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–CH_2 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 $SnOs_3$ cluster **2** apparently forms by a similar process.

The reaction of $SnCl_2$ with **1** is also similar to the reaction of halides with **1**, which give the edge-double-bridged anion $[Os_3(\mu\text{-}I)(\mu\text{-}CH_2)(CO)_{10}]^-$.[4] Similar addition of $SnCl_2$ across an Os–Os bond occurs in forming **2**, except that in the final product the μ-CH_2 ligand bridges two Os atoms that are still bonded to one another.

Finally, it should be noted that the reaction of $SnCl_2$ with **1** to form **2** differs markedly from the reported reaction of SnR_2 ($R = CH(SiMe_3)_2$) with $H_2Os_3(CO)_{10}$.[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 $SnCl_2$ 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 $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$ (2). Dry THF (tetrahydrofuran, 15 mL) was distilled into a 50-mL Schlenk flask containing 0.047 mmol of **1**. Anhydrous $SnCl_2$ (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 $CDCl_3$ solution. Anal. Calcd for $C_{12}H_2Cl_2O_{11}Os_3Sn$: 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 $17° \leq 2\theta \leq 23°$. 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 uniformative background (max 2.16 e/Å^3, 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.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this research, the National Science Foundation for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware, and Dr. G. Steinmetz and R. Hale at the Tennessee Eastman Co., Kingsport, TN, for obtaining the mass spectrum.

Registry No. 1, 77208-32-3; 2, 103148-36-3; $SnCl_2$, 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 $[cis\text{-}\overline{Pt(CH_2N(CH_3)C(CH_3)O})_2\text{-}trans\text{-}Cl_2]$ and $[trans\text{-}Pt(OC(CH_3)N(CH_3)_2)_2\text{-}trans\text{-}Cl_2]$

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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) compounds[16] 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 $Pt(C_4H_8NO)_2Cl_2$ (1) and $Pt(C_4H_9NO)_2Cl_2$ (2). To a volume of 80 mL of dimethylacetamide (dma), 1.0021 g (2.4 mmol) of potassium tetrachloroplatinate(II) (K_2PtCl_4) was added and the resulting slurry was heated and stirred at 60 °C until all of the K_2PtCl_4 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 $Pt(C_4H_8NO)_2Cl_2$; 51.3% based on K_2PtCl_4 as starting material. Anal. Calcd for $Pt(C_4H_8NO)_2Cl_2$: C,

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Table I. Crystal and Intensity Data Collection Summary for **1** and **2**

	1	**2**
mol formula	$Pt(C_4H_8NO)_2Cl_2$	$Pt(C_4H_9NO)_2Cl_2$
M_r	438.22	440.23
a, Å	8.924 (3)	8.626 (3)
b, Å	13.582 (3)	11.548 (4)
c, Å	21.769 (6)	14.025 (4)
V, Å^3	2638 (1)	1397.1 (9)
space group	*Fdd*2	*Pbca*
ρ(calcd), g cm^{-3}	2.21	1.95
Z	8	4
cryst dimens, mm	0.18 × 0.22 × 0.36	0.08 × 0.20 × 0.22
Diffractometer	Nicolet R3	Nicolet R3
radiation[b]	Mo Kα	Mo Kα
abs coeff (Mo Kα), cm^{-1}	115.86	109.46
temp. °C	26	26
scan speed, deg min^{-1}	variable, 3.5–20.0	4
scan type	ω	$2\theta/\theta$
2θ scan range, deg	$4 \leqslant 2\theta \leqslant 55$	$4 \leqslant 2\theta \leqslant 52$
reflcns collcd	$+h,+k,+l$	$+h,+k,+l$
no. of reflcns collcd	808	1219
no. of unique reflcns	728	1036
no. of unique obsd reflcns ($F_o \geqslant 2.5\sigma(F_o)$)	645	574
transmission (max/min)	0.10/0.06	0.14/0.08
std reflcns	3 std/47 reflcns (<1% decay)	3 std/97 reflcns (<1% decay)
ignorance factor, g[a]	0.001	0.003
$R(F)$, %	3.83	5.03
$R_w(F)$, %	3.73	5.02
GOF	1.167	0.999
no. of params refined	69	66

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$. [b] Graphite monochromator.

21.93; H, 3.68; N, 6.39; Cl, 16.18; Pt, 44.52. Found: C, 21.78; H, 3.60; N, 6.39; Cl, 16.11; Pt, 44.45.

Further reduction in volume of the supernatant liquid yielded a small number of darker yellow crystals, which were identified by X-ray diffraction as $Pt(C_4H_9NO)_2Cl_2$.

Similar reactions carried out using *N,N*-diethylacetamide (dea) and *N*-methylpyrrolidinone as solvent/reactant with K_2PtCl_4 by the above procedure yielded small amounts of the KCl byproduct. However, reduction in volume of the resultant supernatant solutions did not result in the formation of crystalline products.

X-ray Structure Determination. Collection and Reduction of X-ray Data. Both **1** and **2** presented many crystal mounting difficulties as a result of the crystals' high solvent vapor pressure (efflorescence) and high solubility of the complexes in their mother liquors. The partial redissolving of the crystals caused by minor temperature fluctuations made mounting in solvent in capillary tubes impossible due to movement of the crystals. Crystals were ultimately attached to glass fibers with a heavy epoxy cement coating. For both **1** and **2**, correction for absorption was empirically performed based upon ψ-scan data for seven reflections (10° increments) fitted to a six-parameter ellipsoidal model. A summary of crystal, data collection and refinement results for **1** and **2** is presented in Table I. Data were collected on a Nicolet R3 diffractometer, and the structures were solved (heavy-atom method) and refined (blocked cascade) by using the SHELXTL (Version 4.1) program system (Nicolet Corp., Madison, WI).

Preliminary photographic classification indicated an *F*-centered orthorhombic lattice for **1**. Systematic absences in the diffraction data combined with the presence of the weakly observed reflections [420],

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $Pt(C_4H_8NO)_2Cl_2$ (**1**)

atom	x	y	z	U[a]
Pt	5000	0	5000	49 (1)
Cl	7554 (5)	226 (4)	5011 (6)	70 (2)
C(1)	4801 (29)	1092 (34)	4395 (24)	59 (9)
C(2)	4611 (53)	2907 (22)	5699 (17)	88 (12)
C(3)	4634 (33)	2012 (21)	5336 (16)	52 (7)
C(4)	4472 (49)	2986 (21)	4374 (15)	76 (10)
O(1)	4720 (23)	1185 (18)	5638 (13)	53 (5)
N(1)	4644 (30)	2042 (16)	4726 (11)	45 (5)

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

Table III. Selected Bond Distances and Angles for $Pt(C_4H_8NO)_2Cl_2$ (**1**)

	(a) Bond Distances (Å)		
Pt–Cl	2.300 (5)	C(2)–C(3)	1.49 (4)
Pt–O(1)	2.15 (2)	C(4)–N(1)	1.50 (3)
Pt–C(1)	1.98 (4)	C(3)–O(1)	1.30 (3)
C(1)–N(1)	1.44 (5)	C(3)–N(1)	1.33 (3)
	(b) Bond Angles (deg)		
Cl–Pt–Cla	178.5 (5)	C(1)–Pt–C(1a)	101 (2)
C(1)–Pt–Cl	90.6 (8)	O(1)–C(3)–C(2)	117 (2)
C(1)–Pt–Cla	90.3 (8)	C(2)–C(3)–N(1)	119 (2)
C(1a)–Pt–Cl	90.3 (8)	O(1)–C(3)–N(1)	124 (2)
O(1)–Pt–C(1)	80.7 (14)	Pt–C(1)–N(1)	113 (2)
O(1)–Pt–C(1a)	178.4 (13)	Pt–O(1)–C(3)	107 (2)
Cl–Pt–O(1)	89.9 (6)	C(1)–N(1)–C(3)	115 (2)
Cl–Pt–O(1a)	89.2 (6)	C(3)–N(1)–C(4)	126 (2)
O(1)–Pt–O(1a)	97.7 (11)	C(1)–N(1)–C(4)	119 (2)

Table IV. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $Pt(C_4H_9NO)_2Cl_2$ (**2**)

atom	x	y	z	U[a]
Pt	0	0	0	49 (1)
Cl	2089 (11)	117 (12)	991 (6)	66 (3)
N(1)	1368 (33)	−2999 (27)	−1446 (22)	53 (8)
O(1)	987 (31)	−1204 (21)	−837 (18)	57 (9)
C(1)	696 (41)	−2323 (39)	−738 (27)	54 (14)
C(2)	−218 (34)	−2790 (25)	−127 (33)	39 (14)
C(3)	2223 (39)	−2453 (38)	−2241 (26)	84 (18)
C(4)	1242 (49)	−4206 (30)	−1481 (30)	71 (16)

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

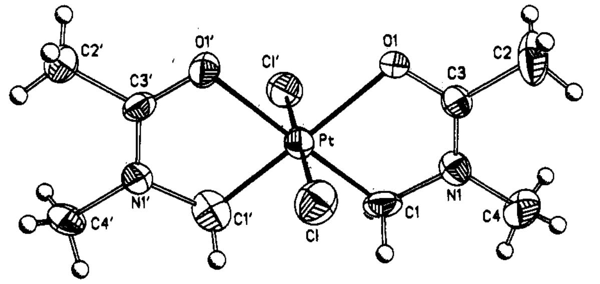

Figure 1. ORTEP drawing for [*cis*-$Pt(CH_2N(CH_3)C(CH_3)O)_2$-*trans*-$Cl_2$] (**1**). The thermal ellipsoids show 50% probability surfaces. Hydrogen atoms are depicted with arbitrary radii.

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Table V. Selected Bond Distances and Angles for $Pt(C_4H_9NO)_2Cl_2$ (**2**)

(a) Bond Distances (Å)			
Pt-Cl	2.278 (8)	N(1)-C(3)	1.44 (5)
Pt-O(1)	2.02 (2)	O(1)-C(1)	1.24 (5)
N(1)-C(1)	1.39 (4)	C(1)-C(2)	1.50 (5)
N(1)-C(4)	1.48 (4)		
(b) Bond Angles (deg)			
Cl-Pt-Cla	180.0	C(3)-N(1)-C(4)	116 (3)
O(1)-Pt-O(1a)	180.0	N(1)-C(1)-O(1)	116 (3)
Cl-Pt-O(1)	90.7 (8)	O(1)-C(1)-C(2)	125 (3)
Cl-Pt-O(1a)	89.3 (8)	N(1)-C(1)-C(2)	119 (3)
C(1)-N(1)-C(3)	121 (3)	C(1)-O(1)-Pt	123 (2)
C(1)-N(1)-C(4)	123 (3)		

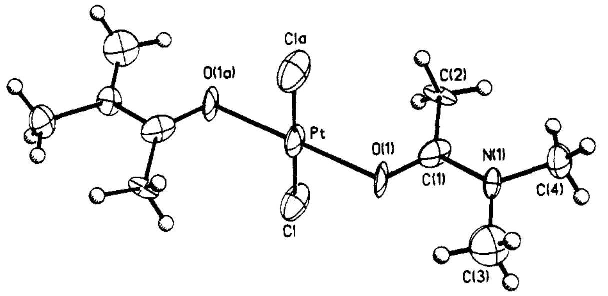

Figure 2. ORTEP drawing for [*trans*-$Pt(OC(CH_3)N(CH_3)_2)_2$-*trans*-Cl_2] (**2**). The thermal ellipsoids show 50% probability surfaces. Hydrogen atoms are depicted with arbitrary radii.

[820], [460], and [680] suggested that the correct space group was *Fdd*2 with the Pt atom on the 2-fold axis. Statistics based upon *E* also strongly indicated a noncentrosymmetric lattice, $|E^2 - 1| = 0.74$. The correctness of the noncentrosymmetric space group was affirmed by the chemically reasonable solution and refinement of the structure.

For both **1** and **2**, all non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were incorporated as idealized updated isotropic contributions (d(C-H) = 0.96 Å). Inversion of the structure for **1** ($x + 0.25$, $y + 0.25$, $-z$) led to significantly inferior residuals, $R(F) = 3.98\%$ and $R_w(F) = 3.88\%$. The highest peak in the final difference map is 1.8 e Å^{-3}. Atomic coordinates for **1** appear in Table II; selected bond distances and bond angles appear in Table III. The labeling scheme and molecular structure are presented in Figure 1.

The structure of **2** was determined by a similar experimental technique. The space group *Pbca* was uniquely determined by systematic absences. A summary of crystal and intensity data for **2** is presented in Table I. The final discrepancy indices were $R(F) = 5.03\%$ and $R_w(F) = 5.02\%$. The highest peak in the final difference map is 2.1 e Å^{-3}. The final positions and thermal parameters of the refined atoms appear in Table IV; selected bond distances and bond angles for **2** appear in Table V. The labeling scheme and molecular structure are presented in Figure 2.

Neither structure is crystallographically very satisfying; each, however, represents the best of several complete data collections, including experimentation with schemes for absorption correction, both empirical and analytical, none of which provided the elimination of effects evident in the high residual electron density and high esd's for the bond parameters.

Other Instrumental Methods. Solid-state ^{13}C CP-MAS NMR spectra were recorded at 75.5 MHz with the use of a Bruker CXP-300 spectrometer. ^{13}C NMR data were obtained on a Bruker WM-250 operating at 62.9 MHz on saturated solutions of **1** in Me_2SO–d_6 referenced to the solvent and on neat samples of reaction mixtures of K_2PtCl_4/dea and K_2PtCl_4/*N*-methylpyrrolidinone externally referenced to Me_4Si. Transmittance IR spectra were obtained on a Perkin-Elmer 180 spectrophotometer; reflectance spectra were obtained by utilizing a Nicolet 7199 infrared interferometer. Mass spectrometric data were collected on a Du Pont 492B double-focusing mass spectrometer. Gas chromatographic analyses were run on a Perkin-Elmer Sigma 2000 using a 0.25-mm-i.d., 10-m methyl silicone column.

Results and Discussion

During our study of the reactions of various platinum(II) compounds with *N*,*N*-dialkylacetamides under mild reaction conditions (60 °C with stirring), a pale yellow crystalline material was isolated from the reaction of potassium tetrachloroplatinate(II) and *N*,*N*-dimethylacetamide which has been shown to have the molecular structure shown in Figure 1, and the molecular formula $Pt(C_4H_8NO)_2Cl_2$ (**1**). The structure suggests that an oxidative addition has occurred with the generation of a platinum(IV) chelate involving N-methyl carbons of two *N*,*N*-dimethylacetamide ligands. When bond lengths expected for the carbonyl and carbon-nitrogen bonds of *N*,*N*-dimethylacetamide are compared with literature values,[19] the X-ray data for C–O and C–N bonds in **1** indicate that charge delocalization has occurred in the chelate ring. Platinum–carbon and C(1)–N(1) bond distances and C(1) bond angles are consistent with sp^3 hybridization of the methylene carbon. The C(1)–N(1)–C(3) bond angle of 115 (2)° suggests approximate sp^2 hybridization. Platinum–carbon, platinum–oxygen, and platinum–chlorine bond lengths are consistent with those for platinum(IV) compounds.[19] Analysis of intermolecular contacts for the crystal does not indicate hydrogen bonding as a factor in unit cell packing. Alkenylization of the *N*,*N*-dimethylacetamide ligand and modification of the square-planar $PtCl_4^{2-}$ to angular geometry would allow formation of **1** according to Saillard and Hoffmann's theory of frontier molecular orbital interactions.[20] Confirmation of carbonyl oxygen chelation and cis conformation of the ligand to the metal center for **1** have been demonstrated through IR and solid-state ^{13}C NMR analyses. The carbonyl IR absorbance of dma (ν = 1639 cm^{-1})[21] was shifted to ν = 1568 cm^{-1} in transmittance IR spectra, indicating chelation.[22] Transmittance and reflectance IR of the compound confirmed cis conformation of the carbon and oxygen ligands (ν(Pt–C) = 618 and 603 cm^{-1} and ν(Pt–O) = 530 and 522 cm^{-1}),[22] while the platinum–chlorine linkage was indicated by single absorbances at ν = 335 cm^{-1} in the transmittance spectrum and ν = 341 cm^{-1} in the reflectance spectrum.[23] Chelation of the metal center to the dma ligand was also indicated by the downfield shift (deshielding) of the carbonyl carbon of dma in solid-state ^{13}C NMR spectra (dma C=O, δ = 169.60; chelated C=O, δ = 177.0).[24] Cis conformation of the methylene carbon atoms was shown by a large platinum–carbon coupling constant (J = 620 ± 20 Hz), indicative of trans carbon–oxygen placement.[25] The molecular formula of the compound is supported by direct chemical ionization (DCI) mass spectrometry, which showed an abundant species with an isotope cluster corresponding to $(M + H–HCl)^+$ from **1**, although no significant amounts of $(M + H)^+$ ions were observed.

A second product, $Pt(C_4H_9NO)_2Cl_2$ (**2**), isolated from the same reaction mixture on further concentration was determined by X-ray crystallography to be a platinum(II) compound having a trans conformation of both the carbonyl oxygens of the dma ligand and the chlorides (see Figure 2). Trans placement of the carbonyl groups of the dma ligand in this case appears to preclude chelate formation.

Crystalline materials have not been isolated from reactions of K_2PtCl_4 with *N*,*N*-diethylacetamide and *N*-methylpyrrolidinone, although solution ^{13}C NMR spectra indicate, in both cases, that carbonyl attachment has occurred (deshielding of the carbonyl carbon) and that some carbon activation has taken place (platinum–carbon constants of approximately 320 Hz).

Gas chromatographic analyses of reaction mixtures of K_2PtCl_4/dma, after removal of the crystalline product, showed

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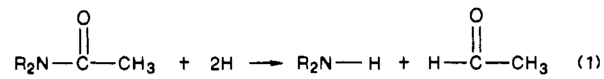
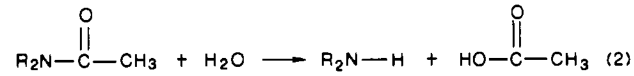
the presence of acetaldehyde, which is consistent with reductive decomposition of excess dma by hydrogen released during the oxidative-addition reaction forming **1** (reaction 1).



$$R_2N{-}C({=}O){-}CH_3 + 2H \longrightarrow R_2N{-}H + H{-}C({=}O){-}CH_3 \quad (1)$$

In contrast, reaction mixtures of K_2PtCl_4/dea, which did not yield crystalline products, did not show the presence of acetaldehyde in gas chromatographic analyses. The latter reaction mixtures were shown to contain trace amounts of acetic acid by gas chromatography, indicating that some hydrolysis of the solvent dea was occurring, rather than reductive decomposition (reaction 2).



$$R_2N{-}C({=}O){-}CH_3 + H_2O \longrightarrow R_2N{-}H + HO{-}C({=}O){-}CH_3 \quad (2)$$

We have structurally and spectroscopically characterized a new platinum(IV)/acetamide chelate prepared under mild reaction conditions. Currently, research is concentrated in the areas of isolation of crystalline analogues of the platinum/*N*,*N*-dimethylacetamide compound and in identification of the organic byproducts of the reactions by NMR spectroscopy, mass spectrometry, and gas chromatography of reaction mixtures.

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Registry No. **1**, 103027-01-6; **2**, 103129-26-6; dma, 127-19-5; dea, 685-91-6; K_2PtCl_4, 10025-99-7; *N*-methylpyrrolidinone, 872-50-4.

Supplementary Material Available: Tables of anisotropic temperature factors and hydrogen atom coordinates (2 pages); tables of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Oxidative Chlorination of Aldehydes and Ketones by Molybdenum(IV): A Synthetic Route to Molybdenum(III) Halide Complexes

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Compounds of the general formula MX_nL_{6-n} are useful sources of monomeric metal halides, particularly when L is readily displaced. Well-known examples include the series of early-transition-metal tetrahydrofuran complexes, $MCl_4(THF)_2$ and $MCl_3(THF)_3$.[1] For M = molybdenum the latter was originally prepared from $MoCl_4(THF)_2$ with metallic zinc as reductant,[2] but a recent modification makes use of metallic tin.[3] In our work we sought similar compounds without oxygen donor atom ligands; while $MoCl_4(NCR)_2$ is available from $MoCl_5$,[4] it has been noted that reduction to $MoCl_3(NCR)_3$ is difficult to control when typical inorganic reducing agents are employed.[2] Presumably, this reflects the need to employ less aggressive reducing agents. Herein we report that $MoCl_4(NCMe)_2$ is effective in the oxidative chlorination of α-branched ketones and aldehydes; this reaction is of interest because it constitutes a simple route to some synthetically useful Mo(III) precursors.

For the bulk of this work we chose to concentrate on isobutyraldehyde, since reactions with this compound proceed at convenient rates. When an acetonitrile solution of this aldehyde was added to an acetonitrile suspension of brown $MoCl_4(NCMe)_2$, the suspension gradually (ca. 20–30 min at 50 °C) transformed into a light yellow solution. The process is apparently that represented in eq 1, in which 2 equiv of Mo(IV) is reduced with

$$2MoCl_4(NCMe)_2 + Me_2CHCHO \xrightarrow[MeCN]{} 2MoCl_3(NCMe)_3{\cdot}MeCN + Me_2CClCHO + HCl \quad (1)$$

concurrent production of chloroaldehyde and HCl. Propylene oxide was used to scavenge the HCl produced; the advantage of this over other bases is the volatility of the resulting neutralization product. In synthetic reactions, all volatiles were removed in vacuo and the resulting residue crystallized from MeCN or MeCN/Et_2O. While the reaction appears to proceed quantitatively, isolated yields are typically in the range 50–60%; in this regard we note the importance of avoiding large excesses of organic reactants, since a secondary reaction darkens the solution and reduces the yield of $MoCl_3(NCMe)_3$. The organic product was identified from a reaction using $MoCl_4(NCCD_3)_2$ in CD_3CN solution; the volatiles were vacuum-distilled and $Me_2CClCHO$ identified via its NMR spectrum,[5] which showed no evidence of the presence of aldehyde condensation products.

While $MoCl_3(NCMe)_3{\cdot}MeCN$ has been prepared previously,[6,7] its geometry has not been determined. A straightforward analysis of the IR spectrum leads to formulation of a *facial* geometry,[8] but we were concerned about the possibility of accidental IR degeneracies and chose to undertake a crystallographic study of the compound.[9] Unfortunately, efforts to solve the structure were hampered by disorder resulting from partial occupation of the site of the lattice MeCN molecule. Because of this the data were not refined to an acceptable degree, but they did allow assignment of a *meridional* goemetry about Mo. Thus, the strong band at 2280 cm^{-1} is likely composed of two degenerate absorptions.

The mechanism by which molybdenum is reduced is of interest since (a) the aldehyde is not oxidized to the corresponding carboxylic acid[10] and (b) $MoCl_4(NCMe)_2$ has been noted to behave as a nonelectrolyte in MeCN solution.[6] Since the reaction reported herein occurs most readily for α-branched aldehydes and ketones, enolization is very likely an important step in the overall reaction. We favor an inner-sphere mechanism involving coordinated carbonyl or enol,[11a] but we note that an outer-sphere process is also viable if electron transfer precedes chloride transfer. This oxidative chlorination is very similar to the $CuCl_2$-mediated oxidative chlorination of aldehydes (eq 2);[11b–d] the latter process can

$$2RCH_2CHO + CuCl_2 \rightarrow 2RCHClCHO + CuCl + HCl \quad (2)$$

be rendered catalytic in $CuCl_2$ by the addition of Cl_2, which serves

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(8) In fact, $MoCl_3(NCMe)_3{\cdot}MeCN$ displays three IR bands (see Experimental Section), but the lowest (energetically) of these is assigned to the free MeCN in the lattice. When the complex is stirred in THF, this band is lost rapidly, while the others persist for ca. 2 days. Hence, the complex itself accounts for only two of the observed bands.

(9) Crystallographic data for $MoCl_3(NCMe)_3{\cdot}MeCN$: $a = 12.255\ (5)$ Å, $b = 15.18\ (2)$ Å, $c = 8.731\ (1)$ Å, $\alpha = 92.53\ (5)°$, $\beta = 105.48\ (2)°$, $\gamma = 82.48\ (7)°$, $Z = 4$, space group $P\bar{1}$; $R = 0.16$ for 4077 reflections, of which 2603 were significant at the 3σ level. These data were sufficient to allow formulation of a meridional geometry (all heavy atoms were located).

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