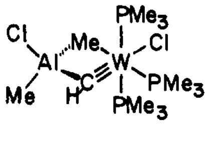
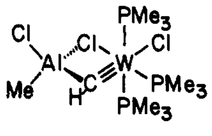


2a



3

[2.525 (5) Å] is consistent with the $AlMe_2Cl$ being removed readily by tmeda. Although more data are required, it is possible that the W–C* bond is long because of a complex interaction of the bridging methyl group with tungsten, e.g., $AlCH_2\cdots H\cdots W$ [cf. $Os_3(CO)_{10}(CH_3)(H)$].[17]

We believe the first step in formation of 1 is alkylation to give $W(Me)(Cl)(PMe_3)_4(AlMe_2Cl)$, since the analogous reaction of $WCl_2(PMe_3)_2(C_2H_4)_2$[18] with $AlMe_3$ proceeds as shown in eq 3.

$$\begin{aligned} & \mathrm{WCl_2L_2L_2'} + \mathrm{AlMe_3} \rightarrow \mathrm{W(Me)(Cl)L_2L_2'(AlMe_2Cl)} \xrightarrow{\text{tmeda}} \\ & \qquad \mathrm{L = PMe_3,\ L' = C_2H_4} \\ & \qquad\qquad \mathrm{W(Me)(Cl)L_2L_2'}\text{[20]} \qquad (3) \end{aligned}$$

One of the major puzzles, however, is how the metal is "oxidized". We do know that 0.9–1.2 equiv of a gas forms which preliminary results suggest is about an 8:2 mixture of methane and hydrogen. The amount of hydrogen formed is too little to account for the oxidation of a $W{-}CH_3$ complex to a $W{\equiv}CH$ complex by loss of H_2, an unprecedented and otherwise attractive explanation.

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(18) Green $WCl_2(PMe_3)_2(C_2H_4)_2$ was prepared from $WCl_2(PMe_3)_4$ and C_2H_4 (30 psi) at 70 °C in toluene.[19] Anal. Calcd for $WC_{10}H_{26}Cl_2P_2$: C, 25.94; H, 5.66. Found: C, 25.71; H, 5.58. This complex will be discussed fully elsewhere.

(19) Sharp, P. R., Ph.D. Thesis, MIT, 1980.

(20) Anal. Calcd for $WC_{11}H_{29}ClP_2$: C, 29.85; H, 6.60. Found: C, 29.73; H, 6.43.[19] Black $W(Me)(Cl)(PMe_3)_2(C_2H_4)$ will be described fully elsewhere.

Preparation of $Fe_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$ from $Fe(CO)_5$

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We have previously reported the preparation of $B_3H_7Fe_2(CO)_6$ and $B_2H_6Fe_2(CO)_6$ from B_5H_9, $Fe(CO)_5$, and $LiAlH_4$.[1] Recently we discovered that if the above synthesis is carried out with Vitride (sodium dihydrobis(2-methoxyethoxy)aluminate: 70% solution in toluene) instead of $LiAlH_4$, the reaction produces not only ferraboranes but also novel alkylidynetriiron nonacarbonyl trihydride complexes. The methyl derivative, $Fe_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$ (I), has been isolated and structurally characterized.

Reaction of $Fe(CO)_5$, B_5H_9, and Vitride (about 2:1:2 molar ratio in toluene) was carried out at 0 °C for 1 h, and then at room temperature for several hours. After treatment with 1 mol of HCl (gas) per mol of Vitride added in several portions, the ferraboranes and the alkylidynetriiron clusteres were separated by trap-to-trap distillation at −15 and −5 °C, respectively. The optimum yield of I is about 10% and is sensitive to reaction temperature and the procedure of acidification. Boranes are required for the production of I. The compound is volatile enough to handle in a standard vacuum line and is readily soluble in a wide range of organic solvents. It is a brown solid at room temperature and decomposes slowly in air.

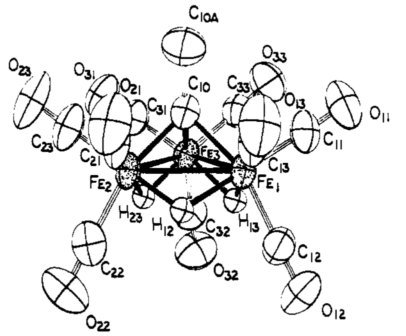

Figure 1. Structure of $Fe_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$. Atoms are represented by 90% ellipsoids (except hydrogens, 50%) and methyl hydrogens are omitted for clarity.

The new compound has been partially characterized spectroscopically. The parent ion in the mass spectrum fragments by the sequential loss of nine CO molecules. The mass spectrometric results also suggest the presence of other triiron analogues, namely $Fe_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CH)$ (II) and $Fe_3(\mu_2\text{-}H)_3(CO)_9(\mu_3CC_2H_5)$ (III) in the product mixture. The 100-MHz ^1H FT NMR spectrum of I in $CD_3C_6D_5$ exhibits two singlets at δ 4.33 and −23.55 (area ratio 1:1), showing that the molecule contains equal numbers of metal bound and carbon bound hydrogens. The 25.2-MHz ^{13}C FT NMR spectrum of I consists of singlets at 206.4 and 46.2 ppm downfield from Me_4Si assigned to CO and methyl carbons, respectively.[2] The proton NMR also suggests the presence of II (δ −24.27).[3] Unambiguous identification of I resulted from an X-ray crystallographic structure determination.

A crystal of 0.3 × 0.4 × 0.7 mm^3 was formed from the gas phase by slow cooling of a pure sample. The crystal was mounted in a capillary under nitrogen and was determined as triclinic (space group $P\bar{1}$) with $a = 7.979$ (2), $b = 9.478$ (3), $c = 12.714$ Å (4); $\alpha = 93.45$ (3), $\beta = 106.94$ (3), $\gamma = 60.79$ (3)°. If $Z = 2$ is assumed, $\rho_{calcd} = 1.87$ g cm^{-3}. The iron atoms were located by direct methods using the MULTAN package.[4] The rest of the nonhydrogen atoms were located by Fourier techniques, and the model was refined to convergence, assuming the atoms to vibrate anisotropically. The bridging hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms. Two of the three methyl hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms, while the calculated position of the third methyl hydrogen atom was included in the model but not refined. Several cycles of full-matrix least-squares refinement (based on 2561 unique observed reflections with $F_0 > 3\sigma F_0$) resulted in convergence with a current $R = 0.077$.

The structure of I with the atoms represented as 90% ellipsoids is shown in Figure 1 (hydrogens represented as 50% ellipsoids). The iron atoms form an equilateral triangular framework with an average Fe–Fe distance of 2.618 Å. The three iron atoms are equivalent, each being coordinated to three terminal carbonyl groups, two bridging hydrogens and one apical carbon. Each pair of iron atoms, the bridging hydrogen atom, and the alkylidyne carbon atom are roughly in the same plane. The Fe–H–Fe angle is about 104° while the $Fe\text{–}C_{apical}\text{–}Fe$ angle is about 85°. The

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(1) Andersen, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 4606. Andersen, E. L.; Haller, K. J.; Fehlner, T. P. *Ibid.* **1979**, *101*, 4390.

(2) These are similar to the absorptions observed for the ruthenium analogue, $H_3Ru_3(CO)_9CCH_3$. As is the case with $H_3Ru_3(CO)_9CCH_3$, as well as $HRu_3(CO)_9C_6H_9$, a resonance for the quaternary carbon was not observed. Canty, A. J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1331.

(3) For the ruthenium analogues the high field metal bound proton resonances are $\delta = -17.45$ ($C\text{–}CH_3$) and $\delta = -17.52$ (CH). Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 477.

(4) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect A* **1971**, *27*, 368. Other programs used as well as a description of data collection and data reduction methods can be found in: Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84.

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apical ethylidyne group, $\equiv CCH_3$, is symmetrically connected to the $H_3Fe_3(CO)_9$ triangular fragment with an average C–Fe distance of 1.947 Å. The C–C bond distance in the ethylidyne group is 1.466 Å. Other bond distances and angles are normal.

The tricobalt analogue of I, $Co_3(CO)_9CCH_3$, a member of a class of compounds that have been extensively studied,[5] has a smaller M–C_{apical}–M angle (81°) and a significantly shorter M–M distance (2.467 Å).[6] The mixed alkylidyne cluster analogue, $HFeCo_2(CO)_9CCH_3$, has also been prepared and characterized.[7] In addition, the ruthenium[3,8] and osmium[8,9] analogues of I have been observed. The X-ray diffraction results on the former[10] reveal the same cluster structure as that determined here for I. The role of the apical carbon[11] and the role of the bridging hydrogens in bonding[12] are two features of cluster bonding that may be fruitfully approached by a comparative study of the electronic structures of these closely related compounds. Also, because ethylidyne has been proposed as the stable species formed from C_2H_2 and C_2H_4 chemisorption on metal surfaces,[13] the properties of I are pertinent to the metal cluster–metal surface analogy[14] as applied to iron.

The aliphatic $\equiv CCH_3$ moiety results from the reduction of CO originally bound to iron. This has been demonstrated by preparing I from ^{13}C enriched $Fe(CO)_5$ (about 30%). The CO's and CH_3 group of the product I exhibited roughly equal ^{13}C enrichments as measured by ^{13}C NMR. Although the specific mechanism for the formation of I is not presently known, there is ample precedent in the literature for the type of reaction that must take place.[15] For example, the reaction of iron bound carbonyl with hydride has been shown to yield formyl complexes,[16] and the reaction of boranes with iron acetyl complexes has been shown to yield alkyliron species.[17] Particularly pertinent is the demonstrated tautomeric interconversion between methyl and hydrido methylene ligands in a triosmium carbonyl cluster and the ultimate conversion of both species to $Os_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CH)$.[18] The conversion of iron bound carbonyl to hydrocarbons by hydride has been demonstrated, e.g., $Cp_2Fe_2(CO)_4$,[19] and I, II, and III must be considered as possible intermediates in such reactions.

The isolation of compound I is of significant interest for other reasons as well. It is the first example of the formation of a member of this class of well-known trinuclear clusters from a mononuclear metal carbonyl. When the general decrease in thermal stability of hydrido derivatives in going from Os to Ru to Fe is considered,[20] the evident stability of I is further proof of the intrinsic stability of alkylidyne trinuclear metal systems.

Details of the structure and other related investigations will be presented in a subsequent publication.

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π- and σ-Acetoxy Radicals

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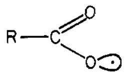
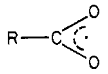
We report here the intermediacy of two types of acetoxy radicals in chain reactions, one as a hydrogen abstractor of low selectivity in alkane halogenation and the other undergoing decarboxylation (Hundsdiecker reaction) exclusively. This behavior is analogous to that shown by succinimidyl radicals,[1] and it is possible that the acetoxys may also be represented as σ and π radicals.



σ



π

All previous work on acetoxy radical recognized cage decarboxylation ($k = 1.6 \times 10^9\ s^{-1}$)[2] as the major pathway, with indications that cage-wall trapping by cyclohexene solvent is the only reaction which competes with decarboxylation; no authenticated noncage reactions were recognized.[3] We observe acetoxy reactions outside the cage which we attribute to π-acetoxy and we attribute all previous work to σ-acetoxy. Acetoxy radical is generated in chain reactions of acetyl hypobromite ($MeCO_2Br$).

Until recently acetyl hypobromite had not been available as the pure substance. We confirm its reported isolation[4] and have improved on the method by using Freon 11 in place of CCl_4, obtaining pure crystalline material in 50–60% yield.

In the absence of H donors, irradiation of solutions of acetyl hypobromite in Freon 11 at −78 °C result in quantitative conversion to methyl bromide and carbon dioxide (Hundsdiecker). These are chain reactions, both in the presence of 10^{-3} M Br_2 or

$$CH_3CO_2Br + CH_3\cdot \rightarrow CH_3CO_2\cdot + CH_3Br$$

$$CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$$

in solutions containing 0.1 M vinylidiene chloride as Br_2 scavenger.[5]

Brominations of alkanes were observed in oxygen-free irradiated solutions of acetyl hypobromite containing 10^{-3} M Br_2. Neo-

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(5) The chain nature of the reactions was demonstrated with propionyl hypobromite whose behavior is the same as that of acetyl hypobromite. Quantum yields for disappearance of propionyl hypobromite were carried out under the conditions described for the acetyl hypobromite reactions. Oxygen-free solutions at −78 °C were irradiated at 313 nm (λ_{max} 320 nm for acetyl hyprobromite)[4] with 10^{-3} M Br_2 or with vinylidiene chloride scavenger with or without 1-bromobutane substrate. All reactions showed an induction period of ~30 min and then rapid loss of the hypobromite. Quantum yields of 25–50 were obtained if one assumes two chains were started by each quantum of light adsorbed; these are minimum values.

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