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# α-Iminoacyl Ligands in Carbonylmetalates

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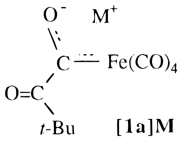
*Summary: Nucleophilic addition of lithium aldimine t-BuN═C(t-Bu)Li to Fe(CO)₅, Mn₂(CO)₁₀, and Cr(CO)₆ affords the corresponding α-iminoacyl carbonylmetalates characterized by NMR and IR spectroscopy. Reaction of these carbonylmetalates with Me₃OBF₄ results in methylation of the acyl oxygen atom.*

## Introduction

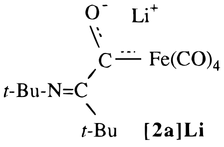
Since the discovery of the first Fischer carbene complexes,[1] considerable attention has been devoted to the reactivity of the metal−carbene bond and, more recently, to that of adjacent substituents.[2] Reactivity studies have particularly shown α,*β*-unsaturated carbene complexes to have potential in a number of reactions.[2,3]

Alkylation of lithium (acyl)carbonylmetalates [R(COLi)M(CO)$_n$] (**1**) is the most general route for the synthesis of neutral Fischer carbene complexes.[4] The synthesis of complexes **1** in which the R group contains an α,*β*-unsaturated function is thus a possible route to α,*β*-unsaturated carbene complexes. We became interested in the synthesis of carbonylmetalates **2** containing the unprecedented α-iminoacyl ligand, akin to the α-ketoacyl ligand, for metals of the first transition row.

Although some α,*β*-unsaturated acylferrates are known,[3,5] only two examples of the sequence [(CO)₄-FeCOCOZ]⁻ have been reported. One is the (ethoxyoxalyl)tetracarbonylferrate (Z = OEt, stable as the sodium salt).[6] The second is the (pivaloylacyl)tetracarbonylferrate (Z = *t*-Bu) **[1a]M** (stable for M = PPN) obtained after a tedious procedure.[7] To the best of our knowledge, the α-ketoacyl ligand has not been described for metalates of the manganese and chromium carbonyls series.[8]



[1a]M



[2a]Li

We report the generation of [**2a**]**Li**, an imino-protected equivalent of [**1a**]**Li**, by reaction of a lithium aldimine on Fe(CO)₅ and extension of this strategy to carbonylmetalates [**2b**]**Li** and [**2c**]**Li** derived from manganese and chromium carbonyls, respectively (Scheme 1).

## Results and Discussion

The lithium aldimine **3**, generated from *t*-BuLi and *t*-BuNC,[9] reacts with Fe(CO)₅ to give the tetracarbonylferrate [**2a**]**Li** stereoselectively (yellow powder, 83% yield). Contrary to [**1a**]**Li**, [**2a**]**Li** is stable at least overnight at 55 °C in THF. It was characterized on the basis of NMR and IR analysis (see Experimental Section). In the $^{13}$C NMR spectrum of [**2a**]**Li** (see Table 1), the carbonyl ligands are equivalent[10] while the *t*-Bu groups are not.

As depicted in Scheme 1, the analogous carbonylmetalates [**2**]**Li** have been obtained for manganese ([**2b**]**Li**, 51% yield, mixture of two isomers[11]) and chromium ([**2c**]**Li**, 74% yield), as well. The characteristic $^{13}$C NMR data for [**2a**−**c**]**Li** are reported in Table 1. Their IR spectra display the characteristic $\nu_{CO}$ absorptions expected for such lithium (acyl)carbonylmetalates.[4]

The reactivity of the new complexes [**2**]**Li** with electrophiles is currently being investigated. As a preliminary result, in situ alkylation of [**2a**]**Li** with Me₃OBF₄ gives the stable methoxycarbene [**2a**]**Me** (mixture of two isomers)[12] in 45% isolated yield. By comparison, [**1a**]**NMe₄** has been reported to react with electrophiles (e.g. FSO₃Et) to give thermolabile products resulting from alkylation at the acyl oxygen atom.[7] On the contrary, [(CO)₄FeCOCOOEt]⁻Na⁺ is alkylated at the metal by reaction with CF₃SO₃Me.[6] For the chromium derivative [**2c**]**Li**, alkylation with Me₃OBF₄ leads to the stable methoxycarbene [**2c**]**Me** (56% isolated yield) as a 70/30 mixture of two isomers.[12]

## Experimental Section

**General Data.** All reactions were performed under argon by standard Schlenk tube techniques, using solvents freshly distilled under argon. Infrared spectra were recorded with a

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

[1] Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3,* 580.

[2] *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A, Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol 12.

[3] See for example: Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10,* 3413−3415 and references therein.

[4] Fischer, H. In *Transition Metal Carbene Complexes;* Verlag Chemie: Weinheim, Germany, 1983; p 1 and references therein.

[5] Mitsudo, T.; Watanabe, H.; Sasaki, T.; Yoshinobu, Y.; Takegami, Y.; Watanabe, Y. *Organometallics* **1989**, *8,* 368−378 and references therein.

[6] Sabo-Etienne, S.; Larsonneur, A.-M.; des Abbayes, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1671−1673.

[7] Dötz, K. H.; Wenicker, U.; Müller, G.; Alt, H. G.; Seyferth, D. *Organometallics* **1986**, *5,* 2570−2572.

[8] Some neutral complexes with α-ketoacyl ligands have been reported; see for example: Sheridan, J. B.; Johnson, J. R.; Beth, J.; Handwerker, B. M.; Geoffroy, G. L. *Organometallics* **1988**, *7,* 2404−2411 and references therein.

[9] Niznik, G. E.; Morison, W. H.; Walborsky, H. M. *J. Org. Chem.* **1974**, *39,* 600−604.

[10] The carbonyl ligands of [(CO)₄FeCOCOZ]⁻ (Z = OEt, *t*-Bu) have also been reported to be equivalent by $^{13}$C NMR analysis; see refs 6 and 7, respectively.

[11] This isomerism is suggested to be due to the *cis* and *trans* positions of the Mn(CO)₅ group and the acyl ligand on the Mn(CO)₄ center.[4]

[12] It is not clear whether this isomerism is due to a *syn/anti* isomerism at the imino group or to different orientations of the methyl (from MeO) in the plane of the carbene ligand.[4]

S0276-7333(96)00343-3 CCC: $12.00

**Scheme 1**

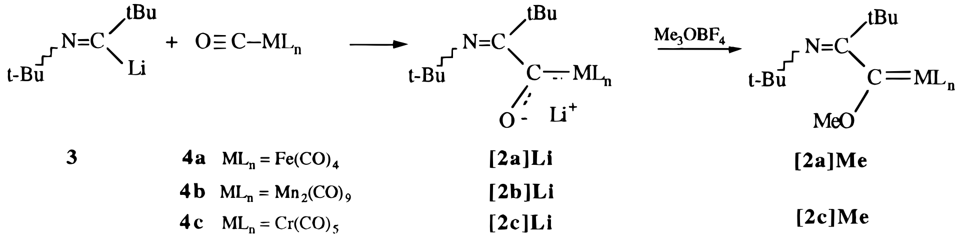

**Table 1. $^{13}$C NMR Data for Complexes [2a−c]E**

| complex | $^{13}$C NMR,[a] δ (ppm) acyl or carbenic C | imino C | terminal CO | |
|---|---|---|---|---|
| *t*-BuN=C(*t*-Bu)(COLi)Fe(CO)$_4$ [**2a**]**Li** | 298.4 | 177.2 | 221.2 | |
| *t*-BuN=C(*t*-Bu)(COLi)Mn$_2$(CO)$_9$ [**2b**]**Li** | 324.4[b] | 177.1[b] | 227.5[b] | 239.3[b] |
| *t*-BuN=C(*t*-Bu)(COLi)Cr(CO)$_5$ [**2c**]**Li** | 332.9 | 180.2 | 221.8 | 225.3 |
| *t*-BuN=C(*t*-Bu)(COMe)Fe(CO)$_4$ [**2a**]**Me** | 335.2[c] | 174.5[c] | 213.9[c] | |
| *t*-BuN=C(*t*-Bu)(COMe)Cr(CO)$_5$ [**2c**]**Me** | 367.0[d] | 172.6[d] | 217.8[d] | 223.9[d] |

[a] Brucker AMX 400 at 100.6 MHz. [b] Major isomer.[11] The minor isomer exhibits signals at 324.4, 170.5, 227.4, and 239.4 ppm. [c] Major isomer.[12] The minor isomer exhibits signals at 333.2, 174.5, and 214.1 ppm. [d] Major isomer. The minor isomer exhibits signals at 371.5, 175.2, 216.7, and 223.2 ppm.

Perkin-Elmer 1725 IRFT spectrometer using a CaF$_2$ cell (0.05 mm). NMR spectra were recorded on an AC 200, AM 250, or AMX 400 Bruker instrument.

**Synthesis of Complexes. Complexes [2]Li.** In a typical experiment, a THF solution of the lithium aldimine **3** is prepared from *t*-BuLi (1.2 mmol) and *t*-BuNC (1.2 mmol) according to the procedure of Walborsky et al.[9] The solution is cooled to −78 °C, and iron pentacarbonyl (1.2 mmol) is added. The solution is then warmed slowly to −15 °C and diluted with cold pentane. After removal of the solvents, the yellow slurry is washed with cold pentane (4 × 3 mL) to yield [**2a**]**Li** as a pale yellow powder (340 mg, 83%). Attempts to obtain crystals of [**2a**]**Li** suitable for X-ray diffraction study were unsuccessful. Similarly attempts to exchange Li$^+$ with either *n*-Bu$_4$N$^+$ or PPN$^+$ failed. Complexes [**2b**]**Li** and [**2c**]**Li** were prepared by a similar procedure but in diethyl ether for [**2b**]**Li**.[13]

**[2a]Li.** $^1$H NMR (THF-$d_8$, 400 MHz, δ (ppm)): 1.14 (bs, 9H), 1.23 (bs, 9H). $^{13}$C NMR (THF-$d_8$, 100.6 MHz, δ (ppm)): 31.4; 32.7; 38.9; 56.2; 177.2; 221.2; 298.4. $^7$Li NMR (THF-$d_8$, 155.5 MHz, δ (ppm)): 3.61 (bs). IR (THF, $\nu_{CO}$ (cm$^{-1}$)): 1902 (s), 1912 (s), 1934 (m), 2021 (m).

**[2b]Li (Mixture of Two Isomers).** $^1$H NMR (C$_6$D$_6$, 400 MHz, δ (ppm)): 1.56 (bs, 9H); 1.59 (bs, 9H). Signals of Et$_2$O complexed at lithium appear at 1.10 (t, 6H) and 3.38 (bs, 4H). $^{13}$C NMR (C$_6$D$_6$, 100.6 MHz, δ (ppm)): Major isomer, 14.9, 31.4, 32.8, 38.9, 55.9, 65.9, 177.1, 227.5, 239.3, 324.4; minor isomer, 14.9, 26.5, 30.6, 36.9, 57.1, 65.9, 170.5, 227.4, and 239.4, 324.4. IR (THF, $\nu_{CO}$ (cm$^{-1}$)): 1916 (w), 1952 (sh), 1976 (vs), 1994 (m), 2013 (m), 2047 (w), 2077 (w).

**[2c]Li.** $^1$H NMR (THF-$d_8$, 400 MHz, δ (ppm)): 1.11 (bs, 9H); 1.19 (bs, 9H). $^{13}$C NMR (THF-$d_8$, 100.6 MHz, δ (ppm)): 31.1; 33.0; 37.9; 55.4; 180.2; 221.8; 225.3; 332.9. IR (THF, $\nu_{CO}$ (cm$^{-1}$)): 1890 (sh), 1906 (vs), 1917 (m); 1979 (m); 2040 (w).

**Complexes [2]Me.** In a typical experiment, a solution of Me$_3$OBF$_4$ (1.3 mmol) in CH$_2$Cl$_2$ (15 mL) is added at −78 °C to a solution of [**2a**]**Li** (1.2 mmol) in THF (6 mL). The reaction mixture is warmed slowly to 0 °C, and the solvents are evaporated. Extraction with cold pentane and evaporation of the latter yield [**2a**]**Me** as an orange oil.

**[2a]Me (Mixture of Two Isomers).** $^1$H NMR (C$_6$D$_6$, 200 MHz, 288 K, δ (ppm)): Major isomer, 1.31 (bs, 9H), 1.35 (bs, 9H), 4.00 (bs, 3H); minor isomer 1.31 (bs, 9H), 1.35 (bs, 9H), 3.16 (bs, 3H). $^{13}$C NMR (C$_6$D$_6$, 100.6 MHz, 288 K, δ (ppm)): Major isomer, 30.7, 31.8, 57.0, 72.0, 81.6, 174.5, 213.9, 335.2; minor isomer, 30.9, 32.0, 58.7, 70.2, 77.5, 174.5, 214.1, 333.2. IR (pentane, $\nu_{CO}$ (cm$^{-1}$)): 1955 (s), 1969 (s), 1995 (m), 2061 (m).

**[2c]Me (Mixture of Two Isomers).** $^1$H NMR (C$_7$D$_8$, 400 MHz, 258 K, δ (ppm)): Major isomer, 1.36 (bs, 9H), 1.38 (bs, 9H), 3.47 (bs, 3H); minor isomer, 1.43 (bs, 9H), 1.46 (bs, 9H), 4.12 (bs, 3H). $^{13}$C NMR (THF-$d_8$, 100.6 MHz, 258 K, δ (ppm)): Major isomer, 29.5, 31.0, 40.3, 57.0, 69.8, 172.6, 217.8, 223.9, 367.0; minor isomer, 30.4, 32.4, 40.4, 57.1, 67.1, 175.2, 216.7, 223.2, 371.5. IR (pentane, $\nu_{CO}$ (cm$^{-1}$)): 1931 (sh), 1956 (vs), 1987 (vs), 2066 (s).

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**Supporting Information Available:** NMR spectra (28 pages). Ordering information is given on any current masthead page.

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