noted when ^{13}C-enriched $W(CO)_5THF$ was added to the $S[Cr_3(CO)_{12}]^{2-}$ anion.

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Registry No. 1, 91670-43-8; 2^{2-} $[PPN^+]_2 \cdot (CH_3)_2CO$, 91670-45-0; $[Na][PPN][\{(CO)_5Cr\}_2S]$, 87039-34-7; $(\mu\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5{}^{2-}$, 87050-03-1; $Cr(CO)_5THF$, 15038-41-2; $W(CO)_5THF$, 36477-75-5.

Methathesis of Molybdenum–Molybdenum Triple Bonds with Acetylenes To Give Alkylidyne Complexes[1]

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Summary: $Mo_2(OCMe_3)_6$ reacts with phenylacetylene in pentane to produce $Mo(CPh)(OCMe_3)_3$ in ~60% yield (by ^1H NMR) in ~2 h. It can be isolated by sublimation in ~30% yield. In the presence of quinuclidine (quin) $Mo_2(OCMe_3)_6$ reacts with phenylacetylene to yield an inseparable 1:1 mixture of $Mo(CPh)(OCMe_3)_3$(quin) and $Mo(CH)(OCMe_3)_3$(quin) in a combined yield of ~60%. Analogous reactions between $Mo_2(OCMe_3)_6$ and 1-pentyne in the presence of quinuclidine yield oily 1-pentyne oligomers containing a mixture of $Mo(CPr)(OCMe_3)_3$(quin) and $Mo(CH)(OCMe_3)_3$(quin) in ~50% yield (by ^1H NMR). In the absence of quinuclidine only $Mo(CPr)(OCMe_3)_3$ is observed by NMR in the oily product mixture. Addition of acetylene to $Mo_2(OCMe_3)_6$ yields what we propose to be $Mo_2(OCMe_3)_6(\mu\text{-}C_2H_2)$, which upon attempted recrystallization loses acetylene to reform $Mo_2(OCMe_3)_6$.

Two years ago we reported that $W_2(OCMe_3)_6$ reacts with disubstituted acetylenes to give alkylidyne complexes of the type $W(CR)(OCMe_3)_3$ and with nitriles to give a mixture of $W(CR)(OCMe_3)_3$ and $[W(N)(OCMe_3)_3]_x$.[2] The reaction appeared to be highly specific in that other W_2X_6 complexes (e.g., X = NMe_2, OCH_2CMe_3, CH_2SiMe_3) either did not react with acetylenes or nitriles or did not give alkylidyne complexes. We thought it peculiar that $Mo_2(OCMe_3)_6$ also did not react with disubstituted acetylenes or with nitriles, especially since reactions between both $W_2(OR)_6$ and $Mo_2(OR)_6$ (R = *i*-Pr, *t*-Bu, CH_2-*t*-Bu) and acetylenes have produced a number of interesting, closely related, dimeric compounds containing one or more acetylenes.[3] Here we report that the $Mo{\equiv}Mo$ bond in $Mo_2(OCMe_3)_6$ *can* be cleaved under mild conditions, but only by terminal acetylenes.

$Mo_2(OCMe_3)_6$[4] in pentane (~50 mg in ~3 mL) reacts immediately with 15 equiv of phenylacetylene to give a brown solution and over a period of 2 h a brown precipitate. The solvent was removed from the filtrate to give a brown residue that by ^{13}C NMR was shown to contain $Mo(CPh)(OCMe_3)_3$ in a yield of 50–60% (^1H NMR vs. an internal standard).[5] $Mo(CPh)(OCMe_3)_3$ can be sublimed from the crude mixture at 65 °C (0.001 μm) in ~30% yield (vs. $Mo_2(OCMe_3)_6$.[7] Lowering the temperature (6 h at 0 °C, 12 h at 25 °C) did not improve the yield (~40% crude). Use of fewer equivalents of phenylacetylene leads to incomplete consumption of $Mo_2(OCMe_3)_6$. The yield also was not improved by adding a dilute solution of the acetylene to a solution of $Mo_2(OCMe_3)_6$ (concentrated or dilute) over a period of 1 h. On the basis of these results we can only conclude that the $Mo{\equiv}Mo$ bond is split by $PhC{\equiv}CH$; we do not know the fate of "$Mo(CH)(OCMe_3)_3$".

Studies in the related tungsten system[6] have shown that $W_2(OCMe_3)_6$ reacts with $PhC{\equiv}CH$ in the presence of quinuclidine (1-azabicyclo[2.2.2]octane) to produce a 1:1 mixture of $W(CPh)(OCMe_3)_3$(quin) and $W(CH)(OCMe_3)_3$(quin) in high yield. The reaction between $Mo_2(OCMe_3)_6$ and $PhC{\equiv}CH$ (3 equiv/dimer) in the presence of quinuclidine (8 equiv) proceeds analogously (eq 1) in ~60% yield (by ^1H NMR vs. CH_2Cl_2 as an internal standard) in 2 h in pentane. The methylidyne proton in $Mo(CH)(OCMe_3)_3$(quin) is observed at 3.98 ppm (in C_6D_6) and the methylidyne carbon atom at 267.2 ppm (in C_6D_6; J_{CH} = 146 Hz) in the crude reaction mixture (cf. $W(CH)(OCMe_3)_3(quin)$[10]). Slow, partial sublimation of the crude reaction mixture at 25 °C and 0.001 μm yields a virtually identical mixture of $Mo(CPh)(OCMe_3)_3$(quin) and $Mo(CH)(OCMe_3)_3$(quin). So far we have not found a way to separate these two compounds. We propose that $Mo(CH)(OCMe_3)_3$(quin) is produced when the primary product $Mo(CH)(OCMe_3)_3$ is trapped by quinuclidine. In the absence of quinuclidine some of the methylidyne complex is *probably* converted into $Mo(CPh)(OCMe_3)_3$, judging from the 50 ± 5% yield quoted above, although whether that conversion consists of a metathesis reaction between $Mo(CH)(OCMe_3)_3$ and $PhC{\equiv}CH$ is unknown.[11]

$$Mo_2(OCMe_3)_6 \xrightarrow[\text{quin}]{PhC\equiv CH} Mo(CPh)(OCMe_3)_3(\text{quin}) + Mo(CH)(OCMe_3)_3(\text{quin}) \quad (1)$$

A reaction similar to that shown in eq 1 in the presence of pyridine (4 equiv) yields only $Mo(CPh)(OCMe_3)_3$(py) in ~50% yield by ^1H NMR (vs. CH_2Cl_2). Attempted sublimation of $Mo(CPh)(OCMe_3)_3$(py) from the crude reaction mixture yielded only $Mo(CPh)(OCMe_3)_3$.

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[1] Multiple Metal-Carbon Bonds. 36. For part 35 see ref 6.

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[5] δ(*C*Ph) 276.7 in $Mo(CPh)(OCMe_3)_3$ in C_6D_6; cf. δ(*C*Ph) 257.0 in $W(CPh)(OCMe_3)_3$ in C_6D_6.[6]

[6] Listemann, M. L.; Schrock, R. R. *Organometallics*, in press.

[7] (a) Anal. Calcd for $MoC_{19}H_{32}O_3$: C, 56.43; H, 7.97. Found: C, 55.73; H, 7.86. (b) We have recently discovered[8] that $Mo(CCMe_3)(OCMe_3)_3$ can be prepared from MoO_2Cl_2 via $(Mo(CCMe_3)(CH_2CMe_3)_3$.[9] Although $Mo(CCMe_3)(OCMe_3)_3$ does *not* react with disubstituted acetylenes, it *will* react with terminal acetylenes to give $Mo(CR)(OCMe_3)_3$ and $Me_3CC{\equiv}CH$ quantitatively McCullough, L., unpublished results). Both $Mo(CPh)(OCMe_3)_3$ and $Mo(CPr)(OCMe_3)_3$ (inter alia) have been prepared by this method. Addition of quinuclidine to $Mo(CPr)(OCMe_3)_3$ gives $Mo(CPr)(OCMe_3)_3$(quin) quantitatively, while addition of pyridine to $Mo(CPh)(OCMe_3)_3$ gives $Mo(CPh)(OCMe_3)_3$(py).

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[10] In $W(CH)(OCMe_3)_3$(quin) the methylidyne proton is observed at 5.15 ppm and the carbon atom at 247.1 ppm (J_{CW} = 287 Hz, J_{CH} = 147 Hz) in C_6D_6.[6]

[11] Chisholm has obtained strong evidence that $W_2(\mu\text{-}C_2H_2)(py)(OCMe_3)_5(\mu\text{-}OCMe_3)$ is in equilibrium with "$W(CH)(OCMe_3)_3$" in the presence of pyridine (probably as an unstable pyridine adduct, $W(CH)(OCMe_3)_3(py)$).[3b] Conceivably, therefore, $Mo(CH)(OCMe_3)_3$ could decompose bimolecularly to reform $Mo_2(OCMe_3)_6$, which could then react with more $PhC{\equiv}CH$.

The reaction between $Mo_2(OCMe_3)_6$ and 1-pentyne (1:10) in the presence of 8 equiv of quinuclidine in pentane (4 h) yields a pentane-soluble crude reaction mixture that contains $Mo(CH)(OCMe_3)_3$(quin) and what can be identified as $Mo(CPr)(OCMe_3)_3$(quin) by comparison of its ^1H NMR spectrum with that of an authetic sample[7b] in ~50% total yield by ^1H NMR (vs. CH_2Cl_2). The formation of oily oligomers has thus far prevented isolation of the product. In the absence of quinuclidine the reaction between $Mo_2(OCMe_3)_6$ and 1-pentyne yields oils (thought to be 1-pentyne oligomers) that contain $Mo(CPr)(OCMe_3)_3$ (δ(*C*Pr) 286.6 in C_6D_6) in about 30% yield by ^1H NMR.[7b]

Addition of 1 equiv of acetylene itself to $Mo_2(OCMe_3)_6$ in the presence or absence of quinuclidine produces what appears to be $Mo_2(OCMe_3)_6(\mu\text{-}C_2H_2)$ by ^{13}C NMR. In particular, the acetylenic carbon atom signal is found at 127.1 ppm in dioxane-d_8 with J_{CH} = 198 Hz and the acetylene proton signal at 5.99 ppm in C_6D_6 (cf. μ-C_2H_2 complexes of tungsten; ref 3c and references therein). The conversion of $Mo_2(OCMe_3)_6$ to $Mo_2(OCMe_3)_6(\mu\text{-}C_2H_2)$ in pentane is high, but attempted recrystallization of the crude red solid reaction product yields more and more $Mo_2(OCMe_3)_6$, apparently due to loss of acetylene from $Mo_2(OCMe_3)_6(\mu\text{-}C_2H_2)$. This reaction is far from definitive but provides some evidence that the first step in the cleavage of the $Mo\equiv Mo$ bond by an acetylene is addition of the acetylene to give a tetrahedral Mo_2C_2 core, as all evidence to date overwhelmingly suggests.[3]

The reactions outlined here do not appear to be as selective for scission of triple bonds as those involving $W_2(OCMe_3)_6$.[2] Apparently other reactions (acetylene dimerization, etc.) compete effectively with the scission reaction. Nevertheless, we have at least demonstrated that the principles, if not yet the synthetic utility, of $W\equiv W$ bond cleavage extend to the analogous $Mo\equiv Mo$ systems. We should note, however, that so far we have not observed scission of acetonitrile or benzonitrile by $Mo_2(OCMe_3)_6$, a reaction in the tungsten system that is qualitatively at least as fast, if not faster than, scission of acetylenes.

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Registry No. $Mo_2(OCMe_3)_6$, 60764-63-8; $Mo(CPh)(OCMe_3)_3$, 91760-26-8; $Mo(CPh)(OCMe_3)_3$(quin), 91780-94-8; $Mo(CH)(OCMe_3)_3$(quin), 91780-95-9; $Mo(CPh)(OCMe_3)_3$(py), 91760-27-9; $Mo(CPr)(OCMe_3)_3$(quin), 91780-96-0; $Mo_2(OCMe_3)_6(\mu\text{-}C_2H_2)$, 91760-28-0; $Mo(CCMe_3)(OCMe_3)_3$, 82209-30-1; $Mo(CPr)(OCMe_3)_3$, 91780-93-7; $PhC\equiv CH$, 536-74-3; quin, 100-76-5; py, 110-86-1; 1-pentyne, 627-19-0; acetylene, 74-86-2.

Selective Reduction of Acyl Chlorides to Aldehydes by Anionic 6B Transition-Metal Hydrides

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Summary: Acyl chlorides can be selectively and rapidly reduced, under mild conditions, by group 6B anionic hydrides, $HM(CO)_4L^-$ (M = Cr, W; L = CO, PR_3), giving the corresponding aldehydes and the metal chlorides $ClM(CO)_4L^-$. The reaction is nearly quantitative for both aliphatic and aromatic acyl chlorides using solvent systems such as dichloromethane, tetrahydrofuran, or acetonitrile. Only in the presence of acid will the aldehydes consume a second equivalent of hydride, subsequently being reduced to alcohols. The anionic hydrides selectively reduce acyl chlorides in the presence of other reducible groups such as alkyl bromides or nitro aromatics. In situ preexchange of hydrogen by deuterium ($HM(CO)_4L^-/CH_3OD \rightarrow DM(CO)_4L^-/CH_3OH$) allows for deuterium delivery, giving RCDO products, as indicated by ^2H NMR.

The monomeric group 6B transition-metal hydrides $HM(CO)_4L^-$, where M = Cr or W and L = CO or PR_3, reduce alkyl halides, with reactivities approaching that of the powerful main-group metal hydrides such as Brown's HBR_3^- reagents.[2] We have now learned that the more reactive acyl chlorides can be selectively reduced to the corresponding aldehydes without further reduction to alcohols—a complication which is unavoidable with Brown's HBR_3^- reagents.[3] This exceptional utility of group 6B hydrides for selective reduction of acyl chlorides has prompted this preliminary report.

Acyl chlorides react within the time of mixing with the group 6B hydrides $HM(CO)_4L^-$ at 25 °C to generate the corresponding aldehydes and the metal chlorides $ClM(CO)_4L^-$ as described in eq 1.[4,5] The organometallic

$$RC(=O)Cl + HM(CO)_4L^- \rightarrow RC(=O)H + ClM(CO)_4L^- \quad (1)$$

product $ClM(CO)_4L^-$ was identified by its IR spectrum, e.g., for $ClCr(CO)_5^-$, ν_{CO} (cm^{-1}) = 2058 (w), 1932 (s), and 1864 (m). The conversion from acyl chloride to aldehyde was monitored in every case by IR and ^1H NMR spectroscopies as well as by GC analysis. In most cases, the deuterium-labeled aldehyde (vide infra) was also identified by ^2H NMR. The benzaldehyde product of reduction of benzoyl chloride was positively identified by GC/MS analysis. Yields as checked by GC analysis always agreed with those checked by spectroscopic means. As shown in Table I, the reaction is nearly quantitative for both aliphatic and aromatic acyl chlorides using solvent systems such as dichloromethane, tetrahydrofuran, or acetonitrile. One reduction (benzoylchloride/$HCr(CO)_5^-$) was done at the synthetic level (0.5 g of $PPN^+HCr(CO)_5^-$, 0.050 g of C_6H_5COCl in 25 mL of THF). The THF solvent was removed by trap to trap distillation (liquid N_2 as trappant) and the benzaldehyde product separated from the oily orange residue by hexane extraction. Following filtration through a short Celite column the hexane was removed by trap to trap distillation. Benzaldehyde, free of any organometallic products, was thus isolated in 59% yield (nonoptimized) based on benzoyl chloride.

To take advantage of the facile hydrogen–deuterium exchange reaction of eq 2,[6] the acyl chlorides were reacted

$$HM(CO)_4L^- + CH_3OD \rightleftharpoons DM(CO)_4L^- + CH_3OH \quad (2)$$

with the hydrides (ca. 0.1 mmol) in THF/CH_3OD, (5 mL

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