tion of O_2^- with the resulting Fe^{II}-EDTA to form the peroxo complex which in turn decomposes to Fe^{III}-EDTA and H_2O_2. Finally, trace C of Figure 2 shows the rate and extent to which equimolar amounts of Fe^{III}-EDTA and H_2O_2 combine to form the peroxo complex. It should be noted that traces A and C converge as nearly equal amounts of total peroxide are present, while in experiment B the final absorbance value is less, consistent with the reduction of Fe^{III}-EDTA to Fe^{II}-EDTA by O_2^- to form O_2 resulting in a lower final concentration of H_2O_2. The results of Figure 2 are thus rationalized in terms of reactions 3-5.

$$\mathrm{Fe^{II}\text{-}EDTA + O_2^- \rightarrow [Fe^{III}\text{-}EDTA\text{-}O_2]^{3-}} \quad (3)$$

$$\mathrm{Fe^{III}\text{-}EDTA + O_2^- \rightarrow Fe^{II}\text{-}EDTA + O_2} \quad (4)$$

$$\mathrm{[Fe^{III}\text{-}EDTA\text{-}O_2]^{3-} \overset{H^+}{\rightleftarrows} Fe^{III}\text{-}EDTA + H_2O_2} \quad (5)$$

From a knowledge of the dead time of the stopped-flow instrument we estimate $k_3 \gtrsim 10^7\ M^{-1}\ s^{-1}$. The values of the other rate constants were estimated from experiments similar to those described in Figure 2 in which the rate of formation and breakdown of the peroxo complex was observed; estimates are $k_4 \sim 6 \times 10^3\ M^{-1}\ s^{-1}$, $k_5 \sim 1\ s^{-1}$, and $k_{-5} \sim 500\ M^{-1}\ s^{-1}$. Equations 3-5 describe a minimal scheme for the catalytic dismutation of superoxide by Fe-EDTA which is qualitatively and quantitatively consistent with all of our observations and which involves the well-known and relatively stable iron-peroxo complex as an obligatory intermediate. The details of this general scheme and its putative relationship to the mechanism of the iron-superoxide dismutase[16] are currently under investigation.

Reaction 3 bears considerable analogy to the oxidation of animopolycarboxylate complexes of several bivalent transition ions by halogens as studied by Woodruff and Margerum.[17] These authors observed that the oxidation of Fe^{II}-EDTA by Br_2 and I_2 proceeded at a rate on the order of $10^7\ M^{-1}\ s^{-1}$, and they suggested that this was determined by the rate at which the oxidant could enter the inner coordination sphere of the complex. This is formally a one-electron oxidative addition reaction as surveyed by Halpern.[18] Reaction 4 appears to be a direct one-electron reduction of Fe^{III}-EDTA; it is not known whether the O_2^- must enter the first coordination sphere or if an outer-sphere reaction occurs.

Acknowledgments. This work was supported by the U.S. Public Health Service, Grant GM 21519 (J.A.F.) and Grant GM 12176 (purchase of rapid scan instrumentation, R. H. Sands and J.A.F.), by the Petroleum Research Fund, administered by the American Chemical Society (J.T.G.), and by The University of Michigan (J.T.G.). G.J.M. is the recipient of a National Science Foundation Graduate Fellowship.

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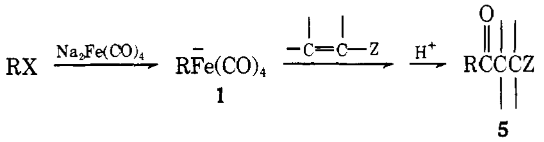
Hydroacylation of Michael Acceptors through Sequential Insertion Reactions of Organotetracarbonylferrates

Sir:

While reagents abound for the introduction of acyl anion equivalents via displacement and carbonyl addition reactions,[1] relatively few methods exist for the introduction of such units in a conjugate manner to Michael-type acceptors.[2] We now wish to report a new method for the direct hydroacylation of such acceptors.

We[3] and others[4] have previously shown that organotetracarbonylferrates, **1**, prepared in high yield through the alkylation of $Na_2Fe(CO)_4$ with ordinary halides and tosylates, undergo facile carbonyl insertion reactions in the presence of suitable ligands to give acylferrate complexes which in turn serve as acyl anion equivalents. We have also shown that in the presence of ethylene, **1** undergoes sequential migratory insertion reactions whereby the olefin is incorporated in the product.[5] We now find that **1** undergoes multiple insertion reactions with a variety of Michael-type acceptors (C=C—Z) giving β-ketoesters, ketones, and nitriles from common alkylating agents as shown in eq 1. Illustrations[6] of this transformation using simple alkyl halides are shown in Table I.

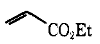
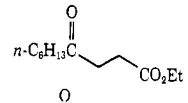
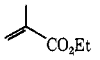
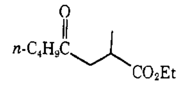
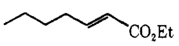
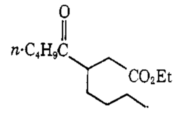
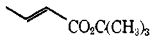
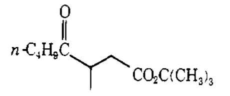
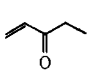
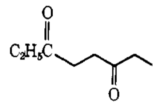
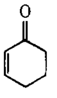
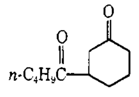
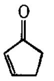
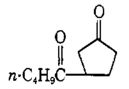
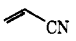
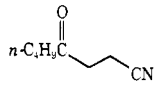
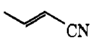
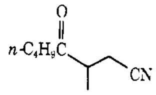
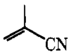
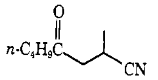


$$\mathrm{RX \xrightarrow{Na_2Fe(CO)_4} \underset{\mathbf{1}}{R\bar{F}e(CO)_4} \xrightarrow{-C{=}C{-}Z} \xrightarrow{H^+} \underset{\mathbf{5}}{RC(=O)C{-}C{-}Z}} \quad (1)$$

In the case of unsaturated esters and nitriles, the transformation may be performed in a single operation by the alkylation of $Na_2Fe(CO)_4$ in the presence of the desired acceptor followed by quenching with acetic acid.[6] The addition of unsaturated ketones, which are often incompatable with $Na_2Fe(CO)_4$ owing to polymerization or reduction, is deferred until formation of **1** is complete.

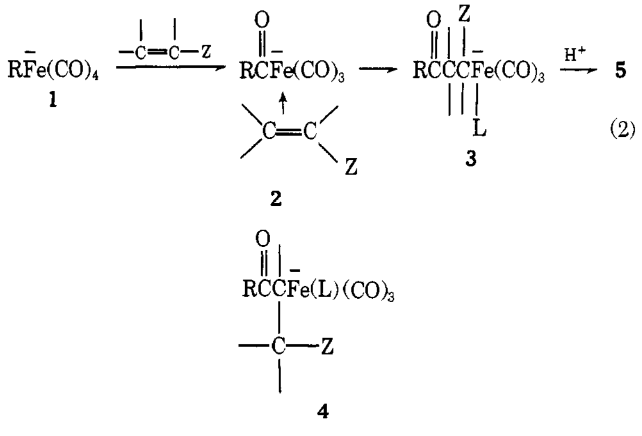
While anionic acyl nickel complexes derived from the addition of alkyllithium reagents to nickel tetracarbonyl have been reported to serve in a similar fashion as acyl donors with Michael acceptors,[2a] it is noteworthy that the potential synthetic utility of the presently reported method is enhanced by the use of the limiting and often more valuable component as the electrophile. Alkylations with $Na_2Fe(CO)_4$ have also been shown to have a wide tolerance for other functional groups.[4a]

Table I. Hydroacylation of Michael Acceptors

RX[a]	Acceptor	Mol equiv	Product[b]	% yield[c]
n-$C_6H_{13}Br$		2.5		92[d]
n-C_4H_9I		2.5		82
		2.5		(61)
		2.5		83
C_2H_5I		2.0[e]		58[f]
n-C_4H_9I		3.5[e]		94 (78)
		3.5[e]		92
		1.2		95 (82)
		1.2		87
		1.2		92 (80)

[a] Reactions typically employed 1.0 mmol of RX and $Na_2Fe(CO)_4$[3,10] from 1.4 mmol of $Fe(CO)_5$.[6] [b] All products were identified through spectra and either comparison with an authentic sample or perparation of a known derivative. Satisfactory elemental analyses were obtained for all new compounds. [c] Determined by GLC; isolated yields are in parentheses. [d] Yield dropped to 79% with 1.2 equiv of acceptor. [e] Acceptor added after alkylation step complete (approximately 10 min) and reaction time increased to 8 h. [f] In a similar experiment methyl vinyl ketone gave the corresponding product in only 20% yield.

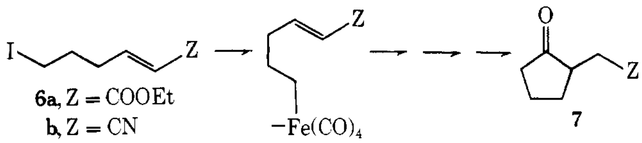
This transformation is believed to proceed through two sequential migratory insertion reactions as shown in eq 2. Migration of the alkyl group in **1** to a metal-bound carbonyl in the presence of the olefinic acceptor gives rise to an acylferrate complex **2** in which the acceptor has been incorporated into the coordination sphere of the metal. Preformed coordinatively saturated acyl ferrates[7] ($RCOFe(CO)_4^-$, $RCOFe(Ph_3P)(CO)_3^-$) do not subsequently react with added olefin indicating that, unlike the labile acyl nickel analogues, the olefin does not gain access to the metal through ligand exchange.[2a] Insertion products are not obtained when **1** is treated with acceptors which are trisubstituted olefins but instead reduction products, RH, arising from the protonation of **1** are observed.[3] This suggests that steric factors play an important role in the initial carbonyl insertion step. Migration of the acyl unit in **2** to the terminus of the bound olefin then gives **3**. The coordination vacancy created by this second migration may be filled by either intramolecular coordination of a functional group within the incorporated acceptor or through complexation with a second olefin (L = -C=CZ). The quantities of acceptors needed to obtain the optimum yields shown in Table I suggest the latter in the case of esters and ketones and the former in the case of nitriles.



(2)

Complex **3** is thought to rearrange to a new σ complex, represented here as **4**,[8] when Z = COOR or CN. The absence of a normal ketone carbonyl band and the presence of a band at 1570 cm^{-1} in the IR spectra of solutions where acrylonitrile served as acceptor[9] suggests that the same $\beta \rightarrow \alpha$ metallocarbonyl rearrangement previously observed in ethylene insertions[5] also operates in these systems. A normal ketone band at 1710 cm^{-1} appears only after addition of the proton source and treatment of unquenched solutions with methyl iodide gives only 3-methyl-4-ketonitrile and ester.

Finally, we have investigated the possibility of the formation of carbocycles through the use of substrates which can undergo intramolecular insertions. Treatment of **6** with $Na_2Fe(CO)_4$ in THF gave after protonation cyclopentanone derivatives **7a** and **7b** in 85 and 82% yield, respectively (eq 3). We are currently investigating other applications of this novel approach to ring construction.



6a, Z = COOEt
b, Z = CN

7

(3)

Acknowledgments. We thank the Research Corporation and the Washington State University Research Committee for support of this research.

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(1) For an excellent review of nucleophilic acylation see O. W. Lever, Jr., *Tetrahedron,* **32,** 1943 (1976).

(2) Direct methods include the use of (a) acyl nickel complexes, E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91,** 4926 (1969); (b) photolytic acylation, D. R. Hicks, R. C. Anderson, and B. Fraser-Reid, *Synth. Commun.*, **6,** 417 (1976); and (c) aromatic cyanohydrins, H. Stetter, M. Schreckenberg, and K. Wiemann, *Chem. Ber.*, **109,** 541 (1976). Less direct methods include the use of (d) protected cyanohydrins, G. Stork and L. A. Maldonado, *J. Am. Chem. Soc.*, **96,** 5272 (1974); (e) nitroalkanes, J. E. McMurry and J. Melton, *J. Org. Chem.*, **38,** 4367 (1973); (f) thioacetal derivatives, J. L. Herrman, J. E. Richman, and R. L. Schlessinger, *Tetrahedron Lett.*, 3271 (1973); 2599 (1973); functionalized cuprates of (g) vinyl ethers, R. K. Boeckman, Jr., K. J. Bruza, J. E. Baldwin, and O. W. Lever, Jr., *J. Chem. Soc., Chem. Commun.*, 519 (1975); C. G. Chavdarian and C. H. Heathcock, *J. Am. Chem. Soc.*, **97,** 3822, (1975); (h) vinyl silanes, R. K. Boeckman, Jr., and K. J. Bruza, *Tetrahedron Lett.*, 3365 (1974); and (i) phenylthioacetals, T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94,** 8641 (1972).

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(5) M. P. Cooke, Jr., and R. M. Parlman, *J. Am. Chem. Soc.*, **97,** 6863 (1975).

(6) A typical example is shown in the preparation of ethyl 4-ketooctanoate from ethyl acrylate and butyl iodide. A slurry of $Na_2Fe(CO)_4$ in 20 mL of dry THF was prepared by reduction of 185 μL (1.4 mmol) of $Fe(CO)_5$ with 2 mL of 1% sodium amalgam.[3] The vessel was purged with N_2 to remove CO, cooled via an ice bath, and treated with 250 μL (2.5 mmol) of ethyl acrylate and then with 120 μL (1 mmol) of 1-iodobutane. The N_2 atmosphere was maintained throughout. The mixture was stirred at room temperature for 4 h, whereupon it was treated with 0.12 mL of HOAc, stirred for 5 min, poured into water and twice extracted with ether. The concentrated extracts were filtered through a short plug of Al_2O_3 (neutral) to remove iron residues. Bulb-to-bulb distillation gave 156 mg (80%) of $C_4H_9COCH_2CH_2COOEt$.

(7) Acylferrates are most conveniently prepared by the addition of CO or Ph_3P to **1**,[3] the addition of acid chlorides to $Na_2Fe(CO)_4$,[4] or by the addition of alkyllithium reagents to $Fe(CO)_5$: W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94,** 2516 (1972).

(8) A structure involving σ bonding through oxygen is also plausible but a π-enolate complex seems unlikely insomuch as the required evolution of CO for π participation is not observed.

(9) A similar band is observed at 1585 cm^{-1} when ethyl acrylate is employed.

(10) Similar results were obtained with commercial $Na_2Fe(CO)_4$ (Ventron Corp.).

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Ditertiary Phosphines as Monodentate Ligands in Transition Metal Carbonyl Complexes

Sir:

Early syntheses of group 6 transition metal carbonyl complexes containing tetraphenyldiphosphinoethane typically involved thermal or photolytic methods, and under these harsh conditions only chelated complexes were isolated. The synthesis of a tungsten carbonyl complex which contains $Ph_2PCH_2CH_2PPh_2$ as a monodentate ligand was reported in 1972 and was achieved by displacing aniline of $(OC)_5WNH_2Ph$ with the phosphine at room temperature.[1]

$$(OC)_5WNH_2Ph + PPh_2CH_2CH_2PPh_2 \rightarrow (OC)_5WPPh_2CH_2CH_2PPh_2 + PhNH_2$$

This reaction has been employed subsequently in the synthesis of a number of carbonyl complexes which contain both symmetrical and unsymmetrical ditertiary phosphines.[2]

The reaction of a pentacarbonylhalo metal anion with a ditertiary phosphine in the presence of trialkyloxonium tetrafluoroborate has been reported as an alternate method for the preparation of complexes of this type.[3]

$$(OC)_5MX^- + PPh_2CH_2CH_2PPh_2 + (R_3O)(BF_4) \rightarrow (OC)_5MPPh_2CH_2CH_2PPh_2 + RX + R_2O + BF_4^-$$

Careful evaluation of the foregoing approaches shows that neither is satisfactory. In each reaction substantial quantities of dimetallic decacarbonyl, $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$, and unreacted free ligand must be separated from the desired product. The formation of the dimetallic product is inevitable since $(OC)_5WPPh_2CH_2CH_2PPh_2$ is itself a good ligand and competes well for available metal sites.[4] An additional disadvantage of both methods is that there is no means of controlling which end of an unsymmetrical ditertiary phosphine will coordinate to the metal. Further, since alkyloxonium salts are good alkylating agents, any excess of this reagent quaternizes the free phosphine.

It was desirable, therefore, to find a method for coordinating one end of a polytertiary phosphine to a metal in high yield or for converting a monodentate ligand of a transition metal complex into a polydentate ligand thereby accomplishing the same thing. We have explored the latter approach by investigating the reaction of diphenylphosphine with pentacarbonyldiphenylvinylphosphinetungsten(0).

The addition of secondary phosphines to vinylphosphines has been studied previously by several groups. Grim and coworkers have used the addition of lithium alkyl and aryl phosphides to vinylphosphines for the preparation of unsymmetrical ditertiary phosphines.[2] King et al. have shown that the addition of secondary phosphines to vinylphosphines is base catalyzed and have prepared a number of polyphosphines by this method.[5] More recently Meek and coworkers have determined that these addition reactions are free radical catalyzed and applicable to a wide range of systems.[6]

We have determined that these approaches to the synthesis of polytertiary phosphines also are effective when a transition metal carbonyl complex which contains a vinylphosphine is employed as a reactant (Scheme I). The reaction of a THF solution of lithium diphenylphosphide with $(OC)_5WPPh_2CH{=}CH_2$ (mp 64-65 °C) followed by hydrolysis is the least reliable of the three reactions and gives an average yield of 12% (based on eight reactions). Stoichiometric quantities of diphenylphosphine react with

Scheme I