Accordingly, both cyclobutyl and cyclopropylcarbinyl cations must be regarded as fully legitimate ionic intermediates, characterized by a significant local minimum on the $C_4H_7^+$ potential surface.

While these conclusions agree with theoretical results pointing to the appreciable stability of the cyclopropylcarbinyl ion in the bisected conformation, and the product distributions are also consistent with the view that acyclic species, such as 1-methylallyl cation, are most stable among $C_4H_7^+$ isomers, the alleged[7] lack of stability of the cyclobutyl cation is not supported by the experimental results.

Finally, the relatively low yields of cyclic neutral products are far from unexpected, and indeed the radiochemical experiments were designed to detect even smaller amounts of cyclobutyl and cyclopropylcarbinyl derivatives among the products.

In fact, even though most decay ions are formed in their electronic ground state,[8] some vibrational excitation necessarily arises from the different equilibrium positions of the constituent atoms in the parent cyclobutane molecule and the daughter cyclobutyl cation, which causes relaxation to the most stable structure of the latter. Following decay leading to such a strained structure as the cyclobutyl cation, even limited vibrational excitation in eq 2 is expected to cause extensive ring cleavage. Furthermore, owing to the exothermicity of eq 3, a certain fraction of the excited onium ions formed is likely to isomerize into more stable acyclic structures.

In conclusion, it appears that the overall results of the joint mass spectrometric[9] and radiochemical investigations begun in 1972 provide direct experimental evidence for the existence of cyclobutyl and cyclopropylcarbinyl cations as free, unsolvated species in the dilute gaseous state. A detailed analysis of their reactivity, equilibration, and competitive isomerization pathways will be reported in a forthcoming paper.

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(12) Deprotonation (eq 4) can readily occur in the presence of a large excess of the nucleophile, following stepwise clustering of several molecules of HY around the charged intermediate, according to the equation $c\text{-}C_4H_{7-n}T_nYH^+ + m\text{HY} \rightarrow c\text{-}C_4H_{7-n}T_nY + \text{H(HY)}^+$. The overall process is exothermic, even though proton transfer to a single HY molecule would be endothermic. For extensive mass spectrometric evidence on such cooperative deprotonation reactions, see K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 360 (1977), and references therein.

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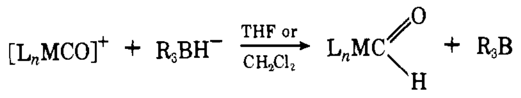
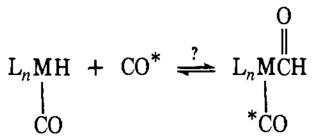
Neutral Metal Formyl Complexes: Generation, Reactivity, and Models for Fischer–Tropsch Catalyst Intermediates

Sir:

The availability of anionic metal formyl complexes from the reaction of hydride donors with neutral metal carbonyl complexes is now well established.[1-3] However, this potentially general methodology has not yet been extended to the preparation of *neutral* metal formyl complexes from *cationic* metal carbonyl precursors. Catalyst-bound formyls are believed to be initially formed intermediates in Fischer–Tropsch type processes,[4] and neutral formyl complexes might be expected to provide more precise models for their reactivity than anionic homologues. We report herein that the reaction of $\mathrm{Li(C_2H_5)_3BH}$[5] with metal carbonyl cations provides a convenient entry into a number of neutral formyl systems (eq 1), one of which can be isolated in crystalline, analytically pure form. Further reactions of these complexes with BH_3, $\mathrm{Li(C_2H_5)_3BH}$, and transition metal hydrides define additional modes of -CO or -CHO reduction which are relevant to (a) possible operative mechanisms of Fischer–Tropsch catalysts, (b) metal hydride carbonylation reactions (eq 2),[6] and (c) important but heretofore unexplained observations of other researchers.[7,8]



$$[\mathrm{L}_n\mathrm{MCO}]^+ + \mathrm{R_3BH}^- \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{THF\ or}} \mathrm{L}_n\mathrm{MC}\overset{\mathrm{O}}{\underset{\mathrm{H}}{}} + \mathrm{R_3B} \qquad (1)$$



$$\underset{\mathrm{CO}}{\mathrm{L}_n\mathrm{MH}} + \mathrm{CO}^* \overset{?}{\rightleftharpoons} \mathrm{L}_n\mathrm{M}\underset{^*\mathrm{CO}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}}\mathrm{H} \qquad (2)$$

Synthesis. The reaction of $[\mathrm{(C_5H_5)Re(CO)_2NO}]^+\mathrm{BF_4}^-$ (**1**)[7b,8] with 1.0 equiv of $\mathrm{Li(C_2H_5)_3BH}$ at −23 °C in THF affords a product in quantitative yield (^{1}H NMR) whose spectral characteristics[9] establish its structure as the neutral formyl $\mathrm{(C_5H_5)Re(CO)(NO)(CHO)}$ (**2**) (Scheme I). Although **2** thus prepared has a half-life of ~3 h at room temperature, extensive attempts at its isolation (via solvent removal, benzene or CH_2Cl_2 extraction, and subsequent concentration and/or addition of hexanes) have to date resulted only in impure powders.

The reaction of $[\mathrm{(C_5H_5)Re(CO)(PPh_3)NO}]^+\mathrm{BF_4}^-$(**3**)[10] with 1.0 equiv of $\mathrm{Li(C_2H_5)_3BH}$ (or $\mathrm{K}(sec\text{-}\mathrm{C_4H_9})_3\mathrm{BH}$) at 22 °C in THF yields the much more stable formyl $\mathrm{(C_5H_5)Re(PPh_3)(NO)(CHO)}$ (**4**) (Scheme I).[11] Solvent removal, silica gel chromatography (under N_2 using hexanes–THF), and THF-hexane recrystallization afford honey-colored, analytically pure crystals[11] in 59% yield (dec pt (gradual) ~91 °C).

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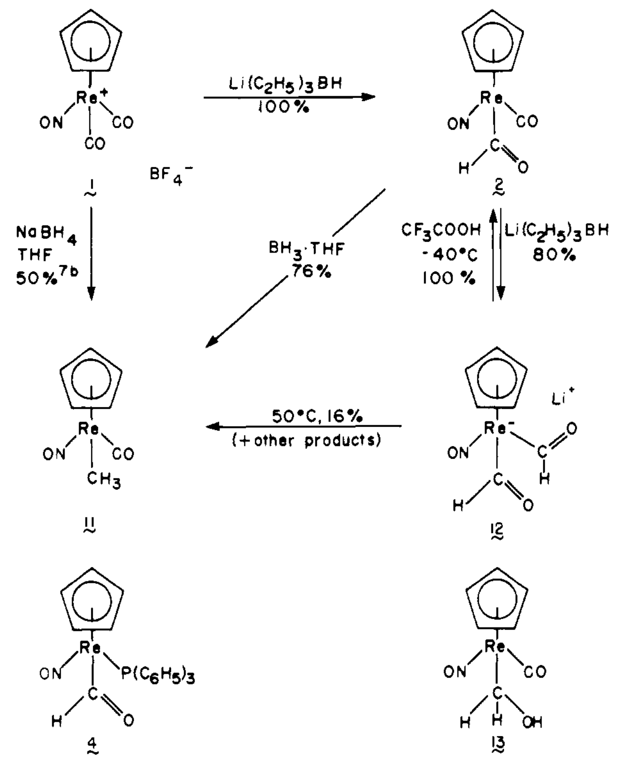
Table I. Data on Unstable Neutral Metal Formyl Complexes Prepared[a]

starting metal carbonyl cation	solvent (temp, °C)	yield, %[b]	^{1}H NMR, δ[c]	thermal stability (temp, °C)
$[(C_5H_5)Mn(CO)_2NO]^+PF_6^-$ (**5**)	THF (−23)	100	13.45 (s)	rapid dec (10)
$[Re(CO)_5PPh_3]^+BF_4^-$ (**6**)	CH_2Cl_2 (−23)	90	13.98 (s)[d]	rapid dec (20)
$[Mn(CO)_4(PPh_3)_2]^+PF_6^-$ (**7**)	CH_2Cl_2 (−22)	71	13.23 (t,[e] 4)	rapid dec (0)
$[Ir(CO)_3(PPh_3)_2]^+PF_6^-$ (**8**)	CH_2Cl_2 (−60)	80	12.85 (t, 17)	rapid dec (−30)
$[(C_5H_5)Mo(CO)_3PPh_3]^+PF_6^-$ (**9**)	CH_2Cl_2 (−41)	41	14.70 (d, 4)	rapid dec (−41)

[a] By reaction with 1.0 equiv of $Li(C_2H_5)_3BH$ in THF with the metal cation dissolved or suspended in the given solvent at the given temperature. [b] By ^{1}H NMR relative to an internal standard. [c] Multiplicity, J in hertz in parentheses. Relative to $(CH_4)_4Si$ at the temperature of generation; chemical shifts are temperature dependent. [d] ^{13}C NMR (−60 °C, 0.03 M $Cr(acac)_3$): 275.6 ppm (d, J = 9 Hz). [e] ^{13}C NMR (−40 °C, 0.03 M $Cr(acac)_3$): 301.2 ppm (br s).

Scheme I. Cyclopentadienylrhenium Formyls Prepared and Related Compounds



Less stable species can be detected by NMR when $Li(C_2H_5)_3BH$ is reacted with metal carbonyl cations **5–9** (Table I).[10] By analogy to **2** and **4**, and in some cases subsequent transformations, these products are formulated as neutral formyl complexes.

The d^8 formyl complex prepared from **8** cleanly decomposes to a metal hydride by the reverse of eq 2 (−40 °C, 20 min, 100% to $HIr(CO)_2(PPh_3)_2$[12]), as does a neutral osmium formyl recently described by Roper.[13] From $(C_2H_5)_3B$-free **2**, small amounts of $(C_5H_5)Re(CO)(NO)H$ (**10**) can be detected. However, the formyl complexes derived from cations **3**, **5**, **6**, **7**, and **9** do not by ^{1}H NMR decompose to metal hydrides. Additional data (vide infra) suggest a possible explanation.

Reactions with BH_3. Cations **1** and **9** have been reported by Graham[7b] and Treichel[7a] to yield methyl complexes **11** (Scheme I) and $(C_5H_5)Mo(CO)_2(PPh_3)CH_3$, respectively, upon treatment with $NaBH_4$ in THF. Our results suggest that the $NaBH_4$ effects the initial formation of formyl complexes (e.g., **2**). The concomitant generation of BH_3 from $NaBH_4$ provides a second reductant which may further reduce the formyl ligand. Accordingly, we find that **2** reacts with BH_3·THF (3 equiv; 1 h at −23 °C followed by 15 min at 25 °C), affording **11** in 76% isolated yield. Intermediates could not be detected in this reaction or the related BH_3·THF reduction of $(CO)_5MnCOC_6H_5$ to $(CO)_5MnCH_2C_6H_5$ (5 min, 25 °C, 100 % by IR).[14] However, the individual steps of Graham's and Treichel's reactions, which constitute the only well-defined conversions of coordinated -CO to -CH_3, have now been clarified.

Reactions with $Li(C_2H_5)_3BH$. The treatment of **2** with an additional equivalent of $Li(C_2H_5)_3BH$ at −23 °C results in the formation of a new species (80% ^{1}H NMR yield) whose spectral characteristics[15] indicate it to be the anionic bis(formyl) **12** (Scheme I). We have previously postulated[1c] a bis(formyl) similar to **12** as an intermediate in the production of formaldehyde and/or methanol when anionic formyl complexes are reacted with additional R_3BH^-. Hence **12**, which is relatively stable at room temperature (half-life 2 h at 23°C), is the first well-defined complex of this type to be generated.

As observed with other anionic formyl complexes,[1a-c,2] **12** acts as a hydride donor toward acids such as CF_3COOH (−40 °C, 100% formation **2**). However, **12** is unreactive toward $Fe(CO)_5$. The thermal decomposition of **12** is first order (k_{obsd} = 1.50×10^{-4} s^{-1} at 38 °C) and results in the appearance of new IR absorptions at 1966 (s) and 1695 (s) cm^{-1} and the eventual formation (50 °C, 2 h) of some **11** (16%). Thus the formyl ligands in **12** can be transformed into methyls; however, formaldehyde, methanol, or other characterizable rhenium complexes are not detectably produced.

Bis(formyl) **12** is compositionally similar to α-hydroxyalkyl **13**, which is claimed to have been isolated (dec pt 69–71 °C; IR 3300–3200 (s), 1980 (s), 1660 (s) cm^{-1}) from the reaction of **1** with $NaBH_4$-C_6H_6-H_2O.[8] Our attempts to reproduce this preparation (we have observed that **1** is converted into **2** under the reported[8] conditions) or effect an independent synthesis by the protonation of **12**, or its decomposition products, have met with failure. Other manganese and rhenium complexes believed to contain an α-hydroxyalkyl ligand are exceedingly unstable.[16] Hence we believe it probable that the structural assignment **13** is in error.

Other anionic bis(formyl) complexes can be prepared from metal carbonyl cations. Reaction of **6** in CH_2Cl_2 with 2.0 equiv of $Li(C_2H_5)_3BH$ at −23 °C affords the corresponding bis(formyl) species in 70% yield (^{1}H NMR).[17]

Reactions with Transition Metal Hydrides. The decomposition behavior of some of our neutral formyl complexes raises the possibility that transition metal hydrides might undergo reactions with neutral formyl complexes. We tested this notion with a prototype reaction between the metal acyl $(CO)_5MnCOC_6H_5$ and metal hydride $HMn(CO)_5$.[18] The admixture of equimolar quantities in THF at room temperature resulted in the formation of $Mn_2(CO)_{10}$ (86% isolated) and benzaldehyde (99%, isolated as 2,4-DNP derivative) over the course of 10 min.

As anticipated, we find that **2** (prepared in situ) reacts rapidly (within 1 h at 0 °C) with the hydrides **10**, $HMn(CO)_5$, and $HMo(C_5H_5)(CO)_3$. While the products of these reactions are still being characterized (with 3 equiv of $HMn(CO)_5$, 8% of **11** is formed from **2**), the present results indicate that the direct observation of metal hydride carbonylation (eq 2) might in some cases be rendered impossible by a competing reaction between the product L_nMCHO and starting L_nMH.[19] The thermal decomposition of neutral formyl complexes by the reverse of eq 2 could also in some cases be complicated by such a competing back reaction.

Summary. The $Li(C_2H_5)_3BH$ reduction of metal carbonyl cations and subsequent reductive transformations of the resulting neutral formyl complexes have served to define numerous new model compounds and reactions which may bear important relationships to operative features of Fischer-Tropsch type catalysts. More detailed investigations of the complexes and reactions reported herein are actively being pursued.

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(17) ^1H NMR (−23 °C, CH_2Cl_2–THF, δ): 14.32 (s, 2 H, $J \leqslant 1$ Hz). ^{13}C NMR (−60 °C, CD_2Cl_2–THF, 0.03 M $Cr(acac)_3$): 293.7 ppm (d, $J = 9$ Hz).

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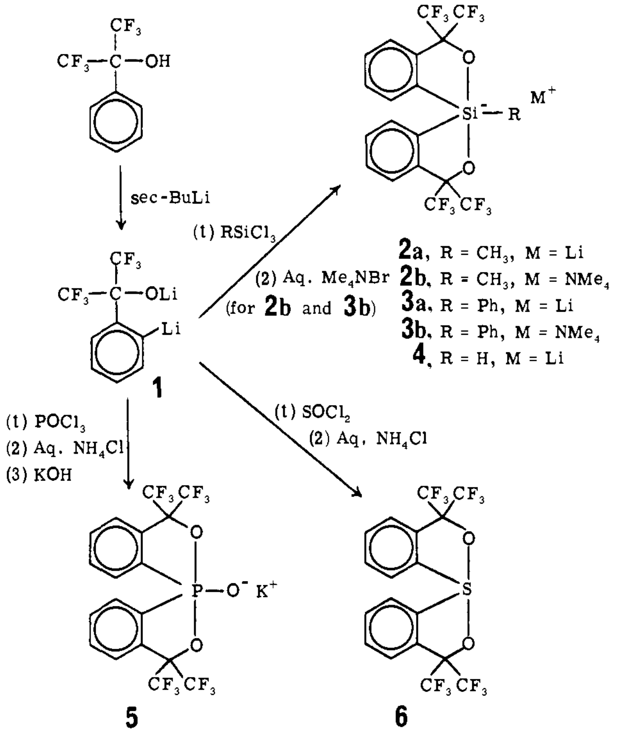
Facile Syntheses of Isolable Organic Derivatives of Hypervalent Sulfur, Phosphorus, and Silicon. Introduction of a Stabilizing Bidentate Ligand via Its Dilithio Derivative

Sir:

We report a very convenient preparation of dilithio derivative **1** by the reaction of *sec*-butyllithium with hexafluorocumyl alcohol. This reagent is used to prepare siliconates[1] **2, 3,** and **4** (anionic pentacoordinate silicon species); potassium phosphoranoxide[2] **5;** and spirosulfurane[3] **6.** These compounds share structural features which have been credited with the extraordinary stabilities earlier noted[4] for certain derivatives of hypervalent sulfur.



Recent success in the isolation of novel anionic hypervalent phosphorus species, phosphoranides[5] (**7c**) and phosphoranoxides[2] (**7d**), isoelectronic with the analogous stable sulfuranes[6] (**7a**) and sulfurane oxides[6] (**7b**), has underscored the postulate[2] that one can, at least qualitatively, assess the probability that a hypervalent species will be stable enough to isolate by extrapolations from a knowledge of stabilities of analogous derivatives of atoms from adjacent columns of the periodic table. Closely analogous (essentially isoelectronic) derivatives of tetracoordinate sulfur(IV)[6] (**7a**), selenium(IV)[7] (**7e**), and anionic phosphorus[2] (**7c**); of pentacoordinate sulfur (VI)[6] (**7b**) and anionic phosphorus(V)[5] (**7d**); and of tricoordinate iodine(III)[8] (**8a**) and anionic sulfur(IV)[9] (**8b**) have been studied with results supporting this postulate.