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[(*N*,*N*-Dimethylamino)carboxymethylene]pentacarbonylchromium(0): The First Fischer Carbene Complex with a Free Carboxyl Group Attached Directly to the Carbene Atom

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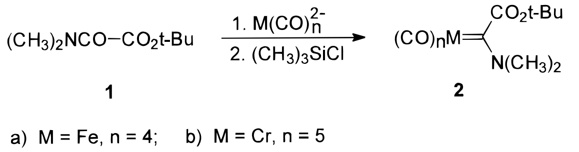
Summary: Ester carbene complexes $(CO)_4Fe{=}C(NMe_2)CO_2t\text{-}Bu$ (**2a**) *and* $(CO)_5Cr{=}C(NMe_2)CO_2t\text{-}Bu$ (**2b**) *can be easily prepared by reaction of* $Me_2NCO{-}CO_2t\text{-}Bu$ (**1**) *with* $Fe(CO)_4^{2-}$ *or* $Cr(CO)_5^{2-}$ *and chlorotrimethylsilane in THF solution. Reaction of* **2b** *with* CF_3CO_2H *affords free acid* $(CO)_5Cr{=}C(NMe_2)CO_2H$ (**3**)*. Comparison of the* pK_a *values of* **3** *(9.36) and* $Me_2NCO{-}CO_2H$ *(9.25) in DMF reveals that the* $(CO)_5Cr{=}C(NMe_2)$ *moiety is a slightly weaker electron acceptor than the* Me_2NCO *group.*

Fischer carbene complexes have become valuable reagents for organic synthesis.[1] This chemistry is based mostly on the reactions of the group 6 elements, especially chromium, while the chemistry of other transition-metal carbenes is less developed. For synthetic applications, easy accessibility of suitably substituted carbene complexes is crucial. One of the most versatile methods for the preparation of chromium aminocarbenes[2] is based on the reaction of $Cr(CO)_5^{2-}$ with tertiary amides of carboxylic acids in the presence of Me_3SiCl. We have recently shown that this method can be used for the preparation of iron aminocarbenes[3] and chromium and iron bis(amino)carbenes[4] as well. However, in the case of iron aminocarbene complexes, the reaction is restricted to nonenolizable tertiary amides. Interesting examples of such amides are ester amides of oxalic acid. Reaction of metal carbonylate anions with these compounds would allow an approach to iron and chromium aminocarbenes bearing a carboxyl functionality attached directly to the carbene atom. Such complexes would be interesting as such and also as potential reagents in organic synthesis. Here, we report our results on the synthesis of the first examples of such complexes.

Scheme 1



Treatment of the ethylester of *N*,*N*-dimethyloxamic acid with $Fe(CO)_4^{2-}$ (generated in situ by reduction of $Fe(CO)_5$ with sodium naphthalenide in THF) and Me_3SiCl afforded a small amount of an unstable product, which could not be obtained in pure form. However, its ^1H NMR spectrum showed, besides signals of the ethyl group, two singlets with chemical shifts at 3.36 and 3.82 ppm characteristic of (dimethylamino)carbene methyl groups. The reaction was therefore repeated with the *tert*-butyl ester in which the ester function should be less reactive. Indeed, *N*,*N*-dimethyloxamic acid *tert*-butyl ester (**1**) reacted with $K_2Fe(CO)_4$ to give the desired iron aminocarbene complex **2a** in more than 50% yield as a bright yellow, relatively stable crystalline compound whose spectral data fully agreed with the proposed structure. In a similar way, the analogous chromium aminocarbene complex **2b** was obtained in 51% yield (Scheme 1).

Attempts to prepare a complex with a free carboxyl group from **2a** were unsuccessful. Treatment of the iron aminocarbene **2a** with trifluoroacetic acid resulted in rapid decomposition accompanied by evolution of carbon monoxide. On the other hand, chromium complex **2b** gave the carboxylic acid **3** cleanly in high yield under the same conditions (Scheme 2).

That carbonylate anions react with amide carbonyl groups in preference to ester carbonyls, which are usually more activated to nucleophilic attack, is in agreement with earlier findings. The formation of alkoxycarbenes has never been observed during the reaction of metal carbonylates with esters of carboxylic acids.[2a,5] Moreover, the *tert*-butoxycarbonyl group in **1**

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[1] For recent reviews on the chemistry of transition-metal carbene complexes, see: (a) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, p 209. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. (d) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 469. (e) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549.

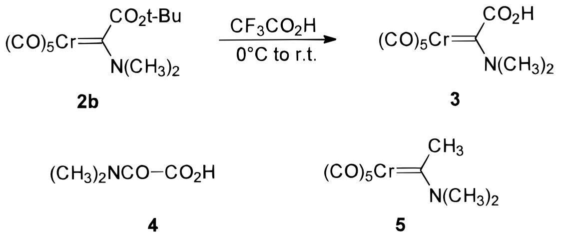
[2] (a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (b) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

[3] Dvořák, D. *Organometallics* **1995**, *14*, 570.

[4] Havránek, M.; Hušák, M.; Dvořák, D. *Organometallics* **1995**, *14*, 5024.

S0276-7333(98)00082-X CCC: $15.00

Scheme 2



is very unreactive, as evidenced by the reaction of mixed ethyl *tert*-butyl oxalate with excess of dimethylamine, which gives almost exclusively esteramide **1** and only traces of *N*,*N*,*N*′,*N*′-tetramethyl oxamide.

The spectral data for the products obtained are in agreement with the aminocarbene structures **2a** and **2b** rather than with the isomeric alkoxycarbene $(CO)_5Cr{=}C(t\text{-}BuO)CONMe_2$. ^{1}H NMR of these compounds show the characteristic nonequivalence of the *N*-methyl signals of aminocarbene moiety. The chemical shifts at 3.37 and 3.80 for **2a** and 3.38 and 3.85 for **2b** are almost identical with those observed for the *N*,*N*-dimethylamino group of $(CO)_5Cr{=}C(Me)NMe_2$ (3.32 and 3.89).[2a] For comparison, the shifts of the *N*,*N*-dimethylamino group in the esteramide **1** and in dimethylacetamide[6] are 2.96, 3.04 ppm and 2.94, 3.09 ppm, respectively. Also, the values of the ^{13}C NMR shifts of the carbons of the $N(CH_3)_2$ group of **2a** (47.19, 49.47 ppm) and **2b** (47.44, 50.55 ppm) are similar to those for $(CO)_5Cr{=}C(Me)NMe_2$ (43.05 and 53.62 ppm). The ^{13}C NMR shifts of the carbons of the $CON(CH_3)_2$ group are lower: for example, 34.44 and 37.56 ppm are the values for esteramide **1**, while for dimethylacetamide exhibits the corresponding peaks at 35.28, 38.13 ppm.[6]

Another piece of evidence in support of the proposed structure comes from the IR spectra. Formation of the carbene complexes **2a** and **2b** from the esteramide **1** results in the disappearance of the amide band at 1661 cm^{-1}. At the same time, the ester absorption of **1** at 1732 cm^{-1} shifts to 1717 cm^{-1} in complex **2a** and to 1706 cm^{-1} in the case of the chromium carbene **2b**. Removing the t-Bu group of **2b** results in a negligible change of the position of the carbonyl band to 1705 cm^{-1}. This absorption disappeared after addition of triethylamine as a result of carboxylate anion formation. At the same time, the carbonyl bands of the $(CO)_5Cr$ group change only slightly from 2062, 1983, and 1938 cm^{-1} to 2055, 1974, and 1929 cm^{-1}. A much larger shift should be expected for the anion of the isomeric hydroxycarbene complex $(CO)_5Cr{=}C(OH)CONMe_2$. For example the carbonyl bands of $(CO)_5Cr{=}C(OH)Me$ at 2070, 1974, and 1951 cm^{-1} are changed to 2041 and 1883 cm^{-1} in the course of anion formation.[7]

The UV spectrum of the chromium compound **2b** shows two bands that can be assigned by analogy[8] as the metal-to-ligand charge transfer (MLCT) at 372 nm ($\log \epsilon = 3.90$) and the $\pi-\pi^*$ transition at 334 nm. On the other hand, the UV spectrum of the iron complex **2a** reveals only one maximum at 366 nm ($\log \epsilon = 3.38$).

The pK_a value of the acid **3** obtained by potentiometric titration in DMF is 9.36 ($s = 0.08$). This value falls between those of *N*,*N*-dimethyloxamic acid **4** (pK_a = 9.25, $s = 0.02$; measured under the same conditions) and formic acid (pK_a = 11.65).[9] This demonstrates the electron-withdrawing ability of the aminocarbene moiety, which however, is weaker than that of the *N*,*N*-dimethylamido group. This is in contrast with the acidity of **5** which is a much stronger C-acid than *N*,*N*-dimethylacetamide and in agreement with earlier findings that the high acidity of **5** and other Fischer carbenes bearing α-hydrogens is due to resonance stabilization of their anions rather than to polar effects.[10]

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. ^{1}H NMR spectral data were recorded in $CDCl_3$ at 300 MHz, and chemical shifts are referenced to TMS. ^{13}C NMR spectra were recorded at 75.46 MHz. All experiments were carried out under argon. The p*K* values in dimethylformamide were measured by potentiometric titration with a glass electrode and a modified calomel electrode. Tetrahydrofuran was distilled from benzophenone ketyl under nitrogen prior to use. Iron pentacarbonyl, chromium hexacarbonyl, chlorotrimethylsilane, dimethylamine, and ethyl oxalyl chloride were purchased from Aldrich and used without purification. Neutral aluminum oxide (Brockman III grade) and silica were obtained from Lachema.

***tert*-Butyl Ethyl Oxalate.** Ethyl oxalyl chloride (23.6 g, 0.173 mol) was added dropwise during 20 min to an ice-cooled solution of *tert*-butyl alcohol (19 mL, 0.199 mol) and pyridine (17.5 mL, 0.216 mol) in diethyl ether (100 mL). The mixture was stirred for 1 h without cooling and then poured into water (300 mL), and the organic phase was washed successively with water (200 mL), 1% hydrochloric acid (200 mL), and 5% $NaHCO_3$ and dried over $MgSO_4$. The ether was evaporated, and the residue was distilled under reduced pressure, giving 25.13 g of crude product (bp 46 °C/1.5 mmHg). Redistillation afforded 20.6 g (68.4%) of pure compound: bp 98.5−99.5 °C/27 mmHg; ^{1}H NMR δ 1.37 (t, $J = 7.2$ Hz, 3, CH_3), 1.56 (s, 9, *t*-Bu), 4.32 (q, $J = 7.2$ Hz, CH_2); IR ($CHCl_3$) ν 3021 (s), 2986 (m), 1759 (s), 1737 (vs), 1372 (m), 1331 (m), 1148 (vs) cm^{-1}. Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.05; H, 8.07.

***N*,*N*-Dimethyloxamic Acid *tert*-Butylester (1).** An excess of gaseous dimethylamine (3.6 g, 80 mmol) was condensed in ice-cooled *tert*-butyl ethyl oxalate (10.84 g, 62.23 mmol), and the mixture was left at room temperature overnight. The excess dimethylamine was then evaporated, and the residue was crystallized from a mixture of *n*-hexane (100 mL) and ethyl acetate (5 mL) to afford 9.51 g (88.2%) of the product. An analytical sample was recrystallized from *n*-hexane: mp 62−64 °C; ^{1}H NMR δ 1.57 (s, 9, *t*-Bu), 2.96 (s, 3, CH_3), 3.01 (s, 3, CH_3); ^{13}C NMR δ 28.63 (q, $C(CH_3)_3$), 34.44 (q, NCH_3), 37.56 (q, NCH_3), 84.78 (s, $C(CH_3)_3$), 162.96 (s, C═O), 163.28 (s, C═O); IR ($CHCl_3$) ν 3018 (m), 2988 (w), 1732 (s), 1661 (vs), 1371 (m), 1123 (s) cm^{-1}. Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.51; H, 8.45; N, 8.24.

[(*tert*-Butoxycarbonyl)(*N*,*N*-dimethylamino)methylene]pentacarbonylchromium(0) (2b). A solution prepared by dissolving potassium (1.14 g, 28.5 mmol) and naphthalene (4.3 g, 33.5 mmol) in THF (80 mL) in an argon atmosphere was slowly transferred via cannula to a stirred suspension of

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chromium hexacarbonyl (2.20 g, 10 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to 0 °C and then cooled to −78 °C, and *N*,*N*-dimethyloxamic acid *tert*-butylester (0.83 g, 4.8 mmol) in THF (10 mL) was added. The mixture was allowed to reach −50 °C within 0.5 h, stirred at this temperature for another 0.5 h, and cooled to −78 °C, and chlorotrimethylsilane (3 mL, 23.6 mmol) was added via a syringe. The cooling bath was removed, the mixture was allowed to warm to 0 °C, and neutral alumina (10 g) was added. The solvent was removed under reduced pressure, and the residue was dried for several hours under high vacuum to remove all the THF. Light petroleum (50 mL) was added, and the mixture was stirred vigorously for several minutes under an argon atmosphere. The suspension formed was then transferred onto a column filled with neutral alumina (75 g). Elution with light petroleum gave (after naphthalene) crude product as a yellow solid (1.085 g). Crystallization from *n*-heptane−ethyl acetate furnished 0.86 g (51%) of pure compound: mp 112.5−114.5 °C; ^{1}H NMR δ 1.60 (s, 9, *t*-Bu), 3.34 (s, 3, CH_3), 3.81 (s, 3, CH_3); ^{13}C NMR δ 28.83 (q, $C(CH_3)_3$), 47.44 (q, NCH_3), 50.53 (q, NCH_3), 85.03 (s, $C(CH_3)_3$), 169.82 (s, C═O ester), 216.93 (s, cis CO), 222.96 (s, trans CO), 260.06 (s, C═Cr); IR (CCl_4) ν 2061 (s), 1982 (m), 1941 (vs), 1707 (w), 1545 (w) cm^{-1}; UV (hexane) λ_{max} 372 nm (log α = 3.90), 334 nm (sh). Anal. Calcd for $C_{13}H_{15}$ $CrNO_7$: C, 44.71; H, 4.33; N, 4.01. Found: C, 44.65; H, 4.45; N, 3.95.

[(*tert*-Butoxycarbonyl)(*N,N*-dimethylamino)methylene]-tetracarbonyliron(0) (2a). *Caution: Potassium and C_8K are pyrophoric!* Iron pentacarbonyl (1.4 mL, 10 mmol) was added at −78 °C via syringe to a suspension of C_8K prepared from potassium (0.62 g, 15.5 mmol) and graphite (1.6 g, 133 mmol) in THF (40 mL). The resulting mixture was stirred 10 min at −78 °C, then a solution of amide **1** (0.865 g, 5 mmol) in THF (10 mL) was added via syringe, and stirring was continued at this temperature for another 10 min. The reaction vessel was then transferred to a cooling bath adjusted to −45 °C, and stirring was continued at this temperature. *(At higher temperature, insoluble and therefore unreactive solvate of $K_2Fe(CO)_4$ precipitates!*[3]*)* After 20 min, the mixture was cooled again to −78 °C and chlorotrimethylsilane (3 mL, 23.6 mmol) was added. Stirring was continued for 20 min at −78 °C, and the mixture was allowed to warm slowly to 10 °C. Alumina (10 g) was added, THF was evaporated at diminished pressure (bath temperature < 30 °C), and the residue was dried in high vacuum. The product was chromatographed as described for the chromium analogue (55 g of alumina, light petroleum; light petroleum−CH_2C_{l2} 5:1; 7:3). The crude product (0.926 g) was dissolved in CH_2Cl_2 (10 mL), heptane (30 mL) was added, and the mixture was filtered under argon. Evaporation of dichloromethane in vacuo, cooling to −30 °C, and filtration under argon gave 0.913 g (56.2%) of pure carbene complex: mp 95−97 °C (dec); ^{1}H NMR δ 1.59 (s, 9, *t*-Bu), 3.37 (s, 3, NCH_3), 3.80 (s, 3, NCH_3); ^{13}C NMR δ 28.89 (q, $C(CH_3)_3$), 47.19 (q, NCH_3), 49.47 (q, NCH_3), 85.58 (s, $C(CH_3)_3$), 169.45 (s, C═O ester), 214.76 (s, CO), 246.34 (s, C═Fe); IR (CCl_4) ν 2049 (s), 1976 (s), 1948 (s), 1948 (vs), 1934 (vs), 1717 (w), 1549 (w) cm^{-1}; UV (hexane) λ_{max} 366 nm (log α = 3.38). Anal. Calcd for $C_{12}H_{15}FeNO_6$: C, 44.33; H, 4.65; N, 4.31. Found: C, 44.39; H, 4.62; N, 4.18.

[(Ethoxycarbonyl)(*N,N*-dimethylamino)methylene]tetracarbonyliron(0). Reaction of $Fe(CO)_5$ (1,4 mL, 10 mmol), sodium naphthalenide (26.5 mmol), *N*,*N*-dimethyloxamic acid ethylester (0.725 g, 5 mmol), and chlorotrimethylsilane (3.0 mL, 23.6 mmol) was carried out analogously to the procedure described for the preparation of [(*tert*-butoxycarbonyl)(*N*,*N*-dimethylamino)methylene]pentacarbonylchromium(0) **(2b)**. Chromatography afforded 0.22 g (15%) of unstable brown oil: ^{1}H NMR δ 1.39 (t, J = 8 Hz, 3, CH_2CH_3), 3.36 (s, 3, NCH_3), 3.82 (s, 3, NCH_3), 4.37 (q, J = 8 Hz, CH_2).

[(Carboxy)(*N,N*-dimethylamino)methylene]pentacarbonylchromium(0) (3). Trifluoroacetic acid (0.8 mL) was added at 0 °C to [(*tert*-butoxycarbonyl)(*N*,*N*-dimethylamino)-methylene]pentacarbonylchromium(0) (0.091 g, 0.26 mmol) under argon. The resulting solution was stirred at this temperature for 1 h (after 0.5 h, the product began to precipitate). Trifluoroacetic acid was then evaporated under reduced pressure, and the residue was washed with *n*-heptane (2 and 0.5 mL) to remove unreacted ester. Drying in vacuo yielded 0.054 g (71%) of the product: ^{1}H NMR (DMSO-d_6) δ 3.37 (s, 3, NCH_3), 3.77 (s, 3, NCH_3); ^{13}C NMR (DMSO-d_6) δ 47.57 (q, CH_3), 49.54 (q, CH_3), 171.22 (s, CO_2H), 216.26 (s, cis CO), 222.55 (s, trans CO), 251.62 (Cr═C); IR ($CHCl_3$) ν 2062 (s), 1983 (s), 1938 (vs), 1705 (w), 1554 (w) cm^{-1}; IR in the presence of Et_3N ($CHCl_3$) ν 2055 (s), 1974 (s), 1929 (vs), 1547 (w). Anal. Calcd for $C_9H_7CrNO_7$: C, 36.87; H, 2.41; N, 4.78. Found: C, 36.55; H, 2.53; N, 4.81.

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