMR (CD_2Cl_2): δ 1.40 (m, CH_3), 1.58 (CH_2P_2), 2.80 (m, CH), 4.36 [d, ^1J(PH) = 410 Hz, PH]. ^{31}P NMR: δ 9.02 [m; ^1J(PtP) = 3300, ^3J(PtP) = 150, ^2J(PP) = 30, ^1J(PH) = 400 Hz], 6.95 [m; ^1J(PtP) = 3300, ^3J(PtP) = 150, ^2J(PP) = 30, ^1J(PH) = 390 Hz], −2.02 [m; ^1J(PtP) = 3360, ^3J(PtP) = 150, ^2J(PP) 30, ^1J(PH) = 420 Hz], −6.39 [m; ^1J(PtP) = 3360, ^3J(PtP) = 150, ^2J(PP) = 30, ^1J(PH) = 390 Hz].

$[Pt_2Me_4(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_2]$ (2). A solution of diphosphine (0.018 g, 0.11 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of $[Pt_2Me_4(SMe_2)_2]$ (0.05 g, 0.087 mmol) in CH_2Cl_2 (2 mL). After 1 h of stirring, the solution was evaporated to 3-mL volume and hexane was added. The resulted yellow precipitate was washed with ether and pentane and dried under vacuum; yield 0.048 g. Anal. Calcd for $C_{18}H_{48}P_4Pt_2$: C, 27.06; H, 6.28. Found: C, 26.42; H, 5.89. MP: 210 °C. ^1H NMR (C_3D_6O): δ 0.35 [m, ^2J(PtH) = 80 Hz, CH_3Pt], 1.20 (m, CH_3), 1.38 (CH_2P_2), 2.25 (m, CH), 4.46 [d, ^1J(PH) ~ 340 Hz, PH], 4.20 [*d*, ^1J(PH) = 350 Hz, PH]. ^{31}P NMR for **2a**: δ 9.29 [m; ^1J(PtP) = 1805, ^3J(PtP) = 75, ^1J(PH) = 380, ^2J(PP) = 44, ^4J(PP) = 28 Hz]. ^{31}P NMR for **2b**: δ 12.8 (m), 10.7 (m), 6.2 (m), −5.8 (m).

$[Pt_2Me_4(\mu\text{-}t\text{-BuHPCH}_2\text{PH-}t\text{-Bu})_2]$ was prepared similarly. Anal. Calcd for $C_{22}H_{56}P_4Pt_2$: C, 31.7; H, 6.7. Found: C, 31.1; H, 6.4. NMR ($CDCl_3$): δ 1.28 (m, MeP), 0.08 [m, ^2J(PtH) = 80 Hz, MePt]; ^{31}P NMR: δ 19.56 [s; ^1J(PtP) = 1741, ^3J(PtP) = 78 Hz; P].

$[Pd_2Cl_4(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_2]$ (4). To $[PdCl_2(C_6H_5CN)_2]$ (0.31 g, 0.8 mmol) dissolved in CH_2Cl_2 (5 mL) was added ligand (0.14 g, 0.82 mmol) in CH_2Cl_2 (5 mL). The resulting white precipitate was filtered off from the yellow solution, giving the isomer **4a**, yield 0.06 g. ^{31}P NMR: δ 21.39 [s, ^1J(PH) = 400 Hz]. The filtrate was reduced in volume to 1 mL, and then ether and pentane were added. The precipitate of isomer **4b** was filtered and washed a number of times with ether and dried under vacuum; yield 0.18 g. A sample was recrystallized from CH_2Cl_2–pentane by slow diffusion. Anal. Calcd for $C_{14}H_{36}Cl_4P_4Pd_2$: C, 24.62; H, 5.31. Found for **4a**: C, 24.52; H, 5.11. Found for **4b**: C, 24.1; H, 4.9. MP: >310 °C (**4a**); 300 °C (**4b**). ^1H NMR (CD_2Cl_2): δ 1.36 (m, CH_3), 1.64 (CH_2P_2), 2.85 (m, CH), 4.96 [d, ^1J(PH) ~ 400 Hz, PH], 4.27 [d, ^1J(PH) ~ 430 Hz]. ^{31}P NMR: δ 25.74 [dd; ^2J(PP) = 11, 15, ^1J(PH) = 420 Hz]; 22.20 [dd; ^2J(PP) = 11, 11, ^1J(PH) = 390 Hz], 15.88 [dd; ^2J(PP) = 15, 15, ^1J(PH) = 400 Hz], 11.87 [dd; ^2J(PP) = 11, 15, ^1J(PH) = 380 Hz].

$[Pt_2Cl_2(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_3][PF_6]_2$ (5b). To a solution of $[Pt_2Cl_2(SMe_2)_2]$ (0.22 g, 0.55 mmol) in CH_2Cl_2 (5 mL) was added ligand (0.18 g, 1.1 mmol) in CH_2Cl_2 (5 mL). After 2 h of stirring, the solvent was removed and the residue was dissolved in methanol. To this solution, ammonium hexafluorophosphate in methanol was added. The resulting yellow precipitate was filtered off and dried under vacuum; yield 0.33 g. Anal. Calcd for $C_{21}H_{54}Cl_2F_{12}P_8Pt_2$: C, 20.28; H, 4.38. Found: C, 20.88; H, 4.40. Mp: 245 °C. ^1H NMR (CD_2Cl_2): δ 1.42 (m, CH_3), 1.64 (CH_2P_2), 2.96 (m, CH), 5.03 [d, ^1J(PH) ~ 380 Hz, PH], 4.78 [d, ^1J(PH) ~ 420 Hz, PH]. ^{31}P NMR : δ 1.34 [m; ^1J(PtP) = 2240, $^2J(P^mP^x)$ = 370, ^1J(PH) = 380, $^2J(P^aP^x)$ = 20 Hz; P^x], −7.48 [m; ^1J(PtP^a) = 3100, $^1J(P^aH)$ = 440 Hz; P^a], −15.57 [m; $^1J(PtP^m)$ = 2200, $^1J(P^mH)$ = 380, $^2J(P^mP^a)$ = 15 Hz; P^m].

$[Pd_2Cl_2(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_3]Cl_2$ (6a). To a solution of $PdCl_2(C_6H_5CN)_2$ (0.27 g, 0.7 mmol) in CH_2Cl_2 (3 mL) was added the diphosphine (0.23 g, 1.4 mmol) in CH_2Cl_2 (5 mL). The clear deep yellow solution was stirred for 1 h. This was then reduced in volume, ether was added, and the resulting precipitate was filtered and washed with ether. The yellow precipitate was dried under vacuum; yield 0.29 g. Anal. Calcd for $C_{21}H_{54}Cl_4P_6Pd_2$: C, 29.60; H, 6.39. Found: C, 29.31; H, 6.23. Mp: 240 °C ^1H NMR (CD_2Cl_2): δ 1.42 (m, CH_3), 2.02 (CH_2P_2), 2.95 (m, CH), 4.64 [d, ^1J(PH) ~ 440 Hz, PH], 4.33 [d, ^1J(PH) ~ 380 Hz, PH]. ^{31}P NMR: δ 2.41 [m, ^1J(PH) = 420 Hz P^a], −3.50 [m; $^2J(P^xP^m)$ = 405, $^1J(P^xH)$ = 385, $^2J(P^aP^x)$ ~ 15 Hz; P^x, −14.92 [m; $^2J(P^aP^m)$ = 405, $^1J(P^mH)$ = 385, $^2J(P^mP^a)$ = 20 Hz; P^m].

$[Pd_2Cl_2(\mu\text{-}i\text{-PrHPCH}_2\text{PH-}i\text{-Pr})_3][PF_6]_2$ (6b). To a solution of compound **6a** (0.15 g) in methanol (10 mL), was added ammonium hexafluorophosphate in methanol. The resulting yellow precipitate was filtered off and dried under vacuum; yield 0.16 g. Anal. Calcd for $C_{21}H_{54}Cl_2F_{12}P_8Pd_2$: C, 23.66; H, 5.10. Found: C, 23.77; H, 5.23. MP: 210–220 °C ^1H NMR (CD_2Cl_2): δ 1.40 (m, CH_3), 1.82 (CH_2P_2), 3.02 (m, CH), 5.10 [d, ^1J(PH) ~ 420 Hz, PH], 4.72 [d, ^1J(PH) ~ 360 Hz, PH]. ^{31}P NMR: δ 7.21 [m, ^1J(PH) = 430 Hz, P^a], 6.10 [m; $^2J(P^xP^m)$ = 420, ^1J(PH) = 385, $^2J(P^aP^x)$ = 15 Hz; P^x], −9.90 [m; $^2J(P^xP^m)$ = 420, ^1J(PH) = 385, $^2J(P^aP^x)$ = 20 Hz; P^m].

$[Pt_2Cl_2(depm)_2(\mu\text{-depm})]Cl_2$. $[PtCl_2(SMe_2)_2]$ (1.19 g, 3.0 mmol) and $Et_2PCH_2PEt_2$ (0.72 g, 3.7 mmol) were mixed in CH_2Cl_2 (20 mL) and stirred for 6 h. Addition of pentane precipitated $[PtCl_2(depm)]$ (0.52 g). Further addition of pentane gave a yellow oil from which a pale yellow solid was obtained with difficulty by slow evaporation of an acetone solution; yield 0.84 g. ^{31}P NMR ($CDCl_3$): δ 10.68 [dd; ^1J(PtP) = 2224, ^2J(PP) = 390, ^4J(PP) = 9 Hz; P^A], −45.54 [dd; ^1J(PtP) = 1898, ^2J(PP) = 390, ^2J(PP) = 66 Hz; P^B], −50.79 [dd; ^1J(PtP) = 2864, ^2J(PP) = 66, ^4J(PP) = 9 Hz; P^C].

$[Pt_2Cl_2(depm)_2(\mu\text{-depm})][PF_6]_2$. The above complex was dissolved in CH_2Cl_2, and a solution of NH_4PF_6 (0.19 g) in acetone was added. The solvent was removed and the product was crystallized from acetone; yield 0.65 g. Anal. Calcd for $C_{27}H_{66}Cl_2F_{12}P_8Pt_2$: C, 24.42; H, 5.01. Found:

C, 24.15; H, 5.19. ^{1}H NMR (acetone-d_6): δ 4.00 [dt; ^2J(PH) = 10.2, ^4J(PH) = 2.0 Hz; CH_2P_2 of chelate depm]; other resonances overlapped. ^{31}P NMR (acetone-d_6): δ 10.16 [dd; $^1J(PtP^A)$ = 2192, $^2J(P^AP^B)$ = 392, ^4J(PP) = 9 Hz; P^A], -45.36 [dd; $^1J(PtP^B)$ = 1880, $^2J(P^AP^B)$ = 392, $^2J(P^BP^C)$ = 66 Hz; P^B], -50.98 [dd; $^1J(PtP^C)$ = 2855, $^2J(P^BP^C)$ = 66, ^1J(PP) = 9 Hz; P^C].

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Registry No. **1a**, 102922-05-4; **1b**, 103001-66-7; **2a**, 102922-06-5; **2b**, 103001-67-8; **3a**, 102922-07-6; **4a**, 102940-22-7; **5b**, 102940-24-9; **6a**, 102940-25-0; **6b**, 103063-14-5; $[Pt_2Cl_2(depm)_2(\mu\text{-depm})]Cl_2$, 102922-08-7; $[Pt_2Cl_2(depm)_2(\mu\text{-depm})][PF_6]_2$, 102922-10-1; *i*-PrMgBr, 920-39-8; $Cl_2PCH_2PCl_2$, 28240-68-8; $PtCl_2(SMe_2)_2$, 55449-91-7; $Pt_2Me_4(SMe_2)_2$, 79870-64-7; *i*-PrHPCH$_2$PH-*i*-Pr, 89915-94-6.

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Insertion of $SnCl_2$ into an Os–Os Bond of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ To Give the Planar Cluster $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$ with a Pentacoordinate Tin Atom

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The methylene-bridged triosmium cluster $Os_3(\mu\text{-}CH_2)(CO)_{11}$ (**1**)[2] has proven to be unusually reactive and gives rise to a number of interesting derivatives. For example, at 22 °C and 1 atm it readily adds CO to give the μ-ketene cluster $Os_3(\mu\text{-}CH_2CO)(CO)_{12}$,[3] it reacts with halides and pseudohalides to give substituted $[Os_3(\mu\text{-}CH_2)(CO)_{10}(\mu\text{-}X)]^-$ clusters,[4] it adds SO_2 to give $Os_3(\mu\text{-}CH_2SO_2)(CO)_{11}$,[5] it adds $Pt(PPh_3)_2$ to yield the tetrametallic cluster $PtOs_3(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2$,[6] and upon heating it loses CO and rearranges to yield $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$.[7] In our continuing studies of the chemistry of **1**, we have found that it also rapidly reacts with $SnCl_2$ to give a novel Os_3Sn cluster formed via insertion of $SnCl_2$ into an Os–Os bond.

Results and Discussion

Addition of anhydrous $SnCl_2$ to a solution of **1** at 22 °C gives formation of the new cluster $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$ (**2**) in high yield (eq 1). This species, isolated as a yellow solid, has been

$$Os_3(\mu\text{-}CH_2)(CO)_{11} + SnCl_2 \xrightarrow[THF]{22\ ^\circ C} \underset{\mathbf{2}\ (91\%)}{(CO)_4Os(SnCl_2)Os(CO)_4(H_2C)Os(CO)_3} \quad (1)$$

1

spectroscopically characterized [m/z 1084 (M^+); ^{1}H NMR δ 5.61 (s, μ-CH_2); IR (hexane) ν_{CO} 2141 (w), 2106 (s), 2066 (vs), 2052 (w), 2029 (s), 2014 (s), 1993 (w), 1983 (w) cm^{-1}] and fully defined by an X-ray diffraction study.

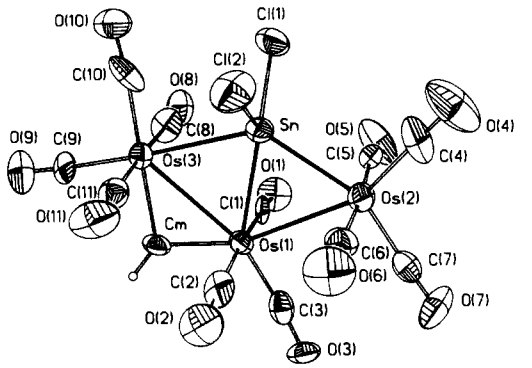

Figure 1. ORTEP drawing of molecule A of $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$ (**2**) with thermal ellipsoids drawn at the 40% probability level.

Table I. Crystal and Refinement Details for $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$ (**2**)

formula	$C_{12}H_2Cl_2O_{11}Os_3Sn$
cryst syst	monoclinic
space group	$P2_1/c$
cryst size	0.30 × 0.25 × 0.20
a, Å	18.655 (3)
b, Å	13.668 (3)
c, Å	17.042 (3)
β, Å	90.926 (15)
V, Å^3	4344.9 (15)
Z	8
density (calc), g cm^{-3}	3.22
μ, cm^{-1}	189.6
max/min transm	0.066/0.035
diffractometer	Nicolet R3
radiation (λ, Å)	Mo Kα (0.710 73)
monochromator	graphite cryst
temp, °C	24
scan technique	Wyckoff[a]
scan speed, deg min^{-1}	variable, 5–20
2θ scan range, deg	$4 \le 2\theta \le 50$
data collcd	$\pm h,+k,+l$
no. of unique data	7654
no. of unique data with $F_o \ge 3\sigma(F_o)$	4867
data/param	9.3
R(int), %	1.66
stds/reflcns	3/197
g[b]	0.001
R_F, R_{wF}, GOF[c]	5.94, 5.79, 1.262
mean shift/esd max, final cycle	0.01

[a] A type of ω scan in which background plus peak tops are measured (Nicolet program package). [b] $w^{-1} = \sigma^2(F_o) + |g|(F_o)^2$. [c] $R_F = \sum[|F_3| - |F_c|]/\sum|F_o|$; $R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$. GOF = $[\sum w(F_o - F_c)^2/(N_{obsd} - N_{param})]^{1/2}$.

The molecule crystallizes in the space group $P2_1/c$ with two independent but structurally similar molecules per unit cell. Figure 1 shows an ORTEP drawing of molecule A, and relevant crystallographic details are given in Tables I–III. The cluster has a near-planar butterfly structure with the Sn and one Os atom forming the butterfly hinge. The [Os(1)–Sn–Os(2)]–[Os(3)–Sn–Os(1)] dihedral angles are 179.7 (2) and 179.5 (2)° for molecules A and B, respectively. The methylene ligand asymmetrically bridges Os(1) and Os(3) but is significantly closer (0.17 Å) to the former than to the latter.

Significant asymmetry also exists in the Os–Sn bond lengths with the Sn atom located 0.159–0.175 Å closer to Os(2) than to Os(1) and Os(3). The Sn–Os(2) distances of 2.641 (2) and 2.636 (2) Å compare well to typical unbridged Sn–Os distances found in other low-valent organometallics (e.g., 2.711 (1) and 2.712 (1) Å in *trans*-$Os(SnPh_3)_2(CO)_4$;[8] 2.653 (1) Å in $HOs_3(\mu_3$-

(1) (a) Pennsylvania State University, Uniontown, PA. (b) Pennsylvania State University, University Park, PA. (c) University of Delaware.
(2) (a) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559. (b) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975.
(3) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783.
(4) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1985**, *4*, 1413.
(5) Morrison, E. D. Ph.D. Thesis, The Pennsylvania State University, 1985.
(6) Williams, G. D.; Lieszkovzky, M. C.; Mirkin, W.; Geoffroy, G. L., to be submitted for publication.
(7) Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.
(8) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

0020-1669/86/1325-3100$01.50/0