

C, 24.15; H, 5.19. ^1H NMR (acetone- d_6): δ 4.00 [dt; $^2J(\text{PH}) = 10.2$, $^4J(\text{PH}) = 2.0$ Hz; CH_2P_2 of chelate depm]; other resonances overlapped. ^{31}P NMR (acetone- d_6): δ 10.16 [dd; $^1J(\text{PtP}^{\text{A}}) = 2192$, $^2J(\text{P}^{\text{A}}\text{P}^{\text{B}}) = 392$, $^4J(\text{PP}) = 9$ Hz; P^{A}], -45.36 [dd; $^1J(\text{PtP}^{\text{B}}) = 1880$, $^2J(\text{P}^{\text{A}}\text{P}^{\text{B}}) = 392$, $^2J(\text{P}^{\text{B}}\text{P}^{\text{C}}) = 66$ Hz; P^{B}], -50.98 [dd; $^1J(\text{PtP}^{\text{C}}) = 2855$, $^2J(\text{P}^{\text{B}}\text{P}^{\text{C}}) = 66$, $^4J(\text{PP}) = 9$ 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; $[\text{Pt}_2\text{Cl}_2(\text{dep})_2(\mu\text{-dep})]\text{Cl}_2$, 102922-08-7; $[\text{Pt}_2\text{Cl}_2(\text{dep})_2(\mu\text{-dep})][\text{PF}_6]_2$, 102922-10-1; *i*-PrMgBr, 920-39-8; $\text{Cl}_2\text{PCH}_2\text{P}(\text{Cl})_2$, 28240-68-8; $\text{PtCl}_2(\text{SMe}_2)_2$, 55449-91-7; $\text{Pt}_2\text{Me}_4(\text{SMe}_2)_2$, 79870-64-7; *i*-PrHPCH₂PH-*i*-Pr, 89915-94-6.

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Insertion of SnCl_2 into an Os-Os Bond of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ To Give the Planar Cluster $\text{Os}_3\text{SnCl}_2(\text{CO})_{11}(\mu\text{-CH}_2)$ with a Pentacoordinate Tin Atom

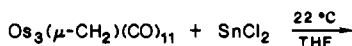
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Received January 24, 1986

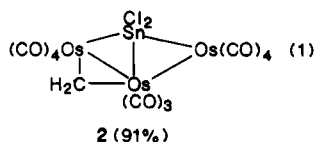
The methylene-bridged triosmium cluster $\text{Os}_3(\mu\text{-CH}_2)(\text{CO})_{11}$ (**1**)² has proven to be unusually reactive and gives rise to a number of interesting derivatives. For example, at 22 °C and 1 atm it readily adds CO to give the μ -ketene cluster $\text{Os}_3(\mu\text{-CH}_2\text{CO})(\text{CO})_{12}$,³ it reacts with halides and pseudohalides to give substituted $[\text{Os}_3(\mu\text{-CH}_2)(\text{CO})_{10}(\mu\text{-X})]^-$ clusters,⁴ it adds SO_2 to give $\text{Os}_3(\mu\text{-CH}_2\text{SO}_2)(\text{CO})_{11}$,⁵ it adds $\text{Pt}(\text{PPh}_3)_2$ to yield the tetrametallic cluster $\text{PtOs}_3(\mu\text{-CH}_2)(\text{CO})_{11}(\text{PPh}_3)_2$,⁶ and upon heating it loses CO and rearranges to yield $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$.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 $\text{Os}_3\text{SnCl}_2(\text{CO})_{11}(\mu\text{-CH}_2)$ (**2**) in high yield (eq 1). This species, isolated as a yellow solid, has been



1



spectroscopically characterized [m/z 1084 (M^+); ^1H NMR δ 5.61 (s, $\mu\text{-CH}_2$); IR (hexane) ν_{CO} 2141 (w), 2106 (s), 2066 (vs), 2052

- (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.
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- (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.

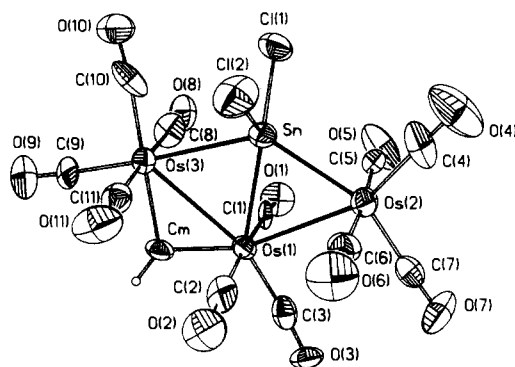


Figure 1. ORTEP drawing of molecule A of $\text{Os}_3\text{SnCl}_2(\text{CO})_{11}(\mu\text{-CH}_2)$ (**2**) with thermal ellipsoids drawn at the 40% probability level.

Table I. Crystal and Refinement Details for $\text{Os}_3\text{SnCl}_2(\text{CO})_{11}(\mu\text{-CH}_2)$ (**2**)

formula	$\text{C}_{12}\text{H}_2\text{Cl}_2\text{O}_{11}\text{Os}_3\text{Sn}$
cryst syst	monoclinic
space group	$P2_1/c$
cryst size	$0.30 \times 0.25 \times 0.20$
<i>a</i> , Å	18.655 (3)
<i>b</i> , Å	13.668 (3)
<i>c</i> , Å	17.042 (3)
β , Å	90.926 (15)
<i>V</i> , Å ³	4344.9 (15)
<i>Z</i>	8
density (calc), g cm ⁻³	3.22
μ , cm ⁻¹	189.6
max/min trans	0.066/0.035
diffractometer	Nicolet R3
radiation (λ , Å)	Mo K α (0.71073)
monochromator	graphite cryst
temp, °C	24
scan technique	Wyckoff ^a
scan speed, deg min ⁻¹	variable, 5-20
2θ scan range, deg	$4 \leq 2\theta \leq 50$
data collcd	$\pm h, +k, +l$
no. of unique data	7654
no. of unique data with $F_o \geq 3\sigma(F_o)$	4867
data/param	9.3
<i>R</i> (int), %	1.66
stds/reflens	3/197
<i>g</i> ^b	0.001
<i>R</i> _F , <i>R</i> _{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 $R_F = \sum[|F_3| - |F_c|]/\sum|F_o|$; $R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)]/[\sum w^{1/2}|F_o|]$. $\text{GOF} = [\sum w(F_o - F_c)^2/(N_{\text{obsd}} - N_{\text{param}})]^{1/2}$.

(w), 2029 (s), 2014 (s), 1993 (w), 1983 (w) cm⁻¹] and fully defined by an X-ray diffraction study.

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 $[\text{Os}(1)\text{-Sn-Os}(2)]$ - $[\text{Os}(3)\text{-Sn-Os}(1)]$ 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*- $\text{Os}(\text{SnPh}_3)_2(\text{CO})_4$,⁸ 2.653 (1) Å in $\text{HOs}_3(\mu_3$ -

(8) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **2**

	x	y	z	U^a
Os(1)	3764 (1)	6695 (1)	371 (1)	33 (1)
Os(2)	4574 (1)	7414 (1)	-1058 (1)	41 (1)
Os(3)	2297 (1)	7563 (1)	477 (1)	36 (1)
Os(1')	1244 (1)	3174 (1)	3037 (1)	42 (1)
Os(2')	253 (1)	3172 (1)	1590 (1)	40 (1)
Os(3')	2703 (1)	2399 (1)	2703 (1)	45 (1)
Sn	3257 (1)	8008 (1)	-772 (1)	39 (1)
Sn'	1588 (1)	2552 (1)	1516 (1)	36 (1)
Cl(1)	2462 (4)	7559 (7)	-1826 (4)	64 (3)
Cl(2)	3187 (5)	9754 (6)	-714 (6)	77 (3)
Cl(2')	1654 (4)	959 (6)	961 (5)	73 (3)
Cl(1')	2236 (4)	3528 (6)	612 (4)	57 (3)
C(1)	3414 (11)	5565 (17)	-220 (13)	31 (7)
O(1)	3238 (10)	4899 (13)	-553 (12)	59 (7)
C(2)	4186 (16)	7730 (20)	1038 (19)	56 (11)
O(2)	4434 (12)	8241 (17)	1507 (15)	83 (10)
C(3)	4555 (14)	5964 (19)	610 (15)	44 (9)
O(3)	5073 (9)	5505 (14)	831 (10)	50 (7)
C(4)	4721 (19)	8166 (27)	-1964 (19)	74 (13)
O(4)	4836 (16)	8684 (20)	-2472 (15)	113 (13)
C(5)	4113 (13)	6381 (23)	-1680 (16)	45 (10)
O(5)	3915 (14)	5727 (16)	-1993 (13)	83 (10)
C(6)	4954 (16)	8435 (23)	-364 (17)	52 (11)
O(6)	5172 (13)	8985 (17)	30 (16)	88 (11)
C(7)	5416 (16)	6643 (25)	-862 (16)	59 (11)
O(7)	5951 (11)	6243 (16)	-757 (15)	79 (10)
C(8)	1926 (15)	6465 (19)	-126 (18)	51 (10)
O(8)	1701 (11)	5845 (15)	-481 (12)	63 (8)
C(9)	1616 (14)	7301 (22)	1282 (16)	56 (10)
O(9)	1186 (12)	7153 (17)	1736 (14)	77 (9)
C(10)	1718 (17)	8477 (21)	-133 (15)	51 (10)
O(10)	1318 (11)	9010 (15)	-451 (12)	61 (8)
C(11)	2710 (13)	8645 (19)	1096 (16)	45 (9)
O(11)	2938 (11)	9245 (15)	1485 (14)	82 (9)
C _m	2963 (13)	6511 (19)	1165 (14)	45 (9)
H _{ma}	2771	5860	1185	54
H _{mb}	3084	6726	1687	54
C(2')	924 (16)	1917 (23)	3390 (18)	65 (12)
O(2')	714 (12)	1177 (15)	3620 (14)	77 (9)
C(1')	1586 (14)	4495 (23)	2776 (17)	53 (11)
O(1')	1680 (12)	5285 (15)	2657 (15)	79 (10)
C(3')	507 (19)	3731 (26)	3654 (17)	73 (13)
O(3')	114 (14)	4090 (20)	4058 (15)	101 (12)
C(4')	-76 (14)	3023 (20)	529 (18)	49 (10)
O(4')	-252 (11)	2880 (20)	-97 (14)	86 (10)
C(6')	-30 (11)	1844 (18)	1881 (16)	42 (9)
O(6')	-167 (10)	1060 (14)	2069 (15)	75 (9)
C(5')	611 (13)	4467 (25)	1292 (20)	64 (12)
O(5')	830 (12)	5179 (14)	1095 (14)	70 (9)
C(7')	-507 (14)	3815 (20)	2192 (18)	50 (10)
O(7')	-969 (13)	4082 (18)	2539 (17)	104 (12)
C(8')	3022 (16)	3740 (23)	2437 (19)	60 (12)
O(8')	3208 (13)	4471 (18)	2284 (14)	83 (10)
C(9')	3473 (24)	2361 (21)	3524 (23)	84 (16)
O(9')	3875 (14)	2302 (19)	4001 (17)	113 (12)
C(10')	3183 (12)	1955 (25)	1775 (19)	59 (11)
O(10')	3498 (11)	1510 (17)	1309 (15)	81 (10)
C(11')	2357 (14)	1066 (19)	2949 (21)	63 (12)
O(11')	2199 (11)	319 (15)	3086 (14)	69 (9)
C _{m'}	2141 (16)	2994 (24)	3734 (18)	70 (13)
H _{m'a}	2339	3593	3936	80
H _{m'b}	2084	2537	4156	80

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

S)(μ_3, η^2 -SCH₂)(CO)₇(PMe₂Ph)(SnMe₃);⁹ 2.645 (3) Å in H₂Os₃(Sn[CH(SiMe₃)₂]₂)(CO)₁₀;¹⁰ 2.658 (0) Å in H₂Os₃(Sn[CH(SiMe₃)₂]₂)(CO)₉(μ -O=CCH(SiMe₃)₂)¹¹. However, the Sn–Os(1) and Sn–Os(3) distances (2.800 (2)–2.886 (2) Å) are

- (9) Adams, T. D.; Katachera, D. A. *Organometallics* **1982**, *1*, 460.
 (10) Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 609.
 (11) Cardin, C. J.; Cardin, D. J.; Power, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 505.

Table III. Selected Bond Distances and Angles for Os₃SnCl₂(CO)₁₁(μ -CH₂) (**2**)

	molecule A	molecule B
Bond Distances (Å)		
Os(1)–Os(2)	3.050 (1)	3.057 (1)
Os(1)–Os(3)	2.989 (1)	2.985 (2)
Os(1)–Sn	2.800 (2)	2.811 (2)
Os(2)–Sn	2.641 (2)	2.636 (2)
Os(3)–Sn	2.868 (2)	2.886 (2)
Os(1)–Cm	2.05 (2)	2.05 (3)
Os(3)–Cm	2.22 (2)	2.22 (3)
Sn–Cl(1)	2.391 (7)	2.383 (8)
Sn–Cl(2)	2.393 (8)	2.378 (9)
Bond Angles (deg)		
Os(2)–Os(1)–Os(3)	112.7 (1)	112.8 (1)
Os(3)–Os(1)–Sn	59.3 (1)	59.6 (1)
Os(1)–Os(3)–Sn	57.1 (1)	57.2 (1)
Os(2)–Os(1)–Sn	53.5 (1)	53.2 (1)
Os(1)–Os(2)–Sn	58.4 (1)	58.6 (1)
Os(1)–Sn–Os(2)	68.1 (1)	68.2 (1)
Os(2)–Sn–Os(3)	131.7 (1)	131.4 (1)
Os(2)–Sn–Cl(1)	110.5 (2)	109.9 (2)
Os(1)–Sn–Cl(2)	128.9 (2)	131.1 (2)
Os(3)–Sn–Cl(2)	98.4 (2)	99.8 (2)
Os(1)–Sn–Os(3)	63.6 (1)	63.2 (1)
Os(1)–Sn–Cl(1)	123.8 (2)	123.5 (2)
Os(3)–Sn–Cl(1)	96.7 (2)	97.2 (2)
Os(2)–Sn–Cl(2)	111.5 (2)	111.6 (2)
Os(1)–Cm–Os(3)	88.8 (9)	88.7 (12)
Cl(1)–Sn–Cl(2)	104.7 (3)	103.0 (3)

significantly longer than the typical Sn–Os distances noted above. The Os–Os distances of 2.985 (2)–3.057 (1) Å are also slightly longer than the average Os–Os distance of 2.877 (3) Å in Os₃(CO)₁₂.¹²

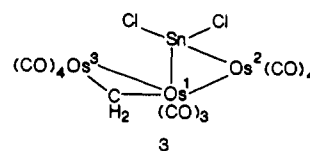
The asymmetry in the Os–Sn bond lengths is also reflected in the Cl–Sn–Os bond angles involving the wing-tip Os atoms, with the Cl atoms bending toward Os(3) and away from Os(2) to which the Sn atom is closest. The coordination geometry about Sn is best described as a distorted trigonal bipyramid; bond angles within the trigonal plane defined by Sn, Cl(1), Cl(2), and Os(1) average 119.1°. An alternative view is to consider the Sn atom to be tetrahedrally coordinated by Os(2), Cl(1), Cl(2), and the midpoint of the Os(1)–Os(3) bond, since the bond angles about Sn defined by Os(2) and the two Cl's average 108.5° for the two molecules.

Cluster **2** has 54 valence electrons within the Os₃Sn framework and adopts the structure predicted by skeletal-electron-pair theory.¹³ There are seven skeleton electron pairs (P_{MM}) calculated with the relationship

$$P_{MM} = \frac{1}{2}[(\text{metal } e^-) + (\text{ligand } e^-) - (12e^-/\text{Os}) - (4e^-/\text{Sn})]$$

Seven electron pairs for a four-metal cluster predicts an arachno octahedral structure; removal of two cis vertices from an octahedron gives a butterfly structure as observed for **2**.

However, it is difficult to rationalize the structure of **2** by application of the EAN rule. That rule would predict structure **3**. The actual structure appears to be a compromise between **3**



and that predicted by skeletal-electron-pair theory. It derives from **3** by Os(3) weakly interacting with the Sn atom, and this is compensated by a corresponding lengthening of the Sn–Os(1) bond and the methylene ligand moving closer to Os(1).

- (12) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
 (13) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

As noted in the introduction, cluster **1** is unusually reactive, especially for osmium clusters which generally require more forcing conditions. The high reactivity of **1** has been attributed to the facile opening of a coordination site by a reversible insertion of CO into the Os-CH₂ bond to give an unsaturated ketene intermediate.^{3,4} Addition of the entering molecule to this site followed by subsequent rearrangements, including CO loss if necessary, accounts for the products noted in the introduction. The SnOs₃ cluster **2** apparently forms by a similar process.

The reaction of SnCl₂ with **1** is also similar to the reaction of halides with **1**, which give the edge-double-bridged anion [Os₃(μ-I)(μ-CH₂)(CO)₁₀]⁻.⁴ Similar addition of SnCl₂ across an Os-Os bond occurs in forming **2**, except that in the final product the μ-CH₂ ligand bridges two Os atoms that are still bonded to one another.

Finally, it should be noted that the reaction of SnCl₂ with **1** to form **2** differs markedly from the reported reaction of SnR₂ (R = CH(SiMe₃)₂) with H₂O₃(CO)₁₀.¹⁰ This reaction involves addition of the tin reagent to the unsaturated cluster to give a planar butterfly cluster with the Sn atom occupying a wing-tip position, in contrast to the hinge position of the Sn atom in **2**.

Experimental Section

Cluster **1** was prepared as previously described.² Anhydrous SnCl₂ was obtained from Aldrich Chemical Co. and was used as received. Solvents were dried by standard methods, and all manipulations were performed under inert atmospheres. Instruments used in this research have been previously described.^{3,4}

Synthesis of Os₃SnCl₂(CO)₁₁(μ-CH₂) (2**).** Dry THF (tetrahydrofuran, 15 mL) was distilled into a 50-mL Schlenk flask containing 0.047 mmol of **1**. Anhydrous SnCl₂ (0.047 mmol) was dissolved in 15 mL of THF and added dropwise to the solution of **1** while being stirred at room temperature. After 30-45 min a clear yellow solution was obtained, which upon evaporation gave **2** as a yellow solid in 91% yield. Recrystallization was accomplished by slow evaporation of a CDCl₃ solution. Anal. Calcd for C₁₂H₂Cl₂O₁₁Os₃Sn: C, 13.32; H, 0.19. Found: C, 14.03; H, 0.43.

Crystallographic Structure Determination. The parameters used during the collection of diffraction data are summarized in Table I. A yellow crystal was attached to a fine glass fiber with epoxy cement. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 17° ≤ 2θ ≤ 23°. Data were corrected for absorption by an empirical procedure that employs six refined parameters to define a pseudoellipsoid used to calculate the corrections. No decay was observed in three standard reflections during the data collection.

The structure was solved by using the direct methods program SOLV, which located six osmium atoms (the asymmetric unit consists of two independent molecules). The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. With the non-hydrogen atoms refined anisotropically and with calculated hydrogen atom positions (*d*(C-H) = 0.96 Å, thermal parameters equaling 1.2 times the isotropic equivalent for the carbon to which it was attached) final residuals of *R_F* = 5.94% and *R_{wF}* = 5.79% were obtained. The final difference Fourier synthesis showed a noisy but chemically uninformative background (max 2.16 e/Å³, 1.0 Å from Os(3)). An inspection of *F_o* vs. *F_c* values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3, SHELXTL (version 4.1), and XP. Atomic coordinates are provided in Table II, and selected bond distances and angles, in Table III. Additional crystallographic data are available as supplementary material.

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Registry No. **1**, 77208-32-3; **2**, 103148-36-3; SnCl₂, 7772-99-8; Os, 7440-04-2; Sn, 7440-31-5.

Supplementary Material Available: A table of anisotropic temperature factors and complete lists of bond lengths and angles for **2** and a stereoview of the unit cell of **2** (6 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

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Oxidative-Addition Reactions of Potassium Tetrachloroplatinate(II) with *N,N*-Dialkylacetamides under Mild Reaction Conditions. Synthesis of

[*cis*-Pt(CH₂N(CH₃)C(CH₃O)₂-*trans*-Cl₂)] and [*trans*-Pt(OC(CH₃)N(CH₃)₂-*trans*-Cl₂)]

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Reactions of platinum(II) compounds with acetamides and the complex systems resulting from these reactions have long been subjects of interest. The original "platinblau",¹ reported by Hofmann and Buggs, has been reformulated recently as either an acetamido derivative of platinum(IV)^{2,3} or as a mixed oxidation state oligomeric compound containing platinum(II), platinum(III), and platinum(IV) species.⁴ Most recently, Lippard, Rosenberg, and others,⁵⁻¹⁵ have characterized platinum(II) and platinum(IV) compounds that are complexes of amide analogues of purine and pyrimidine bases. These have significance in the cytotoxic activity of platinum compounds such as *cis*-diamminedichloroplatinum(II). The platinum(V) species are characterized by bonding of the amide ligands through nitrogen and oxygen and not through platinum-carbon bond formation. Classically, platinum(IV) alkyl and aryl complexes have been prepared by addition of Grignard or alkyllithium reagents to platinum(IV) compounds¹⁶ or by oxidative addition of alkyl and acyl halides, or metal halides, to platinum(II) compounds.¹⁶ Ortho metalation reactions between platinum(II) and palladium(II) compounds and aromatic systems containing a coordinating substituent are well-known.¹⁷ Brookhart et al.¹⁸ have recently generalized these covalent interactions between transition-metal centers and carbon-hydrogen groups by the term "agostic". In the cases of ortho metalation and agostic interaction, however, oxidative addition to the metal center is not postulated.

We have observed that an oxidative-addition, ortho-metalation reaction occurs under mild conditions on combining potassium tetrachloroplatinate(II) with *N,N*-dimethylacetamide: the reaction involves NC-H bond cleavage and NC-Pt bond formation. A platinum(II)/*N,N*-dimethylacetamide compound containing platinum-carbonyl oxygen bonds has also been isolated from the same reaction mixture. Both compounds have been structurally characterized through X-ray diffraction studies.

Experimental Section

Reagent grade *N,N*-dimethylacetamide (dma) and *N,N*-diethylacetamide (dea) were used as received, after IR and NMR analyses of the solvent/reactant showed agreement with literature values. For dma: ν = 3500, 3050, 2930, 2850, 1638, 1538, 1485, 1388, 1254, 1178, 1045, 1005 cm⁻¹; δ = (all singlets) 1.99, 2.86, 3.05. For dea: ν = 3500, 3000, 2960, 1680, 1660, 1500, 1480, 1460, 1450, 1395, 1375, 1330, 1295, 1240, 1180, 1085, 1050, 1005, 800 cm⁻¹; δ = 1.20 (multiplet), 2.00 (singlet), 3.30 (multiplet). *N*-Methylpyrrolidinone was distilled before use. Potassium tetrachloroplatinate(II), a gift of Johnson Matthey, Inc., was used as received. Reactions were carried out under ambient conditions in air.

Synthesis of Pt(C₄H₈NO)₂Cl₂ (1**) and Pt(C₄H₉NO)₂Cl₂ (**2**).** To a volume of 80 mL of dimethylacetamide (dma), 1.0021 g (2.4 mmol) of potassium tetrachloroplatinate(II) (K₂PtCl₄) was added and the resulting slurry was heated and stirred at 60 °C until all of the K₂PtCl₄ had dissolved (approximately 120 h). The resultant golden yellow solution was centrifuged to remove 0.2333 g (3.3 mmol) of KCl. The supernatant liquid was reduced in volume by about two-thirds, until solid product began to form, and then the supernatant was stored for 12 h at 0 °C. The resulting pale yellow crystals were centrifuged from the supernatant liquid, washed with tetrahydrofuran, and dried under vacuum for 12 h. Yield: 0.3392 g (0.77 mmol) as Pt(C₄H₈NO)₂Cl₂; 51.3% based on K₂PtCl₄ as starting material. Anal. Calcd for Pt(C₄H₈NO)₂Cl₂: C,

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