tained at the Midwest Center for Mass Spectrometry, a NSF Regional Instrumentation Facility (Grant No. CHE8211164) at the University of Nebraska, Lincoln.

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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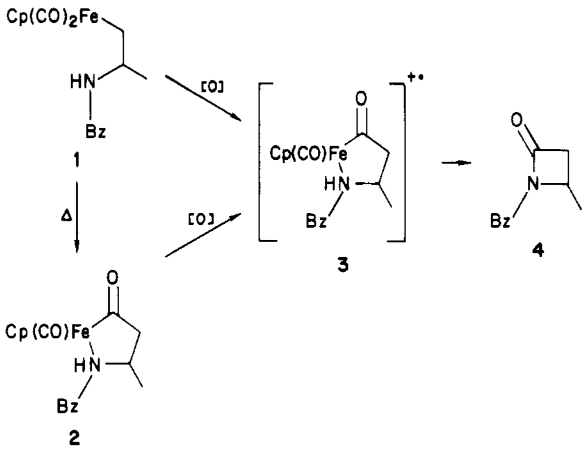
Summary: The results of chemical and electrochemical experiments demonstrate that the β-lactam $\overline{CH_2CHMeNBzCO}$, 4, is generated from $Cp(CO)_2FeCH_2CHMeNHBz$ by deprotonation and cyclization to form $Cp(CO)Fe\overline{CONBzCHMeCH_2}^-$ followed by sequential one-electron oxidations of the 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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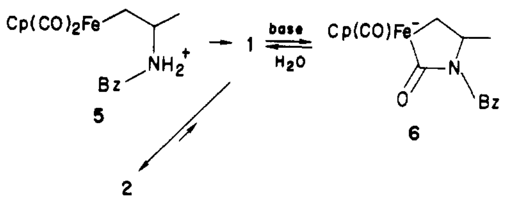

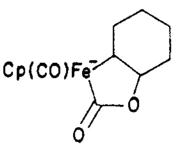

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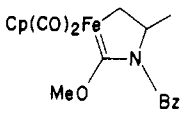

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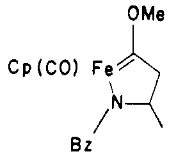

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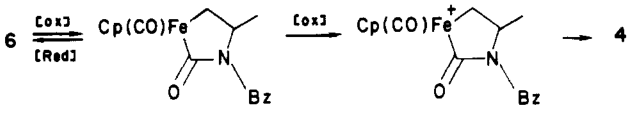
carbonyl complex 7.[9] The NMR spectrum of 6 in either Me$_2$SO-d_6 or dioxane-d_8 is unexceptional and consonant with 6 existing as a pair of diastereomers.[10] Protonation of 6 with water affords high yields of 1 regardless of the origin (1 or 2) of 6. 6 is readily methylated by either the trimethyloxonium ion or dimethyl sulfate to afford carbene complex 8. The NMR spectrum of the resulting carbene complex is also consistent with 8 existing as a pair of diastereomers. One of these diastereomers has been obtained in pure form.[11]

CV analysis of 6 indicates that it undergoes reversible oxidation to 10 ($E_{p_a} - E_{p_c}$ = 60 mV, $E°'$ = −0.590 mV, TBAP, AN, 0 °C, 50 mV s^{-1}, SCE) and a second irreversible oxidation at $E_{p_{a(2)}}$ = 0.95 mV. Chemical oxidation of 6 with ferricenium tetrafluoroborate also affords solutions of 10 that exhibit terminal carbonyl and acyl absorptions at 1970 and 1615 cm^{-1}, an intense ESR signal at g = 2.0518, and voltammograms identical with those of 6. 10 slowly decomposes to the β-lactam 4 and an unidentified dicarbonyliron(II) complex. Immediate oxidation of 10 with another equivalent of ferricenium salt or silver oxide or oxidation of 6 with 2 equiv of ferricenium gives high yields (75%–80%) of 4 with little formation of the dicarbonyliron complex. These chemical and electrochemical results demonstrate that the formation of 4 occurs after further oxidation of the iron(III) complex 10 to the transient iron(IV) complex 11. The formation of 4 during the thermal decomposition of 10 also probably involves 11 formed via the disproportionation of 10.



10 11

It appears that the formation of β-lactams by oxidation with basic metal oxidants involves the intermediacy of iron(III) complexes. Thus chemistry of these iron(III) complexes is crucial to the successful synthesis of β-lactams by this method. For highly reactive iron(III) complexes, it seems likely that the rate of oxidation to the iron(IV) complexes will not be competitive with the rates of alternative decomposition pathways. On the other hand, two-electron oxidation by dioxygen or dihalogens would yield directly iron(IV) complexes. This may account for the observation that complexes such as 2 are readily transformed to β-lactams when treated with dioxygen.[7]

Acknowledgment. We gratefully acknowledge the generous support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Graduate School of Boston University. Also, we wish to thank Prof. Myron Rosenblum and Dr. Todd Price for samples of various iron complexes and helpful discussions.

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[10] 6: NMR (Me$_2$SO-d_6) δ 7.10 (br s, 5, Ph), 4.96 (d + d, 1, PhCH$_2$), 4.15 (s, 5, C$_5$H$_5$), 3.63 (d + d, 1, PhCH$_2$), 3.13 (m, 0.6, CH), 2.09 (m, 0.4, CH), 1.56–0.53 (d + m, 5, CH$_3$, FeCH$_2$).[6] Chemical shift assignments are based upon selective proton decoupling experiments.

[11] 8: ^{1}H NMR[6] (CS$_2$) δ 7.00 (m, 5, PH), 4.86 (d, 1, J = 15 Hz, PhCH$_2$), 4.35 (s, 5, C$_5$H$_5$), 4.20 (d, 1, J = 15 Hz, PhCH$_2$), 3.96 (s, 3, CH$_3$O), 3.47 (m, 1, CHN), 1.86–0.61 (d + m, 5, CH$_3$, FeCH$_2$); ^{13}C NMR$_7$ (CS$_2$) δ 247.46 (carbene C[12]), 222.25 (C=O), 136.76[13] (C$_6$H$_5$, C$_1$), 128.75 (C$_6$H$_5$, C$_3$, 5), 126.89 (C$_6$H$_5$, C$_2$, 6), 126.53 (C$_6$H$_5$, C$_4$), 87.33 (C$_5$H$_5$), 64.56 (CHN), 61.16 (CH$_3$O), 47.82 (PhCH$_2$), 22.03 (CH$_3$), 9.23 (FeCH$_2$). Anal. Calcd for C$_{18}$H$_{21}$FeNO$_2$: Fe, 16.463. Found: Fe, 16.71. Chemical shift assignments are based upon off-resonance ^{1}H decoupling.

[12] This relatively high-field resonance is apparently characteristic of aminoalkoxy carbene ligands and is thereby consistant with structure 8 rather than it isomer 9. Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343.

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A Convenient Route to ^{13}C-Enriched Triruthenium Dodecacarbonyl. Chemistry Relevant to Methyl Formate Production from Carbon Monoxide and Methanol

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Summary: The enhanced carbon monoxide lability exhibited by Ru$_3$(CO)$_{12}$ in the presence of KOMe, where methoxycarbonyl adduct formation occurs, has been utilized in the ready synthesis of highly ^{13}C-enriched Ru$_3$(CO)$_{12}$. The methoxycarbonyl adduct was shown to exist in equilibrium with Ru$_3$(CO)$_{12}$ in methanol or methanol/tetrahydrofuran in the absence of added OMe$^-$, indicative of substantial electrophilic character in the CO ligands of this trinuclear cluster. The possible role of this methoxycarbonyl adduct in the catalytic synthesis of methyl formate from CO/MeOH is discussed.

Recent investigations from our laboratory have suggested that carbomethoxy derivatives of tungsten and ruthenium are intermediates in the homogeneously catalyzed production of methyl formate from carbon monoxide and methanol (eq 1).[1–3] For example, species of the type

$$\mathrm{CO + MeOH} \overset{[\mathrm{cat.}]}{\rightleftharpoons} \mathrm{HCOOMe} \qquad (1)$$

MeOC(=O)W(CO)$_5^-$, and its decarbonylated product MeOW(CO)$_5^-$, have been characterized by ^{13}C NMR and ν_{CO} IR spectroscopy. Both tungsten species were demonstrated to serve as catalysts or catalyst precursors for methyl formate synthesis.[4]

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