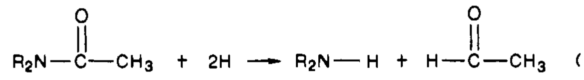
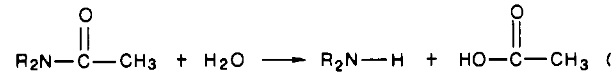
the presence of acetaldehyde, which is consistent with reductive decomposition of excess dma by hydrogen released during the oxidative-addition reaction forming **1** (reaction 1).



$$R_2N-\overset{O}{\overset{\|}{C}}-CH_3 + 2H \longrightarrow R_2N-H + H-\overset{O}{\overset{\|}{C}}-CH_3 \tag{1}$$

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).



$$R_2N-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \longrightarrow R_2N-H + HO-\overset{O}{\overset{\|}{C}}-CH_3 \tag{2}$$

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.

Acknowledgment. The purchase of the X-ray diffractometer was supported by the National Science Foundation.

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

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

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

$$2RCH_2CHO + CuCl_2 \rightarrow 2RCHClCHO + CuCl + HCl \tag{2}$$

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

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(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).

(10) Metal ions are readily able to oxidize aldehydes to carboxylic acids under aerobic/aqueous conditions: March J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; pp 641–643.

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to reoxidize the CuCl produced.[12] The $CuCl_2$ reaction is of greater organic synthetic utility in that it is also effective with unbranched aldehydes and ketones. While $MoCl_4(NCMe)_2$ will chlorinate 2-methylcyclohexanone, we have not completed studies of this reaction or of the general scope of these Mo(IV)-induced oxidative chlorinations.

Previous synthetic routes to $MoCl_3(NCMe)_3$ include the reaction of $Mo_2Cl_9^{3-}$ and MeCN[6] as well as reduction of $MoCl_4(NCMe)_2$ with tetrakis(trimethylsilyl)hydrazine, $[(Me_3Si)_2N]_2$.[7] The route described herein combines the advantages of reasonable yields and readily available starting materials. Furthermore, the THF complex $MoCl_3(THF)_3$ has proved useful as a Mo(III) starting material,[4] and as such we felt it worthwhile to determine if the present chemistry could be utilized in the preparation of this compound. Indeed, if $MoCl_3(NCMe)_3$ is suspended in THF solvent and stirred for 1–2 days (ambient temperature), the result is high-yield conversion to $MoCl_3(THF)_3$ (the latter was identified by comparison of its IR spectrum to that of an authentic sample[4]). Overall, the sequence is as represented in eq 3. Additionally,

$$MoCl_5 \rightarrow MoCl_4(NCMe)_2 \rightarrow MoCl_3(NCMe)_3 \rightarrow MoCl_3(THF)_3 \quad (3)$$

it should be mentioned that the yields of $MoCl_3(THF)_3$ are comparable to those obtained via the intermediacy of $MoCl_4(THF)_2$ and the workups are simplified since all byproducts are volatile and easily removed. The reactions reported here represent unusually mild conditions for the reduction of metal halide species. They are clearly useful in this molybdenum system, and we intend to determine if such reactions are generally applicable to high-valent-metal halide complexes. Additionally, efforts will be directed toward organic applications. Two immediate goals are further exploration of the scope and utility of the process (i.e., with what types of organic carbonyls it is operable) and the development of conditions for making the reaction catalytic in metal halide reagent.

Experimental Section

All manipulations were carried out under an inert atmosphere (argon or nitrogen) using either standard Schlenk techniques or a Vacuum Atmospheres Corp. glovebox. Acetonitrile was distilled from CaH_2 and ether was distilled from sodium benzophenone ketyl, both under nitrogen. Isobutyraldehyde (Aldrich) and propylene oxide (MCB) were stirred over 4A molecular sieves and vacuum-distilled. Molybdenum pentachloride (Aldrich) was used as received and converted to $MoCl_4(NCMe)_2$ via the method of Dilworth.[4] IR spectra were obtained on a Perkin-Elmer M1500 FTIR spectrophotometer and NMR spectra (200 MHz) on a Varian XL-200 FTNMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Tris(acetonitrile)trichloromolybdenum(III). Bis(acetonitrile)tetrachloromolybdenum(IV) (1.0 g, 3.13 mmol) was suspended in 20 mL of acetonitrile. A solution of isobutyraldehyde (0.57 mL, 6.26 mmol) in 20 mL of acetonitrile was then added to the suspension. The system was closed (to avoid loss of aldehyde) and immersed in a warm bath at ca. 50 °C. After being stirred for ca. 20 min, the brown suspension converted to a light yellow solution, at which time propylene oxide (0.28 mL, 4.0 mmol) was added to neutralize the HCl. After being stirred an additional few minutes, the solution was removed from the bath and stripped to dryness in vacuo. The greenish yellow residue was dissolved in a minimum volume of acetonitrile and ether added to the saturation point. Cooling resulted in precipitation of yellow $MoCl_3(NCMe)_3{\cdot}MeCN$ (0.64 g, 55%). Anal. Calcd for $MoCl_3C_8H_{12}Cl_3$: C, 26.22; H, 3.30; N, 15.29; Cl, 29.02. Found: C, 26.31; H, 3.24; N, 14.74; Cl, 29.71. IR (Nujol): 2312 m, 2280, s, 2275 m, 1028 m, br cm^{-1}.

Acknowledgment. This work was supported by Wesleyan University and the donors of the Petroleum Research Fund, administered by the American Chemical Society. S.R. thanks the Shell Foundation for financial support in the form of a summer fellowship. We also thank Dr. James Springer of Merck & Co. for carrying out the X-ray diffraction studies.

Registry No. $MoCl_4(NCMe)_2$, 19187-82-7; $MoCl_3(NCMe)_3{\cdot}MeCN$, 102977-17-3; $MoCl_3(THF)_3$, 31355-55-2; Me_2CHCHO, 78-84-2.

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Effects of Mixed-Ligand Complexation on the Geometry of Copper(II) Complexes. X-ray Study of (Hexafluoroacetylacetonato)(acetylacetonato)copper(II)

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Cu(II) bis chelate complexes are normally found in a square planar or a tetrahedral environment.[1] Square-planar geometries are easily explained by crystal field theory. Distortions toward a tetrahedral environment are less common and are usually explained on the basis of steric and/or anion repulsions. Thus, we had very little expectation of any "surprises" when starting this structural study.[2] However, the previous studies do not include any examples of mixed-bidentate-ligand bis complexes. In this paper, we report the first study of this class of complex and find one completely unexpected result. Although the four oxygens and the Cu(II) are essentially square planar, the planes of the chelate rings form an angle of 163.5° with each other.

An ORTEP[3] drawing is given in Figure 1. The bond lengths and angles are given in Tables I and II. Because the molecule has no imposed symmetry, four Cu–O distances and two O–Cu–O chelate "bite" angles were obtained. The average Cu–O bond length on the hfac side is 1.946 [5] Å. This difference is consistent with our earlier IR and ESR results.[4] The Cu–O bond length on the acac side is shorter than the bond length in the nonmixed $Cu(acac)_2$ complex (1.921 [5] Å).[7] This appears to be direct support for the trans effect model, as the stronger ligand (acac) has a shorter bond when across from a weaker ligand (hfac) than when across from another acac.

The atomic coordinates are given in Table III. Least-squares plane calculations indicated that the four oxygens are within ±0.062 Å of being square planar. The copper is displaced slightly (0.060 Å) from the plane. The surprising thing is that, in the solid state, the molecule as a unit is decidedly folded, the angle between the two chelates being 163.5°. As discussed by Maslen and Waters[5] and by Robertson and Truter,[6] a stepped (chair) type distortion is common in Cu(II) complexes. In Cu(II) acac type complexes, distortion angles ranging from 0 to 14° have been reported (see Table 6 of ref 6). All of these distortions are of the stepped type. A stepped type distortion still leaves the ligand planes parallel to each other and, thus, has only a small effect on inter-ring conjugation (see Figure 11 of ref 5). However, the large umbrella (boat) type distortion observed in the present complex is thought to be inconsistent with significant inter-ring conjugation. The extent of inter-ring conjugation in acac type complexes has been a controversial point in the literature.[8] In a previous paper,[9] we reported that molecular orbital calculations

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(2) A green crystal of dimensions 0.2 × 0.2 × 0.06 mm was mounted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. With Mo Kα ($\lambda = 0.71069$ Å) at room temperature, the crystal data were as follows: triclinic, $P\bar{1}$, $a = 8.775$ (3) Å, $b = 12.052$ (4) Å, $c = 6.978$ (3) Å, $\alpha = 99.87$ (3)°, $\beta = 114.13$ (3)°, $\gamma = 90.70$ (3)°, $Z = 2$, $\mu = 18.1$ cm^{-1}, with no absorption correction applied. Data were collected for 1394 unique reflections up to a 2θ limit of 40.0° by the 2θ–θ scan technique in bisecting mode. The structure was solved by MULTAN.[10] Full-matrix least-squares anisotropic (for all non-hydrogen atoms) refinement converged to $R = 0.053$. The final ΔF synthesis showed two peaks: 0.53 /Å^3 at one fluorine and 0.43 e/Å^3 at the copper.

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