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(24) A mechanism accounting for the data above is eq i, but it fails to account for the kinetics being first order in metal.[21]

$$RCH{=}M + R'CH{=}M \rightleftarrows RCH{=}CHR' + 2M \qquad \text{(i)}$$

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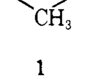
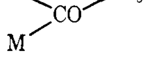
Alkylation and Structural Rearrangement of the Bridging Carbonyl Ligand in $HFe_3(CO)_{11}^-$. The Synthesis of $HFe_3(CO)_{10}(COCH_3)$

Sir:

The interaction of strong carbocation reagents with polynuclear carbonyl anions conceivably might lead to a number of interesting structural features such as metal-alkyl-metal bridges, **1**, and O-alkylation of basic carbonyl groups, **2**. Since neither of these are known in metal carbonyl chemistry, we have recently initiated studies on the alkylation of polynuclear carbonyl species. In this report we present some novel findings on the chemistry of trinuclear iron species.



1



2

The salt [DMTED][$Fe_3(CO)_{11}$] (DMTED = *N,N'*-dimethyltriethylenediamine +2 cation) was prepared by a simple adaptation of Hieber and Brendel's preparation of [$Ni(phen)_3$][$Fe_3(CO)_{11}$].[1] Treatment of the DMTED salt with slightly more than an equimolar quantity of CH_3SO_3F in acetonitrile followed by addition of diethyl ether and filtration yields a solution of crude product, from which solvent is removed under vacuum. The solid is washed with benzene and recrystallized from toluene-acetonitrile. A 0.20-g sample of the resulting [DMTED][$Fe_3(CO)_{11}(CH_3)$]$_2$ was dissolved in 50 ml of CH_3CN, HCl gas was passed over the solution, solvent was removed under vacuum, and the dark red-purple product was sublimed at 45° under a hard vacuum. Anal. Calcd for $HFe_3(CO)_{11}CH_3{\cdot}H_2O$: C, 28.28; H, 1.19; O, 37.67; Fe, 32.87. Found: C, 28.09; H, 1.21; O, 37.21; Fe, 32.67. (Water may have been introduced at the analytical laboratory, as we find no evidence for its presence in any of our experiments.) In a sealed capillary decomposition begins around 135°. A cryoscopic molecular weight determination in benzene solution, conducted under strictly air-free conditions,[2] gave a value of 520. The highest mass peak of appreciable intensity occurs at 492 mass units, in agreement with the parent ion of $HFe_3(CO)_{11}CH_3$. For a large number of peaks, such as those at 492, 464, 436, 408, 380, and 352, a feature is observed two mass units lower with an intensity 0.2 of its high-mass partner. This intensity ratio agrees with the presence of ^{54}Fe at 6% abundance in a Fe_3 cluster. The existence of this cluster over a wide mass range indicates a closed iron triangle rather than an open chain structure.[3] Definitive evidence for the presence of a metal hydride linkage is provided by the presence of a high field resonance 18.2 ppm from TMS. The methyl group is observed at −4.23 ppm with intensity 2.7 of the hydride signal.

A crystal 0.30 × 0.32 × 0.35 mm sealed in a fused quartz capillary was submitted for X-ray structure determination.[4] (See paragraph at end of paper regarding supplementary material.) As may be seen in Figure 1, the molecule con-

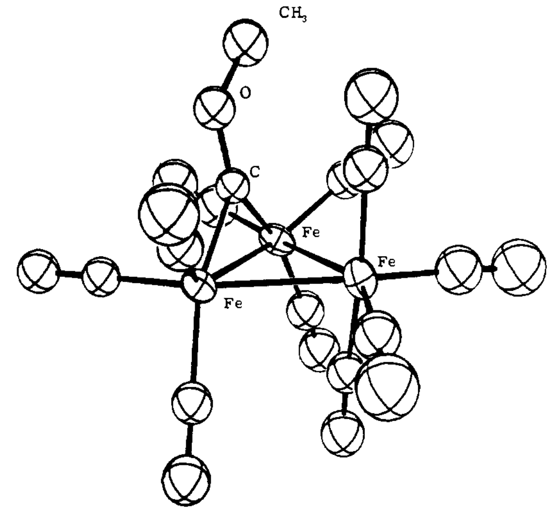
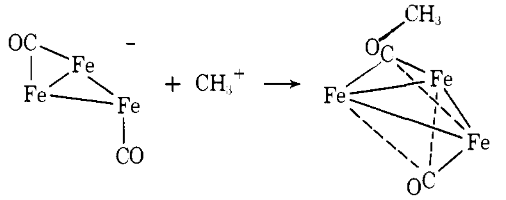


Figure 1. Structure of the HFe(CO)$_{10}$(COCH$_3$) ion. Hydrogen atoms were not included in the refinement.

tains a triangular array of iron atoms with one edge bridged by a CO. Presumably this same edge is bridged by a hydrogen in the fashion postulated for the HFe$_3$(CO)$_{11}^-$ ion.[5] Of particular interest is the attachment of the methyl group to the oxygen of the bridging carbonyl. This is the first case in which this structural feature has been observed. There is, however, some precedent for the structure from the known basicity of bridging carbonyls toward Lewis acids.[6,7] The compound may be viewed as arising via the methylation of the bridging carbonyl of HFe$_3$(CO)$_{11}^-$.[8] There are, however, significant structural differences between the anion and its methyl derivative. Upon formation of the methyl derivative the CO bond length for the bridging carbonyl is increased by 0.1 Å and the average C-Fe distance for the bridging carbonyl to the two nearest iron atoms is decreased by 0.07 Å. These changes indicate that the bridging CO group has become a stronger acceptor toward the metal centers. Of particular interest is the great decrease in the distance between the unique iron and the bridging carbonyl carbon, from 3.00 (1) in the parent anion to 2.70 (1) Å in the methyl derivative. This 0.30 Å shortening is accompanied by a large decrease in the dihedral angle between the iron triangle and the triangle formed by the bridging carbonyl carbon and its two nearest iron neighbors—from 102° in the hydride to 91° in the methylated species.

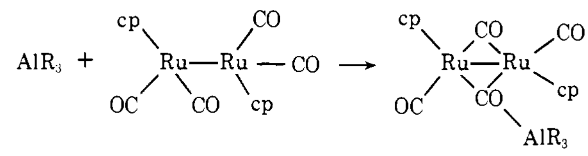
The structural changes associated with the bridging carbonyl are interpreted as the induced shift of CO from a double metal bridge to a triple metal semibridge.[9] This shift which is outlined in reaction 1, presumably occurs because



(1)

[HFe$_3$(CO)$_{11}^-$] [HFe$_3$(CO)$_{10}$(COCH$_3$)]

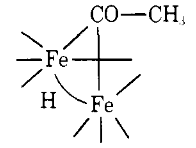
the O-alkylation of CO increases the acceptor character of the carbonyl and therefore promotes close approach of the carbonyl carbon to the third iron. Symmetry in the bonding is achieved by a concomitant shift of another carbonyl toward the opposite face of the iron triangle. (The two relevant nonbonding C-Fe distances in HFe$_3$(CO)$_{11}^-$ are 3.06 (2) and 2.96 (1) vs. 2.85 (1) and 2.95 (1) Å in HFe$_3$(CO)$_{10}$(COCH$_3$).) There is a similarity between this observation of an electron acceptor induced triple metal semibridge, and the known Lewis acid induced rearrangement of CO ligands from terminal to two-metal bridges, reaction 2.[6,10] The general rule from these studies is that the attach-



(2)

ment of an electron acceptor to a carbonyl oxygen increases the propensity for bridge formation at the carbon end.

Returning to the possibility of a metal–alkyl–metal bridge such as **1**, it is clear from the mode of preparation that the O-alkylated metal-protonated form of HFe$_3$(CO)$_{11}$CH$_3$ (**3**) is more stable than its O-protonated metal-alkylated isomer, **4**. Ordinarily the CH$_3^+$ group has a



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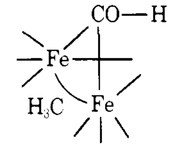

4

strong affinity for basic metal centers, but in the present case it does not successfully compete with the proton for the metal. Another apparent factor in the creation of the oxygen alkylated group is that the connectivity of the irons in HFe$_3$(CO)$_{11}^-$ is six or seven, so there are steric constraints to metal alkylation which are not present in many mononuclear carbonyl anions, where metal alkylation is the rule. Whatever the interpretation, the alkylation of metal cluster compounds deserves further investigation to establish the degree of generality for the carbonyl oxygen alkylation reaction, and to explore further the possibility of other unconventional bonding patterns.

Acknowledgment. We appreciate the generous cooperation of Professor Dahl in providing us with supplementary information on the structure of HFe$_3$(CO)$_{11}^-$ and of D. Greig in the NMR determination. This research was supported by National Science Foundation Grants GP-28878 and MPS74-20004.

Supplementary Material Available. A table of crystal data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche referring to code number JACS-75-1594.

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Synthesis and Reactivity of (Dialkylacetylene)niobium(III) Complexes and Derivatives. Contrast between Protonation and Methylation Pathways

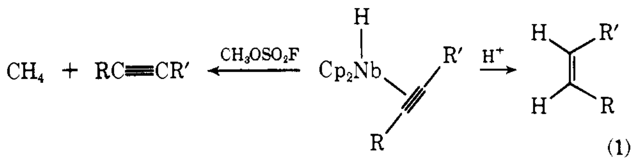
Sir:

We have previously reported[1] the preparation and characterization of the stable complexes $[\eta^5\text{-}(CH_3)C_5H_4]_2TaX$(dialkylacetylene) (X = H, I). We now find that similar Nb(III) species can be prepared under reaction conditions milder than those required for their Ta(III) analogs and that the Nb(III) compounds undergo a variety of transformations which are of interest from the standpoints of both mechanistic considerations and potential utility for organic synthesis.

Acetylene complexes and derivatives were prepared employing Cp_2NbH_3 ($Cp = \eta^5\text{-}C_5H_5$) as starting material. The published preparation[2] of the trihydride, **1**, requires extremely high pressures of hydrogen. We found the following modification of a 1 atm procedure[3] to be a convenient one. A suspension of Cp_2NbCl_2[4] in toluene[5] was stirred with an excess of "Vitride" until all solids dissolved. After hydrolysis with aqueous NaOH, separation, drying, and evaporation of the organic layer, **1** was obtained in up to 55% yield as yellow crystals. Treatment of **1** with a dialkylacetylene in refluxing benzene for 15 min afforded an hydrido(acetylene) complex $Cp_2NbH(RC{\equiv}CR')$, **2** (Table I). The ir and ^1H NMR spectra for **2** are similar to those observed[1] for the analogous Ta(III) complexes (for **2a**, $\nu_{Nb\text{-}H}$ 1720 cm^{-1}; $\nu_{C{\equiv}C}$ 1815 cm^{-1}; $\tau_{Nb\text{-}H}$ 10.8). In contrast to $Cp_2NbH(C_2H_4)$ which readily forms an insertion product, $Cp_2Nb(C_2H_5)(C_2H_4)$, in the presence of excess ethylene,[2] no such reaction of **2** with excess acetylene was observed, even after several hours in refluxing toluene.

The ^1H NMR spectra of complexes **2** are consistent with the structure proposed for the Ta(III) analogs[1] and established crystallographically for the related olefin complex $Cp_2Nb(C_2H_5)(C_2H_4)$;[6] viz., the acetylenic C≡C bond lies in a plane that contains the Nb and H atoms. Thus, for an unsymmetrically substituted acetylene, two isomers for the hydrido(acetylene) complex are possible which are due to the two orientations of the acetylene ligand in the Nb-H-(C≡C) plane. Models suggest that, in the complex, the sterically bulkier substituent on the triple bond will be oriented preferentially toward the small hydride ligand. This supposition is supported by ^1H NMR evidence obtained for a series of hydrido(acetylene) complexes (see Table I). For the mixture of isomeric complexes of a methyl-substituted unsymmetrical acetylene, the major component in this mixture is the one displaying the methyl group resonance at higher field (i.e., the sterically smaller substituent group of the acetylene preferentially occupies the site in the coordination pocket of the metal that gives rise to an upfield shift and the larger group prefers the site that gives rise to a downfield shift). For **3b**, only the lower field resonance displays coupling to the Nb-H ($J_{CH_3\text{-}H}$ = ca. 1 Hz) which indicates that the site associated with the low field resonance (and, hence, the one preferred by the larger substituent group) is the one spatially closest to the hydride ligand.

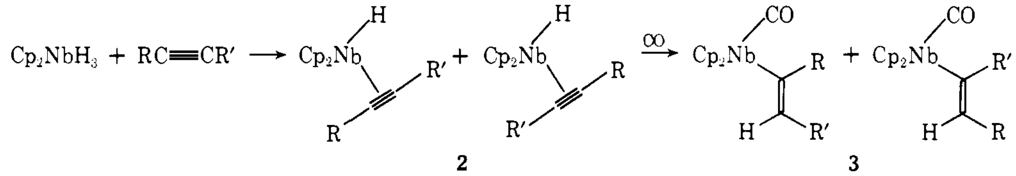
Hydrido(acetylene) complexes **2** are rapidly converted by CH_3I to the orange, crystallize iodo(acetylene) analogs, $Cp_2NbI(RC{\equiv}CR')$, **3**, which were characterized by elemental analysis, ir (for **3a** $\nu_{C{\equiv}C}$ 1825 cm^{-1}), and ^1H NMR. The hydrido(acetylene) complexes also react rapidly with acid to yield, nearly quantitatively, the corresponding cis olefin. Treatment of **2** with methyl fluorosulfonate also causes rapid reaction, but no methylated olefin is obtained; instead, methane is evolved and the original acetylene is liberated. For these complexes, methylation presumably occurs at niobium as does protonation,[7] but reductive elimination of CH_4 from the resulting cationic species is too fast to allow acetylene insertion into the Nb-H bond to compete (reaction 1).



(1)

The above results suggest that alkylation of a coordinated

Table I



2 **3**

RC≡CR'	τ_R	$\tau_{R'}$ (Rel intens)	τ_R	$\tau_{R'}$ (Rel intens)
a, R = $CH_3CH_2CH_2$– R' = $CH_3CH_2\underline{CH_2}$–	7.25	7.20	7.55	7.95
b, R = CH_3– R' = CH_3–	7.58	7.43	8.27	8.30
c, R = CH_3– R' = *i*-C_3H_7–	7.55 (80)	7.37 (20)	8.22 (>95)	(<5)[a]
d, R = CH_3– R = *n*-C_3H_7–	7.53 (60)	7.38 (40)	8.23 (75)	(25)[b]

[a] Not observable within limits of detection. [b] Hidden by other resonances. Determined from relative intensities of C_5H_5 peaks.