found, 439; $C_{17}H_{22}BrNSn$ calcd, 438.

(19) This six-membered ring is puckered both at the CH_2Sn as well as at the $SnN(Me_2)CH_2$ part. In the pentacoordinate {5-MeO-8-Me_2NCM_2naphthyl}MeRSnBr (R = Me or Ph) compounds puckering is restricted to the $SnN(Me_2)CH_2$ part which results in two different conformations for the six-membered chelate ring. Both conformations can be frozen out on the NMR timescale below −30 °C.

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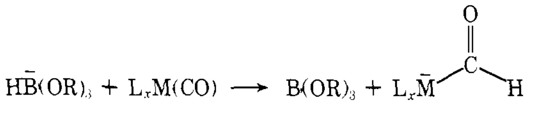
Synthesis of Transition Metal Formyl Compounds by Nucleophilic Attack of Hydride on Coordinated CO

Sir:

There is renewed interest in the conversion of coal to gaseous and liquid fuels. These conversions can be accomplished by the reaction of coal with water to give a 1:1 mixture of $CO:H_2$, which can subsequently be passed over various heterogeneous transition metal catalysts to give methane or methanol or (via the Fischer-Tropsch reaction) gasoline.[1-3] Little is known about the mechanism of these reductions, but transition metal formyl complexes may well be important intermediates in the initiation step for the catalytic reduction of CO by H_2. However, attempts to obtain evidence for the intermediacy of metal formyl complexes in the reactions of metal carbonyl hydrides have uniformly met with failure.[4] Our interest in the mechanism of the Fischer-Tropsch reaction and in the development of a homogeneous catalyst for the reduction of CO has led us to undertake a study of the synthesis and reactions of metal formyl complexes. The only previously reported metal formyl complex, $[(Ph_3P)_2N]^+(CO)_4FeCHO^-$, **1**, was prepared by Collman and Winter in 1973 by the reaction of $Na_2Fe(CO)_4$ with acetic formic anhydride.[7] Here we report (1) a new synthesis of metal formyl complexes from the reactions of metal carbonyl compounds with trialkoxyborohydrides, (2) the isolation of a second stable metal formyl complex, $[Et_4N]^+$ *trans*-$[(PhO)_3P](CO)_3FeCHO^-$, **2**, and (3) the observation of a number of unstable metal formyl complexes.

The reactions of borohydrides with transition metal carbonyl compounds have been used to facilitate the substitution of one or more ligands for CO,[8-10] and to synthesize certain group 6 dinuclear metal carbonyl hydrides.[11,12] We have found that the reaction of $Na^+HB(OCH_3)_3^-$ or $K^+HB(O\text{-}i\text{-}Pr)_3^-$ [13] with various metal carbonyl compounds leads to transition metal formyl compounds according to eq 1. Reaction of $Na^+HB(OCH_3)_3^-$ with $Fe(CO)_5$, followed by cation exchange with $[(Ph_3P)_2N]^+Cl^-$, gives $[(Ph_3P)_2N]^+(CO)_4FeCHO^-$, **1**, in 80–90% yield by NMR analysis[14] and in 39% isolated yield, mp 122–132 °C (sealed tube) dec.[15] The infrared spectrum and ^1H and ^{13}C NMR spectrum of **1** prepared from $Fe(NO)_5$ and $Na^+HB(OCH_3)_3^-$ [16] were identical with the spectra of a sample of **1** prepared from $Na_2Fe(CO)_4$ and acetic formic anhydride.[7] The formyl proton characteristically appears at very low field, δ 14.95, in the ^1H NMR; similarly, the formyl carbon appears at characteristically low field, δ 270.5, in the ^{13}C NMR spectrum. Reaction of **1** (prepared from $Na^+HB(OCH_3)_3^-$ and $Fe(CO)_5$) with HCl in THF gives formaldehyde as previously reported.[7,17] A THF solution of **1** reacts with HCl in the presence of Ph_3P to give $(CO)_4FePPh_3$ (57%) and $(CO)_3Fe(PPh_3)_2$ (20%); similar results were reported in the $NaBH_4$ "facilitated" substitution of $Fe(CO)_5$ by PPh_3, although iron formyl species were not proposed for these reactions.[8]



$$H\bar{B}(OR)_3 + L_xM(CO) \longrightarrow B(OR)_3 + L_x\bar{M}{-}C({=}O){-}H \qquad (1)$$

L = PPh_3, $P(OPh)_3$, CO

R = $-CH_3$, $-CH(CH_3)_2$

The reaction of trialkoxyborohydrides as a hydride source with metal carbonyl compounds is an excellent organometallic synthetic method. The rapidity and ease of the procedure, along with the ability to obtain adequate yields, make the method quite useful. Moreover, this procedure can be extended to the synthesis of metal formyl compounds from systems other than $Fe(CO)_5$, whereas in our hands the reaction of acetic formic anhydride with metal carbonyl anions could not. Reaction of $CH_3C(O)OC(O)H$ with $C_5H_5Fe(CO)_2^-$, $Cr(CO)_5^{2-}$, $(Ph_3P)Mn(CO)_4^-$, and $(Ph_3P)_2Mn(CO)_3^-$ produced no products with ^1H NMR resonances below δ 10 expected for metal formyl compounds. However, reaction of $Na^+HB(OCH_3)_3^-$ with the appropriate metal carbonyl compound in THF in a sealed NMR tube led, in many cases, to the appearance of characteristic formyl ^1H NMR resonances below δ 10. We now have NMR evidence for the formation of metal formyl compounds from $Cr(CO)_6$ (δ 15.2, s),[18] $W(CO)_6$ (δ 15.9, s), $(CO)_5CrPPh_3$ (δ 15.3, s), $(CO)_5WPPh_3$ (δ 15.8, s), and $(CO)_4FePPh_3$ (δ 15.5, d, J = 24 Hz).[19] Quantitative NMR studies on several of the above systems indicated that the extent of the reaction producing the desired metal formyl compound was generally quite low (<10%),[14] and as a result we tried analogous reactions of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ [20] with several metal carbonyl compounds in an attempt to increase the extent of reaction by using a more reactive hydride.[13b] We found that $Cr(CO)_6$ reacts with $K^+HB(O\text{-}i\text{-}Pr)_3^-$ to give a maximum 76% conversion to the formyl compound in 25 min at ambient temperature;[14] the product formyl complex, $K^+(CO)_5CrCHO^-$, is half decomposed in an additional 40 min. In contrast, the reaction of $Cr(CO)_6$ with $Na^+HB(OCH_3)_3^-$ gives a maximum of 4% of the metal formyl after 25 min at ambient temperature.[14] The reaction of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ with $W(CO)_6$ and $(CO)_4FePPh_3$ gives qualitatively similar results.

We have been able to isolate and characterize the second known compound of the metal formyl class by the reaction of a sixfold excess of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ with $(CO)_4FeP(OPh)_3$ in THF.[15] Cation exchange of the resulting potassium salt with $[Et_4N]^+Br^-$ and 1 N NaOH gave $[Et_4N]^+$*trans*-$[(PhO)_3P](CO)_3FeCHO^-$, **2**, as a light tan powder in 64% yield, mp 40–55 °C (sealed tube) dec.[21] Solutions of **2** are rapidly oxidized by air and undergo thermal decomposition at 65° over several hours. **2** shows spectral properties fully consistent with its proposed structure: ^1H NMR (acetone-d_6) δ 1.30 (tt, J = 7.7 Hz, J_{NH} = 1.5 Hz, 12 H, NCH_2CH_3), 3.40 (q, J = 7.7 Hz, 8 H, NCH_2CH_3), 6.8–7.8 (m, 15 H, C_6H_5), 14.82 (d, J_{PH} = 44.4 Hz, 1 H, FeCHO); ir (THF) 2515 cm^{-1} (w, aldehyde C—H[22]), 1960 (m, M≡O), 1872 (vs, M≡O[23]), 1584 (m, formyl C=O).

This new synthesis of metal formyl complexes will enable us to study the kinetic stability of metal formyl complexes, the equilibrium between metal hydrides and metal formyl complexes, and the reaction of metal formyl compounds with hydrogen and other reducing agents.

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Supplementary Material Available: Experimental procedures (2 pages). Ordering information is given on any current masthead page.

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(14) Yields are determined by integration of the characteristic formyl proton resonance with respect to a weighed amount of added toluene.
(15) Detailed procedures for these preparations are included as supplementary material.
(16) Ir (THF) 2690 (w), 2510 (w), 2018 (w), 1930 (s), 1902 (vs), and 1607 (s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 7.44–8.04 (m, 30 H, C_6H_5); 14.95 (s, 1 H, FeCHO). ^{13}C NMR (acetone-d_6) δ 129.8, 130.8, 131.5, 132.5, 133.3, 134.4 (C_6H_5); 221.1 (metal carbonyl), 270.5 (formyl carbon).
(17) Formaldehyde was isolated as the dimedone derivative and characterized by mass spectroscopy, M^+ 292.
(18) Ir spectrum of $Cr(CO)_6 + Na^+ HB(OCH_3)_3^-$ in THF: 2021 (w), 1903 (s), 1888 (s), 1838 (m) cm^{-1}, in addition to frequencies for $Cr(CO)_6$.
(19) We have found, by using identical methods, no evidence for formation of metal formyl compounds from $Mo(CO)_6$, $C_5H_5Mn(CO)_3$, $C_5H_5Fe(CO)(PPh_3)Br$, $(CO)_3Fe(PPh_3)_2$, and (p-xylene)$Cr(CO)_3$.
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A New Structural Type for $M_3(CO)_{12}$ Molecules and Their Derivatives. The Molecular Structure of $Ru_3(CO)_{10}$(1,2-diazine)

Sir:

We have previously called attention to the extreme structural variability of trinuclear metal carbonyl molecules,[1] such as $Fe_3(CO)_{12}$,[2,3] $(\eta^5\text{-}C_5H_5)_3Co_3(CO)_3$,[4] and the related $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$, under the influence of thermal energy, environment, and, more drastically, replacement of one or more CO ligands by other ligands. There are comparable examples among dinuclear species, e.g., $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$,[5] $Co_2(CO)_8$,[6,7] and $Fe_2(CO)_7$(dpy).[8]

We wish to report here some recent work which bears importantly, and interestingly, on this point. It is well known that the solid state structure of $Fe_3(CO)_{12}$ has two unsymmetrical bridges on one edge of the Fe_3 triangle[9,10] while that of $Ru_3(CO)_{12}$ is of D_{3h} symmetry and has no bridges.[11] It is also known that $Fe_3(CO)_{12}$ undergoes CO scrambling with extreme ease[3] and is an example, par excellence, of that class of easily deformable molecules which we have proposed to call *fictile molecules.*[4] $Ru_3(CO)_{12}$, on the other hand, though not fictile (ir spectrum normal in solution) is also readily fluxional, having only one ^{13}C resonance line at the lowest temperature (−100 °C) studied.[12]

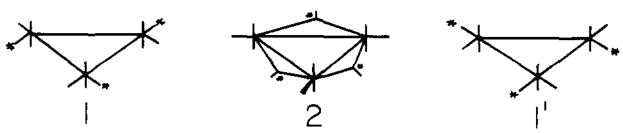

Figure 1. A plausible but undetected pathway for partial CO scrambling in an $M_3(CO)_{12}$ molecule of the $Ru_3(CO)_{12}$ type.

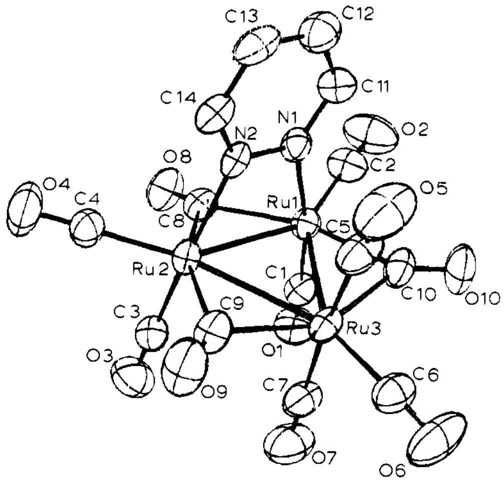

Figure 2. The molecular structure of $Ru_3(CO)_{10}(1,2\text{-}C_4H_4N_2)$. Atoms are represented by thermal vibration ellipsoids at the 50% level.

We have previously proposed[10] a mechanism for CO scrambling in $Fe_3(CO)_{12}$ that involves concerted rotatory motions of CO's on adjacent iron atoms in such a way that a pair of CO bridges is temporarily established across the bond between those two iron atoms. As the proposed process is carried forward, and repeated on the other edges of the Fe_3 triangle, all CO groups are caused to travel over the entire Fe_3 triangle and to have time-average equivalence. It is important to realize, however, that even though this process can account, by itself, for *all* the spectroscopic observations[3] on $Fe_3(CO)_{12}$, one or more other, unperceived, processes, whose spectral effects are masked by the main process may also occur. The unperceived process (or processes) would involve some structurally different intermediate.[13] In the present case, one such process might be that shown in Figure 1, where the intermediate, **2,** has a bridging CO group on each edge and overall D_{3h} symmetry.[17] The process shown in Figure 1 cannot, of course, by itself account for the complete scrambling of CO groups; obviously, it scrambles only half of them. However, it is structurally a very plausible process and may well be occurring, even though its effects might be entirely masked by those of the more extensive scrambling process discussed above.

One form of evidence for the plausibility of any such structure as **2** is the actual observation of it, in slightly modified form, in a closely related system. We now report that sort of evidence for **2.** The reaction of pyridazine (1,2-diazine) with $Ru_3(CO)_{12}$ under appropriate conditions gives a deep maroon crystalline compound of stoichiometry $Ru_3(CO)_{10}(C_4H_4N_2)$. The structure, determined by standard x-ray crystallographic procedures,[18] is shown in Figure 2. Some important bond lengths are given in Table I.

The structure can be thought of as derived from **2** by replacement of two terminal CO groups on Ru1 and Ru2 by the pyridazine nitrogen atoms. As a result of the short N–N distance and preferred orientation of these nitrogen lone pairs, there is a slight tilting of the coordination polyhedra of Ru1 and Ru2 the most notable effects of which are that the CO