direct means of assessing the role of the globin on the reactivity of the heme group.

Acknowledgment. We thank the National Institutes of Health and the National Research Council of Canada for support of this work.

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Received January 31, 1973

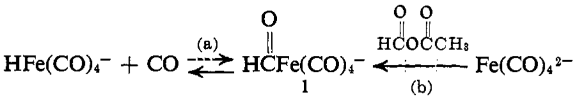
Isolation and Characterization of a Kinetically Stable Transition Metal Formyl Complex

Sir:

Acyl complexes are well known, synthetically useful organotransition metal derivatives;[1-7] however, corresponding formyl complexes have not been characterized.[8] Herein we report the preparation and characterization of a kinetically stable formyl complex, **1**.

Of the two obvious methods for preparing formyl complexes, (a) migratory insertion of a metal carbonyl hydride in the presence of an external ligand such as CO[8] and (b) formylation of a nucleophilic saturated metal carbonyl, we chose the latter because the equilibrium in (a) apparently lies far to the left or the forward rate is imperceptibly slow (eq 1). Previously we had isolated acyl tetracarbonylferrates(0)[3] and found their rate of CO exchange to be very slow.[9] This result suggested that the corresponding formyl tetracarbonylferrate(0) **1** would be kinetically stable with respect to decarbonylation.

Treatment of $Na_2Fe(CO)_4$ with acetic formic anhydride[10] in THF under Ar at 25° cleanly afforded the desired formyl complex $(CO)_4Fe(CHO)^-$ (**1**) which was isolated as the $N(PPh_3)_2^+$ salt.[11] *Anal.* Calcd for $C_{41}H_{31}FeNO_5P_2$: C, 66.95; H, 4.25; N, 1.90. Found: C, 66.94; H, 4.47; N, 1.93.



$$HFe(CO)_4^- + CO \underset{}{\overset{(a)}{\rightleftharpoons}} \underset{\mathbf{1}}{H\overset{O}{\overset{\|}{C}}Fe(CO)_4^-} \xleftarrow[(b)]{H\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3} Fe(CO)_4^{2-} \quad (1)$$

The ir and cmr spectra of **1** closely resemble those of the analogous acyl derivatives $(CO)_4Fe(COR)^-$ (**2**).[12] In addition, the spectra of both **1** and **2** are markedly dependent on the nature of the cation and its state of solvation. The acyl and formyl frequencies in **1** and **2** are raised by 30 cm^{-1} in the ir and their acyl and formyl cmr resonances are shifted upfield by δ 18 and 16, respectively, upon changing the counterion from Na^+ to $N(PPh_3)_2^+$ (Table I). The addition of strongly coordinating solvents such as HMPA or crown ethers to THF solutions of the Na^+ salt of **1** and **2** cause shifts to values near those observed with the $N(PPh_3)_2^+$ counterion. The methyl cmr signal in **2** ($R = C_2H_5$) is insensitive to these changes ($\Delta\delta < 0.1$) exemplifying the small solvent shifts normally associated with cmr. Terminal carbonyls in **1** and **2** show smaller shifts in the ir (5–15 cm^{-1}) and slight cmr shifts ($\Delta\delta < 1$), in each case in the opposite direction from the acyl or formyl shifts.[12,13] These solvent- and cation-induced shifts strongly suggest ion pairing involving primarily association through the acyl or formyl oxygen.[14] Earlier we demonstrated the role of ion pairing in migratory insertion reactions leading to **2**.[17]

Table I. Ir and Cmr Spectra of $Z^+[(YCO)Fe(CO_4)]^-$

Solvent	Z^+	ν(YC=O), cm^{-1} Y = H	Y = CH_3	^{13}C nmr (δ TMS) Y = H	Y = C_2H_5
THF	Na^+	1577	1580	275.8	279.7
THF–HMPA	Na^+	1610	1610	257.6	260.2
THF	$N(PPh_3)_2^+$	1607	1609	260.1	261.5

Although similarities between **1** and **2** have been emphasized, there are important differences. Only the formyl complex **1** exhibits aldehydic ν_{CH} (2690 and 2540 cm^{-1}). The cmr resonance for the formyl carbon in **1** but not acyl carbons in **2** shows nuclear Overhauser enhancement with proton noise decoupling. With off-resonance decoupling the formyl carbon signal is split into a doublet by the aldehydic proton. The pmr spectrum of **1** exhibits a sharp singlet at very low fields (δ 14.95, TMS, in THF).[18]

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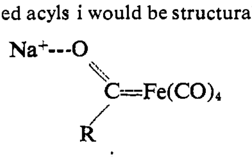
(12) See ref 3 for ir of **2**.

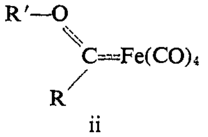
(13) For **1** in THF, Na^+ salt. Ir (ν_{FeCO}) 2018 (w), 1930 (s), 1902 (vs); cmr δ 220.2 (TMS).

(14) Tightly ion paired acyls i would be structurally similar to carbene



i

complexes[14] ii. Carbene complexes have characteristic cmr resonances



ii

at very low field (δ 362.3 for Me(MeO)CCr$(CO)_5$ for example).[15,16] The formyl and acyl frequencies in **1** and **2** are shifted in this direction under conditions favoring ion pairing.

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(18) In THF–HMPA this signal is shifted only slightly to δ 14.78.

Solutions of the formyl complex **1** slowly decompose to $HFe(CO)_4^-$ ($t_{1/2}$ (25°) $\geq$ 12 days (Na^+ salt, THF)) but in the solid state ($[N(PPh_3)_2]^+$ salt) there is no apparent decarbonylation after 13 days at 0.2 mm (25°)). Although the related acyl complexes **2** can be protonated forming aldehydes,[4] oxidized (O_2 + H_2O) affording carboxylic acids,[6] and alkylated yielding ketones,[5] the formyl complex reacts somewhat differently and is not synthetically useful. However, the reactions of the formyl complex have important mechanistic implications. Protonation of **1** afforded the expected formaldehyde (dimedone derivative). Reaction of **1** with O_2 resulted in an explosion upon acidification suggesting the formation of performic acid.[19] Alkylation of **1** with octyl iodide gave octane (75% isolated yield) but only a trace of nonanal—the product expected on the basis of our earlier ketone synthesis.[5,20] Apparently the neutral intermediate iron(II) complex $[(C_8H_{17})(CHO)Fe(CO)_4]$ loses CO and, following hydride migration to iron, reductively eliminates the octyl and hydride groups forming octane.[21]

These diverse experimental results may arise from differences in migratory insertion equilibria and/or from different tendencies of the pairs R, H; RCO, H; RCO, R′; and R, R′ to undergo reductive elimination. In no instance have we observed the reductive elimination of two σ-bonded alkyl groups—a reaction of enormous potential synthetic significance. Further studies are required to clarify these mechanisms.

Acknowledgment. We wish to thank the National Science Foundation, Grant No. GP20273X1, for financial support and Walter Siegl for helpful discussions.

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[19] Performic acid has been reported to explode on heating with metals: "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965, p 2642.

[20] Although $HFe(CO)_4^-$ gives octane when treated with octyl iodide, decarbonylation of **1** to the hydride is too slow to account for the formation of octane by this route.

[21] This neutral iron(II) complex should dissociate CO more easily than the anionic iron(0) formyl complex **1**.

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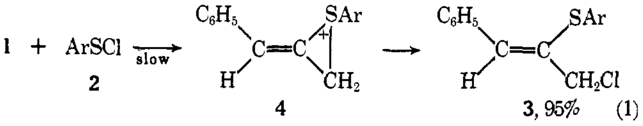
Received March 17, 1973

Orientation and Kinetic Secondary Isotope Effects in the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Phenylallene[1]

Sir:

Allenic compounds show a variety of regioreactivities in electrophilic addition reactions.[2] Phenylallene (**1**) was found to generally give a product of the terminal-bond addition, 2,3 adduct, through the central-carbon attack by an electrophile.[3] However, we have obtained evidence that it is formed in hydrochlorination[3a] and bromination[3b] through a primary electrophilic attack on the internal bond, 1,2 addition, followed by the allylic rearrangement. On the other hand, Jacobs, *et al.*,[4] showed that the allylic rearrangement could not be involved in the sulfenylation of an aliphatic allene. We have found that 2,4-dinitrobenzenesulfenyl chloride (**2**) adds to **1** to give a 2,3 adduct by a direct rate-determining addition to the terminal bond.

The addition of **2** to **1** has been investigated in glacial acetic acid. The product obtained at ~20° was predominantly the 2,3-adduct **3**. The yield was ~95% by nmr spectroscopy. Recrystallization from CCl_4 gave yellow needles in 64% yield, mp 118–119°. *Anal.* Calcd for $C_{15}H_{11}N_2O_4ClS$: C, 51.34; H, 3.16; N, 7.99; Cl, 10.11; S, 9.14. Found: C, 50.98; H, 3.10 N, 8.04; Cl, 10.10; S, 9.15. Nmr ($CDCl_3$): δ 4.44 (2 H, s, CH_2Cl), 7.46 (1 H, s, -CH=), 7.53 (5 H, m, C_6H_5), 7.73 (1 H, d, J = 9 Hz, 6-H of $C_6H_3(NO_2)_2$), 8.33 (1 H, dd, J = 9 Hz, 2.5 Hz, 5-H of $C_6H_3(NO_2)_2$), 9.13 (1 H, d, J = 2.5 Hz, 3-H of $C_6H_3(NO_2)_2$).



Ar = 2,4-dinitrophenyl

The adduct **3** was oxidized by H_2O_2–AcOH to the corresponding sulfoxide, mp 173–174°. Nmr ($CDCl_3$): δ 4.22 and 4.52 (2 H, 2d, J = 13 Hz, CH_2Cl), ~7.48 (5 H, m, C_6H_5), 7.83 (1 H, s, -CH=), ~8.73 (m) and 9.10 (d) (3 H, $C_6H_3(NO_2)_2$). The nmr spectrum of the sulfoxide in the presence of 0.65 mol equiv of the shift reagent, $Eu(C_{10}H_{10}F_2O_2)_3$, showed signals at δ 7.83 and ~8.27 (5 H, 2 m, C_6H_5), ~10.11 (m) and 10.68 (d) (3 H, $C_6H_3(NO_2)_2$), 11.08 (1 H, s, -CH=), and 15.78 and 23.86 (2 H, 2d, J = 13 Hz, CH_2Cl). The comparison of the effects of the shift reagent on the chemical shift of the olefinic proton with those observed for closely related compounds[5] confirmed that the olefinic proton is trans to the sulfinyl group. Hence, **3** can be assigned the structure as shown in eq 1.

Small amounts of the 1,2 adduct, $C_6H_5CHClC(SAr){=}CH_2$, and its rearranged product, $C_6H_5CCl{=}C(SAr)CH_3$, were also isolated. Neither of them was found to rearrange to **3**. This fact indicates that **3** is formed kinetically. Stereochemical purity of **3** obtained in the reaction also conforms to the assumption of its kinetically controlled formation.

Data obtained by the experiments on the kinetic secondary isotope effects are further evidence to substantiate the rate-determining 2,3 attack of sulfur forming an intermediate episulfonium ion. The second-order rate constants[6] measured at 30° are given in Table I for **1** and its deuterated derivatives. The large rate enhancement (k_H/k_D = 0.84) was observed by γ,γ dideuteration while the α deuteration had essentially no effect on the rate (k_H/k_D = 1.01).

The secondary deuterium isotope effects observed here can be taken as a direct indication of the predominant 2,3-bond attack by the sufenyl sulfur in the rate-

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[1] Part V of Electrophilic Additions to Dienes. For part IV, see K. Izawa, T. Okuyama, T. Sakagami, and T. Fueno, *J. Amer. Chem. Soc.*, submitted for publication.

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[6] The rate is first order in each reactant. Kinetic measurements have been made according to the method of Orr and Kharasch.[7]

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