Mo1–C2 bond is about as short as the Mo–C double bond in $[Mo\{C{=}C(CN)_2\}Cl\{P(OMe)_3\}_2(Cp)]$ (1.833 (6) Å)[9] but not as short as the Mo–C triple bond in $[Mo(CCH_2CMe_3)\{P(OMe)_3\}_2(Cp)]$ (1.798 (2) Å).[10] Carbonyl C4–O4 has a much longer Mo–C bond, a C–O bond indistinguishable from the three terminal carbonyls in the structure, a long Zr–O bond, and a bent C–O–Zr linkage. This suggests that O4 is simply acting as a relatively weak, ketone-like σ-donor to the electron-deficient zirconium. The third isocarbonyl, C5–O5, is intermediate in all lengths and angles; its interaction with zirconium is strong, but it is less like a "carbyne" than C2–O2.

The two zirconium amide bonds (to N1 and N2) are the shortest Zr–N bonds that have been reported, comparable to those in $[Zr_2(\mu\text{-}NCMe_3)_2(NMe_2)_4]$ which range from 2.057 to 2.071 Å,[11] suggesting that N to Zr π-donation is important in alleviating the electron deficiency of zirconium. The zirconium–amine (N3) bond (in which π-donation is not possible) is considerably longer, comparable to Zr–N bonds in other zirconium amine complexes (2.43–2.54 Å).[12–14] The bonds from Zr to O4 and N3 are the longest in the structure, suggesting a structural trans influence due to effective π-donation from amides N1 and N2.[15] The major distortions of the zirconium coordination sphere from octahedral symmetry are toward these two weakly bonded ligands.

The 12-membered ring in I resembles that in $[(Cp)_2TiMo(CO)_3(C_5H_4Me)]_2$ (II), recently prepared from $[Mo_2(CO)_4(C_5H_4Me)_2]$ and $[Ti(CO)_2(Cp)_2]$ by Merola and co-workers.[16] One major difference between I and Merola's compound is the absence of cyclopentadienyl ligands on zirconium. The severe electron deficiency of zirconium in I may explain why the isocarbonyls in I are more "carbyne"-like than those in II, with slightly shorter Mo–C distances and more linear M–O–C angles by about 20°. A similar 12-membered $(Al\text{–}O\text{–}C\text{–}W\text{–}C\text{–}O)_2$ ring has been observed in $[AlMe_2\{W(CO)_3(Cp)\}]_2$, prepared from $[WH(CO)_3(Cp)]$ and Me_2AlX (X = H, Me) by Smith and coworkers.[17] In this case, one independent Al–O–C angle is bent (149°) and the second is nearly linear (176°). The origins of structural variation in Lewis acid adducts of metal carbonyls warrant further study.

Infrared spectra of I[6] show weak, low-frequency absorptions at ca. 1725 and 1600 cm^{-1}, characteristic of Lewis acid addition to the oxygen of a metal carbonyl.[18] Proton and carbon NMR spectra[6] suggest that I dissociates into monomers in benzene solution, since only one cyclopentadienyl resonance is observed, whereas there are two distinct environments in the solid state. (Rapid exchange between bridging and terminal sites cannot be ruled out.) Cleavage probably occurs at the weak Zr–O4 bond. Since diethylamine and diethylamido ligands retain distinct magnetic environments in solution, the amine proton does not pass rapidly from site to site. Presumably, the NH resonance itself is too broad to directly observe in the NMR spectrum.[19]

$[Zr\{Mo(CO)_3(Cp)\}_2(NEt_2)_2(NHEt_2)]_2$ reacts with Lewis bases. For example, dissolution in 1,2-dimethoxyethane rapidly causes I to dissociate into ions, as evidenced by the resulting IR spectrum of the $[Mo(CO)_3(Cp)]^-$ anion: $\nu(CO) = 1897$ (s), 1780 (s) cm^{-1}. Dissolution in tetrahydrofuran produced similar spectral changes, which are partially reversed when the product is redissolved in benzene.

$[Zr(NEt_2)_4]$ and $[MoH(CO)_3(Cp)]$ also react in molar ratios other than 1:2. Reaction in a 1:1 ratio produces only I and unreacted $[Zr(NEt_2)_4]$. Reaction in a 1:3 ratio in pentane gives a precipitate of I, whereas the same reaction in toluene leads to $[Zr\{Mo(CO)_3(Cp)\}_3(NEt_2)(NHEt_2)_2]$. The product of the 1:4 reaction is a red solid containing no ethyl groups (by NMR). Full characterization of these products is in progress.

Several important conclusions can be drawn from this work: (1) Dinuclear amine elimination is a useful method for preparing mixed-metal complexes under mild conditions, without competing oxidation–reduction reactions. (2) Multiple amine eliminations can be used to build polynuclear species. (3) Isocarbonyl bridges, rather than direct metal–metal bonds as earlier assumed, may be present in the products. (4) Eliminated amines may be *retained* as ligands.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Institute for Mining and Minerals Research and Occidental Research Corp. for financial support, Ashland Oil for a fellowship to W.J.S., and Dominic Chan for assistance with ref 11–14.

Supplementary Material Available: Listings of positional and thermal atomic parameters (Tables II and III) and experimental and calculated structure factors (Table IV) (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of a Cationic Rhenium Selenoformaldehyde Complex

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Summary: The first cationic selenoformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2{=}Se)]^+$ (3) has been pre-

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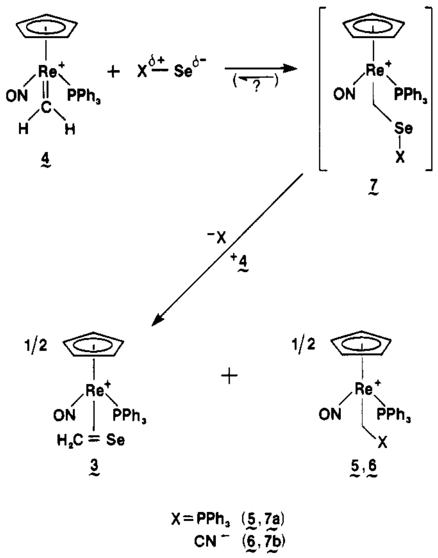
pared from the reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+$ and $PPh_3{=}Se$ or KSeCN. The telluroformaldehyde analogue could not be synthesized. Selenoformaldehyde complex 3 is characterized by ^1H, ^{13}C, and ^{31}P NMR, and IR spectroscopy, FAB MS, and X-ray diffraction.

Chalcoformaldehyde complexes are of current interest as potential model intermediates in catalytic CO/H_2 reactions.[1] A heterogeneous Fischer-Tropsch mechanism that relies heavily on oxygen bound formaldehyde species has been proposed recently.[2] A formaldehyde complex is thought to be a key intermediate in the formation of ethylene glycol and methanol from synthesis gas and homogeneous ruthenium catalysts.[3] In addition to their catalytic importance, chalcoformaldehyde complexes may allow for facile synthetic utilization of the $CH_2{=}E$ (E = O, S, Se, Te)[4] moiety. We therefore chose to investigate this interesting class of compounds and recently reported the syntheses, structures, and some reactivities of the formaldehyde and thioformaldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2{=}E)]^+PF_6^-$ (E = O (1), S (2)).[5] The stabilities of these rhenium complexes prompted investigations into the synthesis of complexes of the then unknown seleno- and telluroformaldehyde ligands. During the course of these studies, the first examples of seleno- and telluroformaldehyde complexes were reported.[6] This communication discloses (a) the synthesis of the first cationic selenoformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2{=}Se)]^+PF_6^-$ (3), (b) its X-ray crystal structure that represents the first structural characterization of a mononuclear selenoformaldehyde complex, and (c) the apparent inability to form a stable telluroformaldehyde complex in the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ system.

The reaction of the electrophilic methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (4)[7] with triphenylphosphine selenide (−78 → 25 °C) yields an equimolar mixture of 3[8] and the known phosphonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (5).[7] The cations are readily separated due to the low solubility of 3 in $CHCl_3$; diffusion crystallization from CH_2Cl_2/hexanes affords 3 and 5 in 39 and 41% isolated yields, respectively. Similar reaction of 4 with potassium selenocyanate forms 3 and a new cyanomethyl complex, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C{\equiv}N)$ (6).[9] Complex 6 is extracted from the evaporated reaction mixture with Et_2O and isolated in 13% yield by toluene/heptane diffusion crystallization at −20 °C. The ether-insoluble residue affords 3 in 45% yield after CH_2Cl_2/hexane crystallization. Monitoring of the reaction between $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$ (which has been shown to react as a stabilized source of 4)[10] and KSeCN by ^1H NMR indicates an equimolar product distribution. The low isolated yield of 6 is a consequence of its solution instability and reluctance to crystallize. An authentic sample of 6 was prepared in 79% yield by the reaction of 4 with NaCN.

Scheme I



The mechanism for the formation of 3 from 4 and $PPh_3{=}Se$ or KSeCN is depicted in Scheme I. Nucleophilic attack at the methylidene carbon of 4 forms intermediate 7 (not observed) that yields 3 upon loss of the nucleophilic leaving group X. However, nucleophile X is now free to react with additional 4 to yield 5 or 6. Stoichiometry, dilution, or order to reagent addition does not seem to affect the equimolar product distribution. A similar mechanism for the formation of 1 and 2 has been proposed.[5]

The stability and ready synthesis of 3 indicated that the tellurium analogue should be accessible by similar techniques. Unfortunately, extensive experimentation has failed to provide conclusive evidence for the existence of the telluroformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2{=}Te)]^+PF_6^-$ (8). Reactions of 4 with $[(PPh_3)_2N^+][TeCN^-]$[11] or $(Me_2N)_3P{=}Te$,[12] under conditions used for the synthesis of 3, lead to the precipitation

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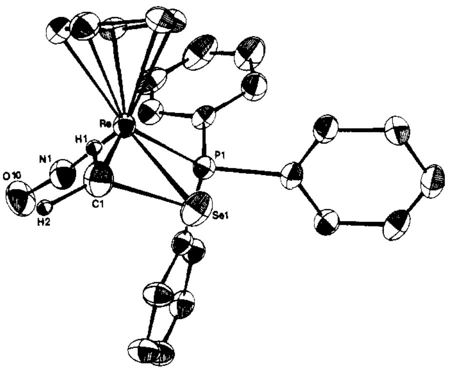

Figure 1. Molecular structure of 3.

of elemental tellurium and the formation of 6 or the new phosphonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(NMe_2)_3)]^+PF_6^-$ (9)[9] as the major identifiable products. Low-temperature, ^1H NMR monitored reactions of 4 and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$[10] with $[(PPh_3)_2N^+][TeCN^-]$ and $(Me_2N)_3P{=}Te$ indicate that the rhenium complexes react rapidly, but resonances assignable to 8 are not unequivocally identified. In all cases, the major products are 6 or 9 and tellurium mirrors. An authentic sample of 9 has been prepared in 74% yield by the reaction of 4 with $P(NMe_2)_3$. The inability to prepare a stable telluroformaldehyde complex in this rhenium system is surprising considering the accessibility and stability of telluroformaldehyde complexes in other metal systems.[6] In addition, $TeCN^-$ has recently been used to convert an alkylidene ligand into a telluroketone ligand.[13]

The golden orange selenoformaldehyde complex 3 is air stable in solution and in the solid state. Comparison of the spectral features of 3[8] with 1 and 2[5] indicates the chalcoformaldehyde ligands are electronically very similar. Complexes 2 and 3 have identical nitrosyl stretches (1752 cm^{-1}) in their infrared spectra. The ^1H and ^{13}C NMR chemical shifts for the C_5H_5 ligands (^1H δ 6.40 ± 0.01; ^{13}C 100.5 ± 0.4 ppm) are essentially the same for all three chalcoformaldehyde complexes. Fast atom bomardment MS of 2[14] and 3[8] reveal strong molecular ion peaks with the major fragmentations being the loss of S or Se and the loss of the chalcoformaldehyde ligand. Relative intensities indicate that loss of Se from 3 is more facile than loss of S from 2. Facile loss of chalcogen could account for our inability to observe the telluroformaldehyde complex.

Since the structures of 1 and 2 have been determined[5] while no structures of mononuclear selenoformaldehyde complexes have been reported, we undertook an X-ray diffraction analysis of 3. X-ray data on a rectangular prism of 3 was collected at 25 °C and refined as described in the supplementary material. Of the 5702 reflections measured ($\theta \leq 27$°C), 4152 were considered observed [$F_0^2 \geq 1.0\sigma(F_0^2)$] and were used in the refinement. The crystal belongs to the monoclinic system of space group $P2_1/c$ ($Z = 4$) with $a = 9.689$ (2) Å, $b = 18.608$ (3) Å, $c = 15.054$ (3) Å, and $\beta = 104.98$ (1)°. Complex 3 is essentially isostructural with 2. The selenoformaldehyde hydrogens were located from a difference map, and their positions were refined isotropically. The molecular structure of 3 is shown in Figure 1, and pertinent bond lengths and angles are listed in Table I. Final R indices were $R = 0.038$ and $R_w = 0.047$ with a goodness of fit of 1.89.

Table I. Selected Bond Lengths (Å) and Angles (deg) in 3

Bond Lengths (esd)			
Re-C1	2.173 (6)	Re-P1	2.447 (1)
Re-Se1	2.522 (1)	C1-H1	0.87 (5)
C1-Se1	1.879 (6)	C1-H2	1.09 (6)
Re-N1	1.765 (5)	N1-O10	1.169 (6)
$Re\text{-}C_5H_5$[a]	2.299		

Bond Angles (esd)			
Re-C1-Se1	76.6 (2)	P1-Re-C1	123.8 (2)
Re-Se1-C1	57.0 (2)	Re-N1-O10	173.2 (5)
C1-Re-Se1	46.5 (2)	H1-C1-H2	101 (5)
N1-Re-P1	88.9 (1)	H1-C1-Se1	114 (4)
N1-Re-C1	89.6 (3)	H2-C1-Se1	135 (3)
P1-Re-Se1	81.08 (3)	H1-C1-Re	112 (4)
N1-Re-Se1	107.5 (2)	H2-C1-Re	117 (3)

[a] Average distance from Re to C_5H_5 carbons.

The bonding parameters for the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety are very similar to those found in related structures.[5,15] The $CH_2{=}Se$ ligand is η^2 bound with the $\overline{Re{-}C{=}Se}$ plane twisted 21.8° away from the Re-P bond vector (toward the C_5H_5 ligand). This conformation allows good overlap of the rhenium HOMO[15a] with the $CH_2{=}Se$ π^* orbital. The C-Se bond length of 1.879 (6) Å is very close to those found in selenoureas (1.82-1.87 Å).[16] It is somewhat shorter than a typical C-Se single bond (1.95-1.99 Å)[16] but is significantly longer than the C=Se bond found in CSe_2 (1.6917 (15) Å).[17] It is also shorter than the bond length determined for the $\mu,\eta^2\text{-}CH_2{=}Se$ ligand of a dimanganese selenoformaldehyde complex which was assumed to be a single bond.[6b] The Re—C(selenoformaldehyde) bond length (2.173 (6) Å) is slightly shorter than those normally found for Re-C single bonds (2.2-2.4 Å).[15,18] The Re-Se distance (2.522 (1) Å) in 3 is also shortened relative to the Re-Se distance in $[(Me_3P)_2(CO)_3Re]_2Se$ (2.653 (4) Å).[19]

In summary, chalcoformaldehydes are becoming generally available ligands in organometallic chemistry. Our methods, in conjunction with those of other groups,[6] could lead to a broad series of seleno- and telluroformaldehyde complexes. Formaldehyde and thioformaldehyde derivatives may be even more readily available.[5] The chemistry of these complexes is of great interest in regards to their synthetic potential and suitability as catalysis models. The reactivities of 2 and 3 are currently under investigation, and preliminary results indicate they are dominated by nucleophilic attack at the chalcoformaldehyde carbon. Details of these studies will be reported in due course.

Acknowledgment. Professors L. Pignolet and D. Britton (University of Minnesota) are thanked for their invaluable assistance with the structure determination. I also thank the 3M Analytical and Properties Research staff (especially Drs. R. Newmark and P. Lyon) for the analytical and spectroscopic data. The FAB MS were ob-

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Supplementary Material Available: Analytical and spectral data for **6** and **9**, description of structure solution, and tables of atomic positions, thermal parameters, bond lengths and angles, and observed and calculated structure factors for **3** (31 pages). Ordering information is given on any current masthead page.

Evidence for the Intermediacy of an Iron(IV) Carbonyl Complex during the Oxidative Degradation of a (β-Aminoalkyl)iron Complex

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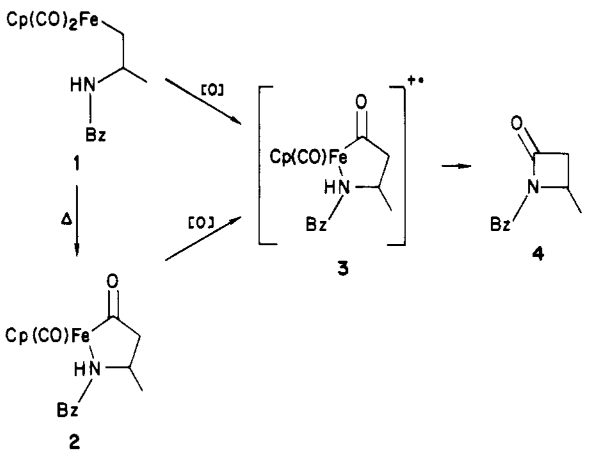
Summary: The results of chemical and electrochemical experiments demonstrate that the β-lactam $CH_2CHMeNBzCO$, **4**, is generated from $Cp(CO)_2FeCH_2CHMeNHBz$ by deprotonation and cyclization to form $Cp(CO)FeCONBzCHMeCH_2^-$ followed by sequential one-electron oxidations of the anion to give a transient iron(IV) complex. This iron(IV) complex then collapses to the β-lactam.

Electrochemical, chemical and spectroscopic evidence indicate that the formation of the β-lactam **4** during the oxidative degradation (via metal oxidants) of the β-aminoalkyl (**1**) or β-aminoacyl (**2**) iron complexes occurs by reductive elimination of the β-lactam from an iron(IV) complex, **11**.

Syntheses of β-lactams via transition-metal complexes has been accomplished by the rhodium-catalyzed ring expansion of aziridines in the presence of carbon monoxide,[1] the photochemical reactions between chromium carbene complexes and imines,[2] the oxidative degradation of allyliron tricarbonyl complexes,[3] and the oxidative degradation of β-aminoalkyl or (β-aminoacyl complexes[4]) of the type η-$Cp(CO)_2FeCH_2CHRNHR$.[5,6] Although this latter class of compounds is readily available, their utilization in the syntheses of penicillin precursors has not been successful.[7]

The reasons for this failure remains obscure. In part this is attributable to a lack of knowledge concerning the mechanism of the oxidative degradation of the (β-aminoalkyl)iron complexes. In his recent papers Rosenblum suggested that the iron(III) radical cation **3** is the immediate progenitor of the β-lactam formed during the oxidative degradation of either **1** or **2**.[5] This hypothesis is strongly supported by the demonstrated kinetic and thermodynamic enhancement of the alkyl to acyl migratory insertion reaction in the iron(III) state as compared to the iron(II) state[8] and the often facile transformation of **1** to **2** in the iron(II) state.[5]



Experimental evidence now shows that **3** is not the precursor of the β-lactam **4**. Complex **3** is readily prepared chemically by the oxidation of **2** by ferricenium tetrafluoroborate in methylene chloride at 24 °C. The addition of petroleum ether effects the precipitation of **3** as a green solid that has been obtained in analytically pure form. The structure of **3** is conclusively established by consideration of its chemical and spectroscopic properties. Thus, the IR spectrum of **3** exhibits terminal and acyl carbonyl absorptions at 2010 and 1730 cm^{-1}, respectively. A single intense signal is observed in the ESR spectrum of **3**. The cyclic voltammetry behavior of **2** and **3** are identical ($E_{p_a} - E_{p_c}$ = 60 mV, $E°'$ = 0.06 mV, $LiClO_4$, AN, 24 °C, 20 mV s^{-1}, SCE), thereby indicating that **3** does not differ structurally from **2** in a significant manner. **3** is quantitatively reduced to **2** by triethylamine. **3** is the most stable of the organoiron(III) carbonyls that we have studied. It decomposes slowly ($t_{1/2}$ = 11 h at 22 °C) via a process that is first order in complex for at least 3 half-lives. At no time during the decomposition was more than a trace of β-lactam observed. Attempts to force the transformation of **3** to **4** by deprotonation of **3** with sodium hydroxide or silver oxide (one of the oxidants that transforms **2** to **4**) resulted in gross decomposition. Complex **3** also decomposes in the presence of **1** without formation of any β-lactam.

Since the basic oxidants Ag_2O and PbO_2 are most effective in transforming **1** or **2** to **4**, it was thought that deprotonation may occur before oxidation. Surprisingly the deprotonation of either **1** or **2** with sodium hydride does not afford deprotonated **2** but rather the isomeric anion **6**. Thus, treatment of **1** with excess sodium hydride in tetrahydrofuran or treatment of **5** with greater than 2 equiv of sodium hydride affords the anionic aminocarbonyl complex **6** in 10–20 min at room temperature. Complex **2** is also transformed to **6** but only under more drastic conditions—5 h in refluxing tetrahydrofuran. The anion **6** was characterized by IR and NMR spectroscopy and its chemical reactivity. Thus, **6** exhibits a terminal carbonyl absorption at 1850 cm^{-1} that is characteristic of an anionic iron carbonyl. The acyl absorption is observed at 1495 cm^{-1}, some 35 cm^{-1} lower than for an analogous alkoxy-

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