

manganate) afforded the carboxylic acid, and subsequent esterification (diazomethane) and then methoxymethylation [methoxymethyl chloride (MOMCl) and diisopropylethylamine] produced the protected ester **6** [92%, oil, $[\alpha]_D^{20} + 11^\circ$ (CHCl₃)]. The N-blocking group was first removed by reduction to give the γ -lactam with cyclization and the silyl group removed (tetrabutylammonium fluoride) to yield the diol **7** [93%, oil, $[\alpha]_D^{20} - 11^\circ$ (CHCl₃)]. Selective methoxymethylation of **7** (1.5 equiv of MOMCl) gave a mixture of trimethoxymethyl derivatives **8** [51%, oil, $[\alpha]_D^{20} + 1.0^\circ$ (CHCl₃)] and **9** [34%, oil, $[\alpha]_D^{20} - 52^\circ$ (CHCl₃)]. The major product **8** was found to be converted to the desired mesylate **10** [93%, oil, $[\alpha]_D^{20} - 12^\circ$ (CHCl₃)], the structure of which was supported by the ¹H NMR spectrum. The minor product **9** could be effectively recycled to **7** by selective hydrolysis (80%, a catalytic amount of camphorsulfonic acid in methanol). Treatment of **10** with 4.5 equiv of borane-methyl sulfide¹⁰ to give the pyrrolizidine skeleton with intramolecular S_N2 displacement of the intermediary pyrrolidine derivative, followed by cleavage of MOM protecting group (0.5 N HCl) afforded (-)-rosmarinic acid [**1**: 54%, $[\alpha]_D^{21} - 121^\circ$ (EtOH); picrate (needles from EtOH): mp 175 °C, $[\alpha]_D^{21} - 60^\circ$ (MeOH)] identical in all respects with that obtained from natural sources.^{3c,11}

With the use of similar strategy, the stereoselective synthesis of (-)-isoretronecanol (**2**) was accomplished as outlined in Scheme II, starting again from the key intermediate **3**. The ditrityl derivative **11**, obtained from **3** [trityl (Tr) chloride, pyridine, 70 °C, 26 h], was subjected to Wittig reaction [3 equiv of (methoxycarbonyl)methylenetriphenylphosphorane] to give the unsaturated ester **12** [85%, mp 210 °C, $[\alpha]_D^{29} - 14^\circ$ (CHCl₃)]. Reduction of **12** gave the γ -lactam, which was in turn treated with Amberlyst 15 resin (H-type) in methanol to remove the trityl group and then mesylated to afford the dimesylate **13** [80%, oil, $[\alpha]_D^{30} + 1.5^\circ$ (MeOH)]. Borane reduction of **13** to give the monomesyl pyrrolizidine derivative, followed by treatment with 3.5 equiv of potassium acetate gave the monoacetate **14** (90%), which was deacetylated by methanolic ammonia to afford (-)-7-deoxyrosmarinic acid [**15**: 84%, $[\alpha]_D^{25} - 115^\circ$ (EtOH); picronate (needles from EtOH): mp 206 °C].¹² On the other hand, by the standard procedures,¹² **14** was converted to (-)-isoretronecanol [**2**: 74%, $[\alpha]_D^{20} - 91^\circ$ (EtOH); picrate (needles from EtOH): mp 199 °C, $[\alpha]_D^{20} - 29^\circ$ (MeOH)].¹³ The synthetic products **15** and **2** were identical in all respects with (-)-7-deoxyrosmarinic acid and (-)-isoretronecanol obtained from natural sources, completing the stereoselective synthesis of natural pyrrolizidine mono- (**2**), di- (**15**), and triol (**1**).

Acknowledgment. We are grateful to the Institute of Microbial Chemistry for the generous support of our program and thank Y. Kanemura for his technical assistance. We also are indebted to Professors S. E. Drewes,^{3c} L. W. Smith,^{11,13} H. Kakisawa,¹³ and H. W. Pinnick¹³ for kindly providing the authentic samples and/or the ¹H NMR spectra.

Registry No. **1**, 520-61-6; **2**, 526-63-6; **3**, 85781-28-8; **4**, 85781-29-9; **5**, 85781-30-2; **6**, 85781-31-3; **7**, 85781-32-4; **8**, 85781-33-5; **9**, 85781-34-6; **10**, 85781-35-7; **11**, 85781-36-8; **12**, 85781-37-9; **13**, 85781-38-0; **14**, 85781-39-1; **15**, 85848-68-6; TBDMS, 18162-48-6; TrCl, 76-83-5; (methoxycarbonyl)methylenetriphenylphosphorane, 2605-67-6; allyl bromide, 106-95-6; benzyl *S*-(4,6-dimethylpyrimidin-2-yl)thiocarbonate, 42116-21-2; methyl 2-amino-2,3-dideoxy-3-*c*-formyl- α -D-xylofuranoside-3'-*R*-5-hemiacetal, 84034-70-8.

Supplementary Material Available: Characterization data for compounds **1**, **2**, **5**, **7-10**, and **15** (9 pages). Ordering information is given on any current masthead page.

(10) Ohfuné, Y.; Tomita, M. *J. Am. Chem. Soc.* **1982**, *104*, 3511-3513.

(11) The ¹H NMR of the natural product was provided by Prof. L. W. Smith, CSIRO, Australia.

(12) Aasen, A. J.; Culvenor, C. C. J. *J. Org. Chem.* **1969**, *34*, 4143-4147.

(13) Authentic samples of the natural and racemic products were provided by Prof. L. W. Smith, CSIRO, Australia and Prof. H. Kakisawa, The University of Tsukuba, respectively, and the ¹H NMR spectra were also provided by them and Prof. H. W. Pinnick, The University of Georgia.

Do Complexes of Composition MnLX₂ (L = Tertiary Phosphine) Really Exist? Do They Reversibly Bind Dioxygen?

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McAuliffe and co-workers have reported the preparation and partial characterization of a series of manganese(II) complexes of the general formula MnLX₂ (L = tertiary phosphine, X = anion) that they claim resemble hemoglobin and myoglobin in that the complexes reversibly interact with dioxygen and other small molecules.¹ Such compounds would be expected to have extensive industrial application in the purification of gas streams, for oxygen storage devices, and possibly even as catalysts for important oxidation reactions. However, Green and co-workers have cast doubt on the early work of McAuliffe by claiming that they were not able to prepare the complexes and observe reversible interaction with dioxygen.² In fact they suggest that the dramatic color changes that the MnX₂/L system undergoes upon exposure to dioxygen are due to a transient Mn(III) species that ultimately decomposes by oxidizing the tertiary phosphine present; they further postulate that color changes upon dioxygen uptake would continue as long as tertiary phosphines remain present. McAuliffe has recently rebutted the claims of Green and co-workers by emphasizing the need for preparing the MnLX₂ complexes under "absolutely anhydrous" conditions and by ensuring that excess phosphine is not present during the dioxygen uptake experiments.³ In these laboratories work has been undertaken aimed toward answering the questions that have been raised concerning the existence of the MnLX₂ complexes and the nature of the interaction of the complexes, if they do exist, with dioxygen. The primary approach here has been to use infrared spectroscopy as a probe in investigating the possible binding of dioxygen to the alleged complexes.

A considerable amount of effort was expended here in attempting to isolate the MnLX₂ complexes by the procedures used by McAuliffe et al. under anhydrous conditions in the absence of oxygen. Complexes could be produced that did reversibly interact with dioxygen, did undergo the marked color changes reported earlier,^{1,2} and did provide elemental analyses in accord with the formula MnLX₂; however, even the most meticulous sample deposition and pellet preparation procedures under inert, anhydrous conditions always provided solid-state samples that exhibited infrared bands near 3500-3450, 1600, and 550 cm⁻¹ attributable to moisture contamination. Such samples did indeed uptake some dioxygen (not quantitative) and change color reversibly, but any cycling of intensity of infrared bands upon exposure/evacuation cycles bore a direct relationship to the intensities of the "water bands" such that no definitive conclusions could be made. It was apparent that the samples were undergoing decomposition to phosphine oxide and/or the MnL'X₂ (L' = phosphine oxide) complexes as was evidenced by intense infrared bands growing with time at ca. 1150 cm⁻¹. Ultimately these complexes were no longer active in dioxygen uptake or color change.

It was decided that a new approach for preparation of the infrared samples was necessary. After considerable work, we have developed a means of preparing MnLX₂ complexes in an infrared

(1) McAuliffe, C. A.; Al-Khateeb, H.; Jones, M. H.; Levason, W.; Minten, K.; McCullough, F. P. *J. Chem. Soc., Chem. Commun.* **1979**, 736. Hosseiny, A.; McAuliffe, C. A.; Minten, K.; Parrott, M. J.; Pritchard, R.; Tames, J. *Inorg. Chim. Acta* **1980**, *39*, 227. Hosseiny, A.; Mackie, A. G.; McAuliffe, C. A.; Minten, K. *Ibid.* **1981**, *49*, 99. Barber, M.; Bordoli, R. S.; Hosseiny, A.; Minten, K.; Perkin, C. R.; Sedgwick, R. D.; McAuliffe, C. A. *Ibid.* **1980**, *45*, L89. McAuliffe, C. A.; Al-Khateeb, H. *Ibid.* **1980**, *45*, L195.

(2) Brown, R. M.; Bull, R. E.; Green, M. L. H.; Grebenik, P. D.; Martin-Polo, J. J.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *201*, 437.

(3) McAuliffe, C. A. *J. Organomet. Chem.* **1982**, *228*, 255.

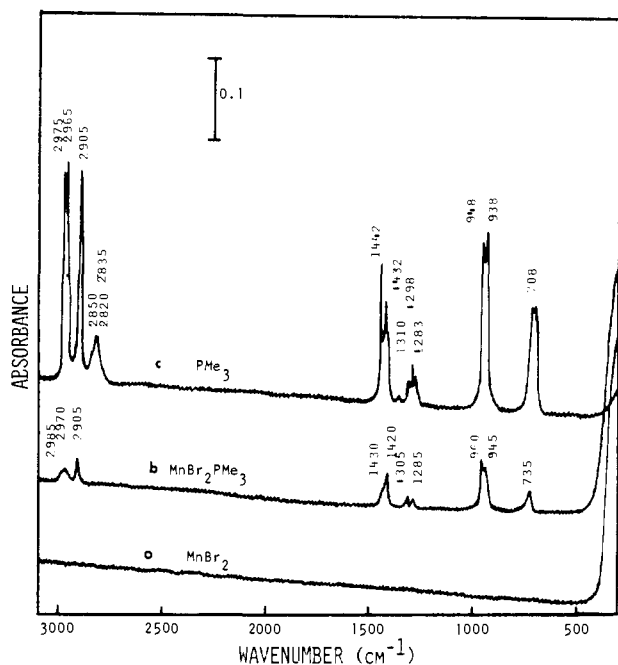


Figure 1. Infrared spectra of MnBr_2 , $\text{MnBr}_2\text{PMe}_3$, and PMe_3 : (a) film of MnBr_2 (0.5 mg cm^{-2}) on KBr prepared by sublimation at 10^{-5} torr and 600°C followed by evacuation at 10^{-6} torr for 2 h at 200°C ; (b) film in a exposed to PMe_3 gas at its vapor pressure for 1 h followed by evacuation for 30 min; (c) 10.1 torr of PMe_3 gas.

cell under completely anhydrous and inert conditions.⁴ Briefly, a manganese(II) salt such as MnBr_2 is either sublimed or sprayed in an anhydrous solvent onto a KBr infrared cell window. This window containing a film of MnBr_2 is then placed in an infrared cell designed here. The cell is attached to a clean vacuum system and evacuated while heating (to ca. 200°C) at ca. 10^{-6} torr. This process is continued until all infrared bands attributable to water have vanished. At this time the film of MnBr_2 is exposed to anhydrous tertiary phosphine vapor from a reservoir attached to the vacuum system. Under these conditions the complex MnLX_2 forms readily as a film on the infrared window. Then the cell is evacuated for several hours at ca. 10^{-5} torr to remove all traces of "excess phosphine". The resulting complexes may then be exposed to dry oxygen (Matheson UHP usually at 100 torr) at various exposure times followed by evacuation with infrared spectra (Perkin-Elmer 580) being monitored before and after evacuation.

Figure 1 shows the infrared spectra in the $500\text{--}4000\text{-cm}^{-1}$ region for the anhydrous MnBr_2 film, the $\text{MnBr}_2\text{PMe}_3$ film, and free PMe_3 vapor. It is obvious that the spectra for PMe_3 and for what is presumably $\text{MnBr}_2\text{PMe}_3$ are substantially different, indicating most probably that chemical reaction has occurred. In other experiments $\text{MnBr}_2\text{PMe}_3$ has been driven to $\text{MnBr}_2\text{OPMe}_3$ by lengthy exposure to oxygen and mild heating. Comparison of the precise weights of the MnBr_2 film with the final oxide film indicates that the stoichiometry is as indicated.⁵

Figure 2 shows the infrared spectra in the $300\text{--}1500\text{-cm}^{-1}$ region for the complex (a), the dioxygen adduct (b), an oxide complex (c), and free OPMe_3 sublimed onto a KBr window (d). Again the considerable differences in spectra c and d indicate that an authentic $\text{MnBr}_2\text{OPMe}_3$ complex has been formed upon reaction of MnBr_2 and OPMe_3 . Comparison of spectra a and b indicates that new bands at 409, 570, 755, 862, 1060, and 1132 cm^{-1} have developed upon exposure to dioxygen. The bands near 400, 755,

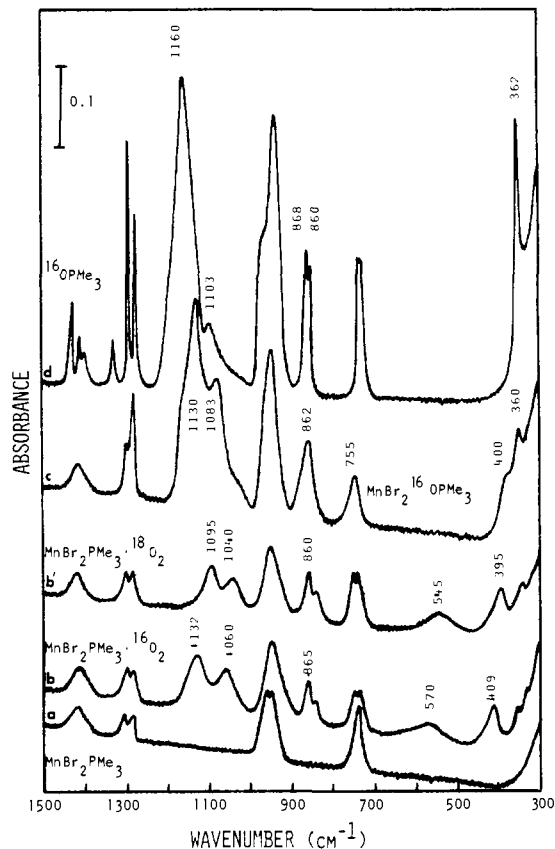


Figure 2. Infrared spectra of $\text{MnBr}_2\text{PMe}_3$, $\text{MnBr}_2\text{PMe}_3\cdot\text{O}_2$, $\text{MnBr}_2\text{OPMe}_3$, and OPMe_3 : (a) complex film prepared as in Figure 1b; (b) following exposure to 100 torr of $^{16}\text{O}_2$ for 5 h; (b') a second complex film following exposure to 100 torr of $^{18}\text{O}_2$ for 30 min; (c) MnBr_2 film exposed to OPMe_3 for 13 h at room temperature followed by evacuation for 2 h; (d) OPMe_3 sublimed onto KBr held at -110°C followed by evacuation at 35°C for 12 min.

and 862 cm^{-1} can clearly be assigned to the phosphine oxide complex which has begun to form. A portion of the band at 1132 cm^{-1} can also be assigned to the phosphine oxide complex. However, the 570- and 1132-cm^{-1} bands do diminish upon heating and evacuation in conjunction with a color change (blue \rightarrow off-white); the band near 1130 cm^{-1} grows again as the final oxide state is approached. Thus a portion of the band at 1132 cm^{-1} must be due to the dioxygen complex. This band shifts to 1095 cm^{-1} upon exposure of $\text{MnBr}_2\text{PMe}_3$ to $^{18}\text{O}_2$. It is well-known that for dioxygen complexes, a band in the $1100\text{--}1200\text{-cm}^{-1}$ region is most representative of an O-O stretch for a dioxygen species bonded in an end-on bent configuration.⁶⁻⁹ We suggest that the dioxygen is present as a superoxide species that would have manganese in a III oxidation state, thus providing the chromophore. A similar suggestion has been made for the manganese phthalocyanine-dioxygen adduct.⁹ The 570-cm^{-1} band, which shifts to 545 cm^{-1} upon $^{18}\text{O}_2$ exposure, would then be assigned to the Mn-O stretch in that superoxide species. The 1060-cm^{-1} band disappears upon heating before complete breakdown to $\text{MnBr}_2\text{OPMe}_3$ occurs (a spectrum nearly identical with that in c is obtained upon driving the sample represented by b to its inactive oxide form). We see a similar band near 1060 cm^{-1} for a gaseous mixture of PMe_3 and O_2 , although such a band is not apparent in the spectrum for OPMe_3 (see d). Work is in progress to identify the new species

(4) Complete details will be published in due course.

(5) The films on the KBr plate were difficult to weigh accurately, but 0.2990 g ($1.392 \times 10^{-3} \text{ mol}$) of MnBr_2 was converted to 0.4197 g ($1.368 \times 10^{-3} \text{ mol}$) of $\text{MnBr}_2\text{OPMe}_3$ in a sealed tube by heating $\text{MnBr}_2\text{PMe}_3$ in the presence of oxygen until the blue color disappeared; all weighings were made in a drybox. Anal. Calcd (Atlantic Microlab, Inc.) for $\text{MnBr}_2\text{OPMe}_3$: C, 11.74; H, 2.96; Br, 52.08. Found: C, 11.81; H, 2.96; Br, 51.99.

(6) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139 and references therein.

(7) Jones, R. D.; Budge, J. R.; Ellis, P. E.; Linard, J. E.; Summerville, D. A.; Basolo, F. *J. Organomet. Chem.* **1979**, *181*, 151.

(8) Suzuki, M.; Ishiguro, T.; Kozuka, M.; Nakamoto, K. *Inorg. Chem.* **1981**, *20*, 1993.

(9) Lever, A. B. P.; Wilshire, J. P.; Quan, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 3668; *Inorg. Chem.* **1981**, *20*, 761.

causing this band at 1060 cm^{-1} .

To summarize our preliminary observations on the $\text{MnBr}_2\text{PMe}_3$ system: (1) the complex does exist in the solid state in accord with claims by McAuliffe; (2) the dioxygen is present as a superoxide species in the solid state leaving Mn with a III oxidation state as claimed by Green; (3) although reversible oxygenation/evacuation cycling has been reported for some complexes,¹ this process is very slow if present at all in the solid state for the $\text{MnBr}_2\text{PMe}_3\cdot\text{O}_2$ complex and is accompanied by slow irreversible transformation to the inactive phosphine oxide complex. We have learned that the relative rates of the competing process of reversible interaction with dioxygen and irreversible formation of a phosphine oxide complex for MnLX_2 complexes in the solid state are highly dependent on the nature of the phosphine employed.⁴

Acknowledgment. We are grateful to the Research Corp., the National Science Foundation through Grant CHE-7920825, and the Auburn University Energy Grant-in-Aid program for partial support for this work.

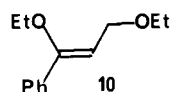
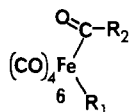
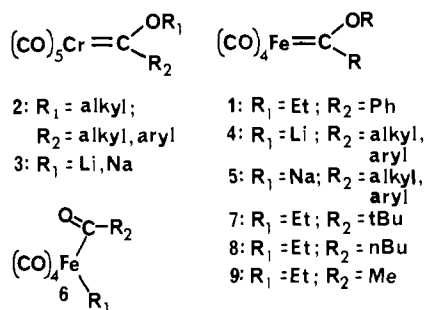
Control over Site of Alkylation in Iron Acylate Complexes: General Preparation and Reactions of Alkylidene-Iron Tetracarbonyl Complexes

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Fischer-type carbene metal complexes¹ of iron (e.g., **1**) have



been relatively inaccessible,²⁻⁴ and little information on the pattern

(1) For reviews, see: (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1-32. (c) Fischer, E. O. *Rev. Pure Appl. Chem.* **1972**, *30*, 353. (d) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651.

(2) Complexes of type **1** have been prepared by photochemical exchange of a CO ligand in $\text{Fe}(\text{CO})_5$ with an alkylidene ligand in a molybdenum complex: (a) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162-172. (b) Fischer, E. O.; Beck, H. J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72-74.

(3) Special examples of Fischer-type carbene complexes of iron are known: (a) Nakatsu, K.; Mitsudo, T.; Nakanishi, H.; Watanabe, Y.; Takegami, Y. *Chem. Lett.* **1977**, 1447-1448. (b) Petz, W.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 934-935. (c) Darenbourg, D. J.; Darenbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691-1694. (d) Petz, W.; Jonas, W. *J. Organomet. Chem.* **1976**, *120*, 423-432.

(4) Systematic attempts at O-alkylation of tetracarbonyliron acylate anions were generally unsuccessful. In certain special cases, reaction of trimethyl-oxonium fluoroborate in dichloromethane gave the desired methoxy-alkylidene-iron species.⁵ In a study concerning several aspects of the reaction of iron acylate anions with alkylating agents, with emphasis on (phosphine)tricarboxyliron acylates, H. Conder and M. Darenbourg considered the effect of leaving group on the efficiency of O-alkylation.⁶ This work showed that complexes in the series $\text{L}(\text{CO})_3\text{Fe}=\text{C}(\text{OEt})\text{Ph}$ could be prepared where L = various phosphines using triethylxonium fluoroborate and methyl fluorosulfonate; the parent compound with L = CO appears as an entry in a table without experimental detail. No alkyl-substituted alkylidene ligands were prepared.

Table I. Reaction of Iron Acylate Salts with Alkylating Agents

$$(\text{CO})_4\text{Fe}=\text{C} \begin{array}{l} \text{O}^- \text{M}^+ \\ \text{Ph} \end{array} \xrightarrow[\text{(b) FeCl}_3]{\text{(a) R-X}} \text{PhCO}_2\text{R} + \text{PhCOR}$$

entry	M^+	R-X	solvent	A		B	
				yield, ^a %	ratio A:B	yield, ^a %	ratio A:B
1	Li	EtOSO ₂ F	ether/HMPA (4:1) ^b	80	89:11		
2	Li	EtOSO ₂ F	ether	70	24:76		
3	NMe ₄ ^c	EtOSO ₂ F	CH ₂ Cl ₂	78	64:36		
4	Li	EtOSO ₂ F	CH ₂ Cl ₂	57	16:84		
5	Li	MeOSO ₂ F	ether/HMPA (4:1)	79	14:86		
6	NMe ₄ ^c	MeOSO ₂ F	CH ₂ Cl ₂	61	10:90		
7	Li	EtOSO ₂ tol	THF/HMPA (1:1) ^d	20	90:10		
8	Li	EtI	THF/HMPA (1:1) ^e	53	0:100		

^a The yields were determined by quantitative GLPC analysis using standard samples of the products for calibration. ^b The reagents were mixed at -78 °C and stirred for 4 h and then allowed to warm to 25 °C over 2.0 h. ^c The ammonium salt was prepared by metathesis with tetramethylammonium bromide (see ref 10). ^d Heated at 65 °C/18 h. ^e 25 °C/24 h.

of reactivity has been reported.⁷ The analogous chromium complexes (**2**) are well-known, from alkylation of acylate salts (**3**), and show reactivity of significant potential in organic synthesis.^{8,9}

We were drawn to consider the iron analogue **1** for several reasons. The iron acylate salts (e.g., **4** and **5**) can be prepared by reaction of organolithium¹⁰ or organomagnesium derivatives¹¹ with $\text{Fe}(\text{CO})_5$, by reaction of carboxylic acid chlorides with tetracarbonyliron(II) dianion,¹² and by addition of an alkyl halide to the dianion followed by migratory insertion of CO.^{12,13} The tetracarbonyliron(II) dianion is readily available and relatively easy to handle.¹² However, alkylation of iron acylate salts (**4** and **5**) generally leads not to alkylidene complexes (i.e., **1**) but instead to alkylation at iron (to give **6**) and subsequent coupling to form unsymmetrical ketones (Collman's reaction).^{4,12}

We analyzed the problem using the hard-soft acid-base picture, which serves to rationalize O- vs. C-alkylation in enolate anions.¹⁴

(5) In special cases, the alkylation of analogues of **5** has been successful: Fischer, E. O.; Beck, H. J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

(6) Condon, H. L.; Darenbourg, M. Y. *Inorg. Chem.* **1974**, *13*, 506-511.

(7) We are aware of no systematic study or isolated example pertaining to the reactivity pattern of complex **1** nor of the previously more accessible analogue with a phosphine ligand replacing CO.⁵

(8) (a) For a review, see: Casey, C. P. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, pp 190-234. (b) An extensive study of reactions of **2** with alkynes has been initiated by K. H. Dötz and co-workers. For a recent paper and leading references, see: Dötz, K. H.; Pruski, I.; Mühlemeier, J. *Chem. Ber.* **1982**, *115*, 1278-1285. For a recent application in β -lactam synthesis, see: McGuire, M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538-5540.

(9) An obvious alternate preparation of **3** from reaction of pentacarbonylchromium(II) dianion with a carboxylic acid chloride has not been reported. We studied this possibility using benzoyl chloride and $\text{Cr}(\text{CO})_5^{2-}$, generated by several different procedures: (a) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79. (b) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7825. (c) Maher, J. M. PhD Thesis, Harvard University, 1981. We thank Dr. Maher for this procedure: (d) Maher, J. M.; Beatty, R. P.; Cooper, J. M. *Organometallics* **1982**, *1*, 215.

Under the best conditions, the salt (**3**, $\text{R}_1 = \text{Na}$; $\text{R}_2 = \text{Ph}$) was obtained and methylated to give **2** ($\text{R}_1 = \text{Me}$; $\text{R}_2 = \text{Ph}$) in 50% yield, using $\text{Cr}(\text{CO})_5^{2-}$ from reduction of $\text{Cr}(\text{CO})_6$ with sodium in liquid ammonia. Rigorous air-free work is necessary to minimize the formation of polynuclear anionic complexes. (10) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *23*, 215.

(11) For a recent example and leading references, see: Yamashita, M.; Miyoshi, K.; Nakazono, Y.; Suemitsu, R. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1663-1664.

(12) For a review, see: Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342-356.

(13) Collman, J. P.; Finke, R. G.; Cawsi, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515-2526.

(14) HSAB theory successfully correlates trends in the effect of leaving group on C- vs. O-alkylation of enolate anions: Pearson, R. G.; Songstad, J. *J. Org. Chem.* **1967**, *34*, 2899; *J. Am. Chem. Soc.* **1967**, *39*, 1827. For a general discussion of factors influencing O- vs. C-alkylation, see: House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: New York, 1972; pp 522-529.