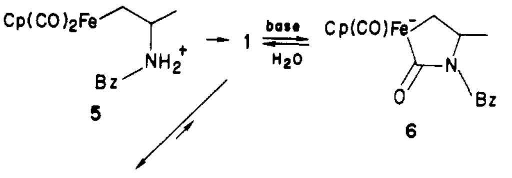

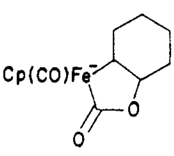

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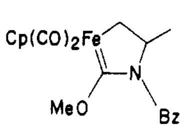

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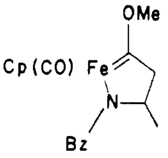

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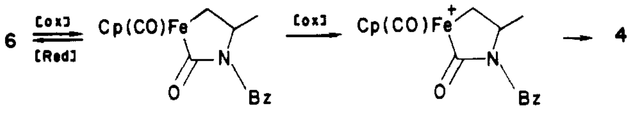
carbonyl complex 7.[9] The NMR spectrum of 6 in either Me_2SO-d_6 or dioxane-d_8 is unexceptional and consonant with 6 existing as a pair of diastereomers.[10] Protonation of 6 with water affords high yields of 1 regardless of the origin (1 or 2) of 6. 6 is readily methylated by either the trimethyloxonium 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, $E^{\circ\prime}$ = −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.



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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(9) Klemarczyk, P.; Price, T.; Priester, W.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *135*, C25.

(10) 6: NMR (Me_2SO-d_6) δ 7.10 (br s, 5, Ph), 4.96 (d + d, 1, $PhCH_2$), 4.15 (s, 5, C_5H_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_5H_5), 4.20 (d, 1, J = 15 Hz, $PhCH_2$), 3.96 (s, 3, CH_3O), 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_6H_5, C_1), 128.75 (C_6H_5, C_3, 5), 126.89 (C_6H_5, C_2, 6), 126.53 (C_6H_5, C_4), 87.33 (C_5H_5), 64.56 (CHN), 61.16 (CH_3O), 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.

(13) The positions were assigned from the calculated values. Simmon, W. W. "The Stadtler Guide to Carbon-13 NMR Spectra"; Simons, W. W., Ed.; Stadtler Research Laboratories, 1983; p 606.

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

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

$MeOC(=O)W(CO)_5^-$, 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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(1) Darensbourg, D. J.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc.* **1983**, *105*, 5937.

(2) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750.

(3) Darensbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. *J. Mol. Catal.*, in press.

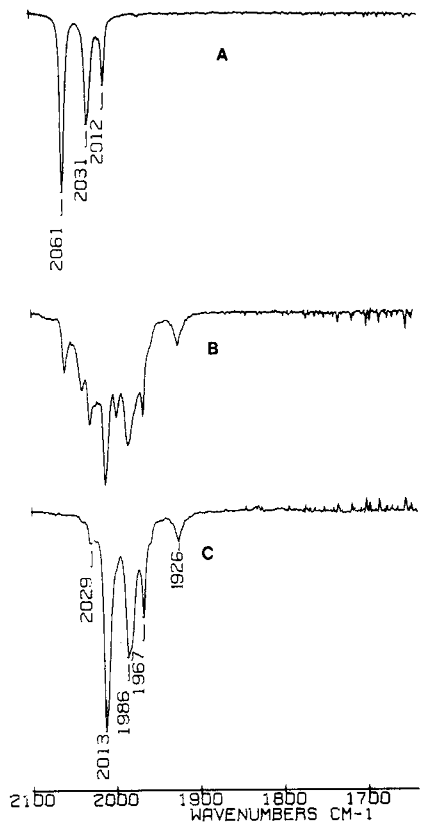

Figure 1. Infrared spectra in ν_{CO} region of $Ru_3(CO)_{12}$ in hexane determined on samples from the ^{13}CO ligand exchange reaction which was run in THF/MeOH at 50 °C: A, initial spectrum; B, after 4 h; C, after 8 h, low-frequency band at 1925.8 cm^{-1} due to $^{13}C^{18}O$ enriched species.

While investigating reaction 1 in the presence of $Ru_3(CO)_{12}/OMe^-/^{13}CO$, it became apparent that facile carbon monoxide exchange occurs in the parent triruthenium dodecacarbonyl under these reaction conditions. This in turn implied that $Ru_3(CO)_{12}$ might indeed undergo CO ligand exchange reactions readily in methanol in the presence of catalytic quantities of methoxide ions, hence providing a convenient route to ^{13}C-enriched $Ru_3(CO)_{12}$ which serves as an ubiquitous catalyst precursor. Indeed while this work was in progress, the methoxycarbonyl adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$ was shown to have CO ligand lability orders of magnitude greater than that of the parent compound $Ru_3(CO)_{12}$ as evidenced by phosphite substitution reactions.[5]

The carbon monoxide ligand exchange reactions of $Ru_3(CO)_{12}$ were carried out in THF/MeOH (2:1, v/v) because of the limited solubility of the carbonyl trimer in methanol alone. In a typical experiment 20 mg (0.031 mmol) of $Ru_3(CO)_{12}$ contained in a 50-mL Schlenk flask was degassed and dissolved in 10 mL of solvent under a 99.98% ^{13}C-enriched CO atmosphere. The yellow-orange solution was heated in a thermostated bath at 50 °C, and ^{13}CO incorporation was monitored by periodically withdrawing samples for FT-IR analysis in the CO stretching region. Figure 1 depicts spectra of the $Ru_3(CO)_{12}$ (where the THF/MeOH has been removed and the solid redissolved in hexane) as a function of reaction time. Complete exchange was observed after about 8 h. Similar, but much slower, exchange was noted at ambient temperature. *The reaction was found to be catalyzed by small quantities of KOMe, for example, the presence of 0.014 equiv of KOMe resulted in complete ^{13}CO incorporation at 50 °C within 1 h.*

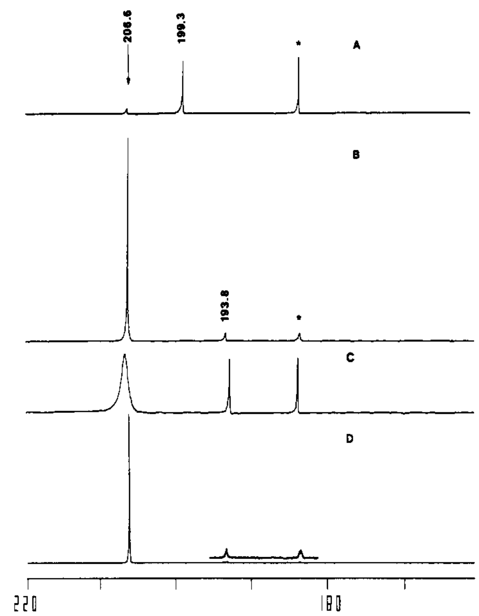

Figure 2. ^{13}C NMR spectra of ^{13}C-enriched $Ru_3(CO)_{12}$ in THF/MeOH (2:1 by volume), peak marked by asterisk at 184.1 ppm due to free ^{13}CO: A, sample with no additive; B, sample as in A with 1 equivalent of KOMe (peak at 193.8 ppm assigned to the carbonyl unit of the methoxycarbonyl ligand); C, sample in B determined at −100 °C; D, sample in C after sample returned to ambient temperature.

The CO-labilizing ability of the methoxycarbonyl ligand may be a fairly general property in metal carbonyl derivatives in the absence of competing processes. For example, $CH_3OC(=O)Co(CO)_4$ undergoes rapid CO substitution by triphenylphosphine.[6] An alternative process for facile ^{13}CO enrichment of $Ru_3(CO)_{12}$ has been reported by Shore and co-workers[7] where trace quantities of KH catalyze CO exchange in THF (eq 2).

$$Ru_3(CO)_{12} + KH \overset{^{13}CO}{\rightleftharpoons} KHRu_3(CO)_{11} + CO \quad (2)$$

Gross and Ford have investigated the kinetics of the reaction of methoxide ions with $Ru_3(CO)_{12}$ in MeOH and/or THF under a carbon monoxide atmosphere.[8] These researchers concluded that formation of an adduct 1, resulting from nucleophilic addition of OCH_3^- at a coordinated CO ligand in $Ru_3(CO)_{12}$, is in rapid equilibrium with starting reagents (eq 3).[9] We further find in this

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[4] In all instances we have examined, group 6B metal carbonyls combined with alkali-metal alkoxides are more active catalysts than the alkali-metal alkoxides alone. However, it is recognized that the Brendlein Process, alkali-metal alkoxide catalyzed carbonylation of methanol to yield methyl formate, is quite sensitive to trace quantities of water. Hence, metal carbonyls might be simply additives that react with hydroxide to provide anionic metal hydrides that subsequently yield hydrogen with regeneration of OMe^-. Every precaution was taken to exclude trace quantities of water; i.e., CO was dried by slowly passing it over sodium alumina silicate 13X molecular sieve (Matheson purifier), and methanol was distilled over magnesium turnings under nitrogen immediately prior to use. A series of isochronous experiments involving metal carbonyls/KOMe and KOMe alone as catalysts were carried out under identical reaction conditions.

[5] Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696. Similar observations have recently been noted for $Ru_3(CO)_{12}$ in the presence of PPN^+ salts of other nucleophiles, e.g., CN^- or $CH_3CO_2^-$ by: Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. We thank Professor Kaesz for personal communication of these results prior to publication.

[6] Milstein, D. W.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

[7] Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444.

[8] Gross, D. C.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 1702.

[9] The infrared spectrum of the adduct 1 in THF in the CO stretching region displays bands at 2069 (w), 2015 (s), 1997 (s), 1963 (m), and 1595 (w) cm^{-1} with the last band being attributed to the $-CO_2CH_3$ function.[7]

$$Ru_3(CO)_{12} + CH_3O^- \rightleftharpoons \underset{1}{Ru_3(CO)_{11}(CO_2CH_3)^-} \rightleftharpoons Ru_3(CO)_{10}(CO_2CH_3) + CO \qquad (3)$$

investigation infrared spectral data for $Ru_3(CO)_{12}$ in pure methanol that indicate partial formation of the adduct species 1, with the principal metal containing component in solution being $Ru_3(CO)_{12}$. Whereas ν_{CO} bands attributed only to 1 prepared from an equimolar mixture of $Ru_3(CO)_{12}$/KOMe were observed in THF/MeOH at 2072 (w), 2015 (s), 1990 (s), 1965 (m), and 1603 cm^{-1}, the ν_{CO} infrared spectrum of $Ru_3(CO)_{12}$ in methanol displayed bands due to both 1 and $Ru_3(CO)_{12}$. Similarly the ^{13}C NMR spectrum of an equimolar mixture of $Ru_3(CO)_{12}$/KOMe in ^{13}CO displayed a single resonance at 206.6 ppm ($Ru_3(CO)_{12}$ in THF/MeOH has a ^{13}C signal at 199.3 ppm) at ambient temperature due to 1 that broadens below −100 °C. In the absence of KOMe the minor component (16.8%) in a MeOH/THF solution of $Ru_3(CO)_{12}$ exhibits ^{13}C NMR spectral characteristics identical with that described in the presence of KOMe, and the major species in solution is $Ru_3(CO)_{12}$ (see Figure 2).[10]

Hence both ν_{CO} infrared and ^{13}C NMR spectral data indicate that in MeOH or MeOH/THF, $Ru_3(CO)_{12}$ has acid (electrophilic) sites, presumably the carbon centers of coordinated CO ligands, for interaction with OMe^- which are moderately competitive with H^+ (eq 4). This is consistent with the high CO stretching frequencies observed for $Ru_3(CO)_{12}$.[11] In contrast, $W(CO)_6$, which possesses a considerably lower CO stretching force constant, does not show adduct formation in methanol alone nor does it display CO lability. However, $W(CO)_5CO_2Me^-$, prepared from $W(CO)_6$ and KOMe displays drastically enhanced CO lability over that of $W(CO)_6$.

$$Ru_3(CO)_{12} + MeOH \rightleftharpoons Ru_3(CO)_{11}CO_2Me^- + H^+(\text{solvated}) \qquad (4)$$

Since catalysis of methyl formate synthesis via CO/MeOH occurs in the presence of equimolar quantities of $Ru_3(CO)_{12}$ and PPNOMe or KOMe in methanol, it is possible that species 1 is an intermediate in this catalytic process.[12] Consistent with the solution species described in eq 4, $Ru_3(CO)_{12}$ in the absence of added methoxide ions is a modest catalyst for methyl formate production from CO/MeOH.[12] This is an important observation in light of the fact that alkoxides alone are catalysts for this process. Protonation of 1 by MeOH leads to HCOOMe and the cocatalyst OMe^-, with subsequent rapid uptake of carbon monoxide by $[Ru_3(CO)_{11}]$ to reform the metal catalyst component $Ru_3(CO)_{12}$. It is generally assumed that the most easily protonated site in 1 is the $-OCH_3$ unit which leads to reformation of $Ru_3(CO)_{12}$ and CH_3OH. For example, it was shown by Gross and Ford[8] that the addition of excess CF_3COOH to 1 regenerated $Ru_3(CO)_{12}$, quantitatively. An analogous process has been employed in the synthesis of several monomeric metal carbonyl derivatives of manganese and rhenium from the corresponding MC(=O)OEt species provided by M^- and ClC(=O)OEt coupling reactions.[13] Nevertheless, we feel that there are other sites for protonation, most notably the metal centers, which would lead to methyl formate production via reductive elimination.[14] Indeed the reverse process, oxidative addition of methyl formate to a transition-metal center to provide an hydrido methoxycarbonyl complex has been reported in the literature.[15] We are currently investigating mechanistic aspects of protonation reactions of methoxycarbonyl adducts of low-valence transition-metal derivatives in order to gain a better understanding of these processes.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

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[10] ^{13}C NMR spectra were determined in THF/MeOH (2:1, v/v) because of the limited solubility of $Ru_3(CO)_{12}$ in methanol. Spectra were measured on a Varian XL-200 spectrometer.

[11] Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691.

[12] A 0.30-mol sample of $Ru_3(CO)_{12}$ and KOMe was dissolved in 15 mL of degassed methanol (distilled under nitrogen over magnesium turning and iodine), and the internal standard (hexane) was added. This reaction mixture was transferred to a stirred (magnetically activated, packless impeller system) 300-mL Parr reactor in a drybox. The reactor was then sealed and pressurized to 250 psi (at 25 °C) with pure CO and heated to 125 °C (reaching a final total pressure of 500 psi). After 24 h, the reactor was cooled and the pressure released. The reactor was then returned to the drybox and opened, and the reaction solution was transferred to a septum-capped vial. This solution was analyzed by GC (Perkin-Elmer Model Sigma 2, column used was 10% Carbowax 20M over Chromosorb) which showed 23 mmol of HCO_2Me was produced. This represents a turnover number (mol of HCO_2Me/mol of catalyst) of 80. Independent experiments were performed in a completely analogous manner employing $Ru_3(CO)_{12}$ or KOMe alone as catalysts, with turnover numbers of 21 and 115 being determined. Hence, although $Ru_3(CO)_{11}CO_2Me^-$ is the principal species present in solutions of $Ru_3(CO)_{12}$ and OMe^-, catalysis could be proceeding (at least in part) by way of uncomplexed methoxide.[4]

[13] (a) Kruck, T.; Noack, M. *Chem. Ber.* **1964**, *97*, 1693. (b) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713. (c) Darensbourg, D. J.; Darensbourg, M. Y.; Drew, D.; Conder, H. L. *J. Organomet. Chem.* **1974**, *74*, C33. (d) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579.

[14] It is important to note here that we are quite certain that methyl formate is not produced via hydrogenation of the methoxycarbonyl ligand by H_2 afforded from water-gas shift chemistry. Ford and co-workers have reported that such a process does occur.[5] In our catalytic conversion of CO/MeOH to HCO_2Me little water-gas shift chemistry occurs simultaneously. In addition the other product of the WGS reaction CO_2 has been shown to effectively inhibit catalysis by reacting with the cocatalyst OMe^- to provide carbonates.

[15] Thorn, D. C. *Organometallics* **1982**, *1*, 197.

Silicon–Carbon Unsaturated Compounds. 18. Nickel-Catalyzed Reactions of (Phenylethynyl)polysilanes with Phenyl(trimethylsilyl)acetylene and Molecular Structure of 3-Phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene

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Received August 13, 1984

Summary: The reactions of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene (**2**) in the presence of a catalytic amount of $NiCl_2(PEt_3)_2$ gave products arising from isomerization of the (phenylethynyl)polysilanes, followed by addition to **2**. Similar reaction of (phenylethynyl)pentamethyldisilane in the absence of **2** afforded

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[1] (a) Kyoto University. (b) Osaka City University.

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