ORGANOMETALLICS

Reactivity of a bridged vinyl dinuclear iron complex anion [Fe2(CO)6(.mu.-CO)(.mu.-CHCH2)]- toward dicobalt octacarbonyl: synthesis of a mixed dinuclear iron cobalt bridged vinyl complex FeCo(CO)7(.mu.-CHCH2) and its thermal conversion into a bridged vinylalkylidene mixed trinuclear cluster FeCo2(CO)9(.mu.3-CCH2) and an ethylidyne mixed trinuclear cluster Fe2Co(CO)10(.mu.3-CCH3)

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applications of sonic waves to the hydrosilation reaction and to other metal-catalyzed transformations.

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Registry No. n-$C_6H_{13}SiCl_3$, 928-65-4; n-$C_6H_{13}SiMeCl_2$, 14799-94-1; n-$C_6H_{13}SiEt_3$, 13810-04-3; $(CH_3)_2CHCH_2CH_2CH_2SiCl_3$, 20170-36-9; $(CH_3)_2CHCH_2CH_2CH_2SiMeCl_2$, 25959-94-8; $(CH_3)_2CHCH_2CH_2CH_2Si(OEt)_3$, 85356-49-6; $PhCH_2CH_2SiCl_3$, 940-41-0; $PhCH_2CH_2SiMeCl_2$, 772-65-6; $CH_3CH_2CH_2CH(CH_3)CH_2SiCl_3$, 18151-51-4; $CH_3CH_2CH_2CH(CH_3)CH_2SiMeCl_2$, 54008-58-1; $HSiCl_3$, 10025-78-2; $HSiMeCl_2$, 75-54-7; $HSiEt_3$, 617-86-7; $HSi(OEt)_3$, 998-30-1; Pt, 7440-06-4; *trans*-(trichlorosilyl)styrene, 3412-59-7; phenylacetylene, 536-74-3; 1-hexene, 592-41-6; 4-methyl-1-pentene, 691-37-2; styrene, 100-42-5; 2-methyl-1-pentene, 763-29-1.

Reactivity of a Bridged Vinyl Dinuclear Iron Complex Anion, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]^-$, toward Dicobalt Octacarbonyl: Synthesis of a Mixed Dinuclear Iron Cobalt Bridged Vinyl Complex, $FeCo(CO)_7(\mu\text{-}CHCH_2)$, and Its Thermal Conversion into a Bridged Vinylalkylidene Mixed Trinuclear Cluster, $FeCo_2(CO)_9(\mu_3\text{-}CCH_2)$, and an Ethylidyne Mixed Trinuclear Cluster, $Fe_2Co(CO)_{10}(\mu_3\text{-}CCH_3)$

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Summary: The reaction of $[Fe_2(CO)_7(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$ with $Co_2(CO)_8$ at room temperature results in the formation of $FeCo(CO)_7(\mu\text{-}CHCH_2)$ (**1**) as well as the salt clusters $[Fe(Co_2(CO)_9(\mu_3\text{-}CCH_3)][P(C_6H_5)_4]$ (**2**) and $[Co(CO)_4][P(C_6H_5)_4]$. Heating **1** in refluxing hexane results in redistribution to give the trinuclear clusters $Co_3(CO)_9(\mu_3\text{-}CCH_3)$, $FeCo_2(CO)_9(\mu_3\text{-}CCH_3)$ (**3**), and $Fe_2Co(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CCH_3)$ (**4**).

In a recent study[2] we have shown that $[HFe_3(CO)_{11}]^-$ reacts at room temperature with acetylene to give the μ_3-ethylidyne trinuclear iron complex anion $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^-$ and the μ-vinyl dinuclear iron complex anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]^-$. This ease of conversion of acetylene to a μ_3-ethylidyne ligand suggests a facile rearrangement of a μ-vinyl intermediate to a μ_3-ethylidyne ligand on a trinuclear iron unit. For this reason, it was thought that the dinuclear bridged vinyl iron anion might serve as a percursor for a variety of triply bridged ethylidyne mixed-metal clusters by addition of a metal-ligand system. A similar type of study has been developed with a bridged vinylalkylidene complex as a starting material.[3]

Dicobalt octacarbonyl was chosen as the metal-ligand system in the first approach, in the hope that dicobalt octacarbonyl should play a supplementary role, the one of the oxidizing agent, i.e., the reaction shown in eq 1.

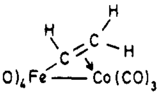

Figure 1. Proposed structure for complex 1.

$$[Fe_2(CO)_7(\mu\text{-}CHCH_2)]^- + Co_2(CO)_8 \rightarrow Fe_2Co(CO)_{10}(\mu_3\text{-}CCH_3) + Co(CO)_4^- + CO \quad (1)$$

Furthermore, cobalt also seemed to favor the transformation of acetylene into the ethylidyne ligand, just as acetylene has been shown to lead to $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ at low temperature with the cluster $HCo_3(CO)_9$.[4] Actually, as is often the case, the reaction is more complex than expected, and even though formation of $Co(CO)_4^-$ has been observed, the reaction does not lead directly to the trinuclear cluster unit.

When stoichiometric amounts of $Co_2(CO)_8$ and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$ are dissolved at room temperature in dichloromethane, a rapid reaction occurs and, after 1 h, no starting material is detected. After solvent evaporation, extraction of the residue with pentane gives a brown solution from which the very volatile brown solid 1 can be isolated with difficulty upon keeping a concentrated pentane solution in dry ice. Both its low melting point and its volatility prevented us from obtaining pure, solvent-free crystals, and it was mainly characterized by infrared, NMR, and mass spectroscopy (Table I). The proton NMR spectrum shows the presence of a vinyl group. In the mass spectrum, a parent ion is detected with a m/z value of 338, while the ions corresponding to the successive loss of seven CO's are observed. The m/z value of 338 agrees with $FeCo(CO)_7CHCH_2$ formula for 1, and the FeCo ion is detected (m/z 115).

A structure is proposed for 1 with a metal-metal bond between the iron and the cobalt atom. The iron is σ bonded to the vinyl group and to four CO groups, while the cobalt is π bonded to the vinyl group and surrounded by three CO groups (Figure 1). This seems to be the first case of an heterodinuclear complex bridged by a vinyl group.

Upon treatment of the residue of the pentane extraction with diethyl ether, a further complex is dissolved, which can be purified by crystallization from methanol. The infrared spectrum in the CO stretching region (Table I) shows the presence of only terminal CO groups. In the proton NMR spectrum, a complex signal that is characteristic of a $P(C_6H_5)_4$ group and a singlet at 3.65 ppm are observed with an intensity ratio 20/3 that suggests the presence of a CH_3 group in 2.

Protonation of this anion by trifluoroacetic acid leads to the isolation of the known $CH_3CFeCO_2(CO)_9H$.[5] This result shows 2 to be the $[FeCo_2(CO)_9(\mu_3\text{-}CCH_3)][P(C_6H_5)_4]$ complex. Extraction with ether only leaves $[Co(CO)_4][P(C_6H_5)_4]$ as an insoluble material. The presence of 2 is somewhat surprising and could be the result of the action of $Co(CO)_4^-$ on 1. Accordingly, we mixed $Co(CO)_4^-$ with 1 and, indeed, 2 is slowly formed at room temperature. Equations 2 and 3 summarize our observations.

$$[Fe_2(CO)_7CHCH_2]^- + Co_2(CO)_8 \rightarrow FeCo(CO)_7CHCH_2 + Co(CO)_4^- + Fe(CO)_4 \quad (2)$$

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Table I. Spectroscopic Data of Isolated Complexes

		IR,[a] ν_{CO} (cm^{-1})	^1H NMR,[b] δ (Me_4Si)
$FeCo(CO)_7(CHCH_2)$	1	2098 w, 2051 sh, 2045 s, 2037 m, 2017 s, 1980 w	CH, 7.95 dd (J_1 = 8Hz, J_2 = 13 Hz) CH_2, 3.05 d (J = 13 Hz), 2.82 d (J = 8 Hz)
$[CH_3CFeCo_2(CO)_9][P(C_6H_5)_4]$	2	2050 w, 1982 s, 1970 sh, 1915 w (br)	CH_3, 3.72
$CH_3CFeCo_2(CO)_9H$		2100 m, 2063 sh, 2052 s, 2047 s, 2036 s, 2012 m, 1988 m	CH_3, 2.58 d (J = 2.6 Hz); H, −9.80 (br)
$CH_3CCo_3(CO)_9$		2102 m, 2050 s, 2037 s, 2018 m	CH_3, 3.18
$CH_2CFeCo_2(CO)_9$	3	2102 m, 2053 s, 2047 s, 2037 s, 2015 m, 1987 m	CH_2, 3.78 (^{13}C NMR CO, 204.1 ppm, CH_2, 79.5 (J_{CH} = 162 Hz))
$CH_3CFe_2Co(CO)_{10}$	4	2098 w, 2047 s, 2030 s, 2008 m, 1840 w	CH_3, 4.08

[a] Hexadecane solutions except 2 (CH_2Cl_2 solution). [b] C_6D_6 solutions except 2 ($(CD_3)_2CO$ solution).

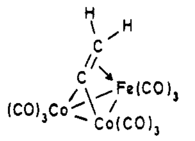

Figure 2. Proposed structure for complex 3.

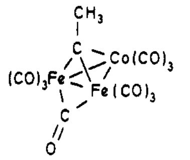

Figure 3. Proposed structure for complex 4.

$$FeCo(CO)_7CHCH_2 + Co(CO)_4^- \rightarrow [FeCo_2(CO)_9CCH_3]^- + 2CO \quad (3)$$

As complex 1 is quite easily accessible (ca. 50% yield), its thermal stability has been checked. Considerable redistribution is observed upon refluxing a solution hexane of 1 for 1 h. The proton NMR spectrum of the resulting mixture shows the presence of three new products while 1 has disappeared. The three products have been separated by chromatography on Florisil. The first product isolated is the pink $CH_3CCo_3(CO)_9$ identified by infrared and NMR spectra compared with literature data.[6,7] The second product is the brown solid 3 which crystallizes in hexane. Its infrared spectrum in the CO terminal stretching region is quite complex and very similar to that of the compound described as $H_2Fe_2Co(CO)_9CCH_3$.[8] Nevertheless, the proton NMR spectrum shows no hydride resonance. 3 has been identified by its mass spectrum. The parent ion has an *m/z* value of 452, and the ions corresponding to the successive loss of nine CO's are observed. The other ions observed have *m/z* values of 200 and 174, respectively. The latter corresponds to the ion $FeCo_2$, and the difference of 26 between these two ions corresponds to a C_2H_2 group. The formula of 3 is therefore $FeCo_2(CO)_9C_2H_2$, and the exact nature of the C_2H_2 group is ascertained by a gated ^{13}C NMR spectrum which shows a triplet at 79.5 ppm (J_{CH} = 162 Hz). From this observation, we conclude that the C_2H_2 group is a vinylalkylidene ligand and the structure shown in Figure 2, which is consistent with the proton NMR spectrum, is proposed for 3.

The third product, which is less abundant, is the brown solid 4. The presence of bridging CO's is observed in the CO stretching region of the infrared spectra (Table I), and the proton NMR spectrum shows no hydride resonance. 4 has also been identified by its mass spectrum. A parent ion with an *m/z* value of 478, and the ions corresponding to the successive loss of 10 CO's are observed. The other ions are Fe_2Co (*m/z* 171), Fe_2CoC (*m/z* 182), Fe_2CoC_2H (*m/z* 196), and $Fe_2CoC_2H_3$ (*m/z* 198). From these observations, we can conclude that the formula of 4 is $Fe_2Co(CO)_{10}CCH_3$. Its proposed structure is shown in Figure 3.

Thus, thermal rearrangement of 1 is seen to lead to trinuclear cluster units resulting from the scrambling of the two metals in one homonuclear tricobalt cluster and two heteronuclear clusters with an $FeCo_2$ or Fe_2Co core. Furthermore, the vinyl ligand generated both a vinylalkylidene (complex 3) and an ethylidyne ligand (complex 4) which stabilize the $FeCo_2$ and the Fe_2Co cores. Such rearrangements of vinyl groups are commonly encountered in cluster chemistry[9] but usually with second- and third-period metals.

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Registry No. 1, 85236-19-7; 2, 85236-21-1; 3, 85249-99-6; 4, 85236-22-2; $Co_2(CO)_8$, 10210-68-1; $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$, 85236-24-4; $Co(CO)_4^-$, 14971-27-8; $CH_3CFeCo_2(CO)_9H$, 69493-75-0; $CH_3CCo_3(CO)_9$, 13682-04-7; Co, 7440-48-4; Fe, 7439-89-6.

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Apparent Syn Elimination of Palladium Oxide from a β-Hydroxy Organopalladium Intermediate

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Summary: Reaction of 1,4-anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol (**1**) with (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate (**2**) in the presence of palladium(II) acetate forms an adduct which possesses adjacent cis hydroxyl and palladium(II) substituents. The observed decomposition of this adduct to (2′-*S*-*trans*)-5-[2′,5′-dihydro-5′-[(methoxymethoxy)methyl]-2′-furanyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione is most reasonably formulated as involving