Notes

A Convenient Entry to Substituted Cationic Iron–Carbene Complexes

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Summary: The alkoxycarbene complex [Fe(Cp)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (1) readily undergoes specific substitution of one or two carbonyl ligands, depending on the photochemical conditions. This method opens a route to various mono- and disubstituted methoxycarbene complexes which are otherwise not accessible.*

Electrophilic iron—carbene complexes form a very important class of molecules, both as models and intermediates in organic synthesis.[1] The reactivity of such species is highly sensitive to the environment of the metal. Fe(Cp*)–carbene complexes (Cp* = η^5-C$_5$Me$_5$) are generally prepared from acyl and alkyl derivatives[2] but the lack of a general route to substituted complexes has precluded the extensive development of this chemistry. This is in particular due to the reluctance of the alkyl derivatives [Fe(Cp*)(CO)$_2$(R)] to undergo substitution of both terminal carbonyl ligands.[3] Moreover, by contrast to the Cp complexes, insertion of a carbonyl ligand into the Fe—R bond leading to the desired phosphine-substituted acyl complex[1] is unefficient in the case of the permethylated Cp analogues. Cationic complexes, in which the carbene ligand is already formed, appear to be good candidates for such substitution reactions. For these reasons, we have investigated the reactivity of the methoxycarbene complex[2d] [Fe(Cp*)(CO)$_2$(=C(OMe)Me)]$^+$; such alkoxycarbene complexes, easily accessible and thermally stable, are known to be useful precursors of very reactive nonheterostabilized carbene species.[1] In addition, the access to carbene complexes possessing a labile ligand (such as CH$_3$CN) would open a new field of investigation, as precursors of neutral carbene derivatives and chiral at metal carbene complexes. We report here the preparation and spectral characterization of new various substituted complexes [Fe(Cp*)(L)(L')(=C(OMe)Me)][CF$_3$SO$_3$]. The sequence described hereafter provides a general method for the synthesis of complexes of this type which are otherwise not accessible.

Results and Discussion

The access to disubstituted complexes[4] generally involves photochemical displacement of both carbonyl ligands in the presence of a suitable substrate. We have previously found that from *neutral alkyl species*, such a method is only efficient in the two following cases: the methyl and methoxymethyl complexes [Fe(Cp*)(CO)$_2$(R)] (R = Me, CH$_2$OMe), by using as incoming ligand the chelate diphosphine dppe.[3] Similar reactions with PMe$_3$ or PPh$_3$ do not lead to the desired disubstituted complexes; the second decarbonylation step is, in the former case, promoted by the chelating effect of the diphos ligand. Moreover, this substitution reaction cannot be extended to other alkyl complexes, in particular those possessing a β-hydrogen atom, due to side reactions.[5] By contrast, it has been shown that photolysis of cationic species is easier: for example, complete formation of the tris(acetonitrile) complex [Fe(Cp*)(CH$_3$CN)$_3$][PF$_6$] from [Fe(Cp*)(CO)$_3$][PF$_6$] is achieved within 3 h of near-UV irradiation.[6] Furthermore, Geoffroy and co-workers[7] have recently published the original reactivity pattern of a PPh$_3$-substituted manganese carbene complex [Mn(Cp)(CO)(PPh$_3$)(=C(OMe)Me)], in which the presence of the phosphine ligand has a dramatic effect; the coordinated carbene fragment remains intact under the photochemical conditions necessary to prepare this latter species.

Methoxy(alkyl)carbene complexes, which are obtained by O-methylation of the corresponding acyl complexes, constitute interesting starting materials, since a wide variety of acyl complexes [Fe(Cp*)(CO)$_2$(C(O)R)] are synthetically available. The methoxy(methyl)carbene complex[2d] [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (1), is converted upon irradiation into either the mono(acetonitrile) derivative [Fe(Cp*)(CH$_3$CN)(CO)(=C(OMe)Me)][CF$_3$SO$_3$] (2) or the bis(acetonitrile) derivative [Fe(Cp*)(CH$_3$CN)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (3). The reactions are chemospecific: monodecarbonylation occurs by carrying out the irradiation reaction in a glass vessel, whereas near-UV photolysis of 1 leads to the formation of 3 (Scheme I). The air-sensitive complexes 2 and 3 are isolated in quantitative yield. Complex 3 is stable only in CH$_3$CN solution; the ^{1}H and ^{13}C NMR signals of CH$_3$CN are

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(1) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411 and references therein.

(2) (a) Guerchais, V.; Thépot, J.-Y.; Lapinte, C.; Toupet, L. *Organometallics* **1988**, *7*, 604. (b) Roger, C.; Toupet, L.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1988**, 713. (c) Tudoret, M.-J.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1991**, *414*, 373. (d) Nlate, S.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, *434*, 89.

(3) Roger, C.; Harmon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045.

(4) For the synthesis of some diphosphorus complexes, see: (a) Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C.; Raabe, E. *Chem. Ber.* **1987**, *120*, 1987. (b) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1987**, 411.

(5) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005.

(6) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

(7) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735.

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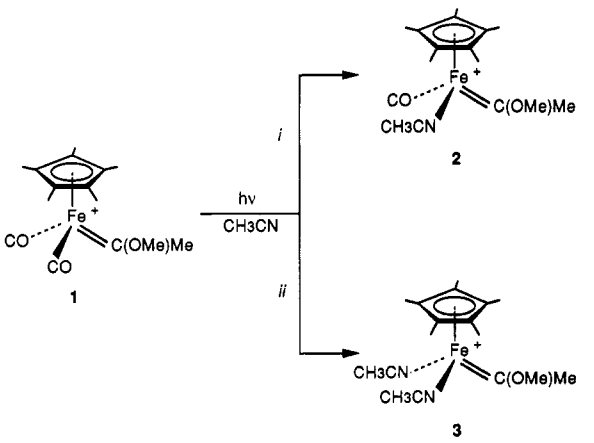
Scheme I[a]



[a] Key: *i*, irradiation in a glass vessel; *ii*, irradiation in a quartz vessel.

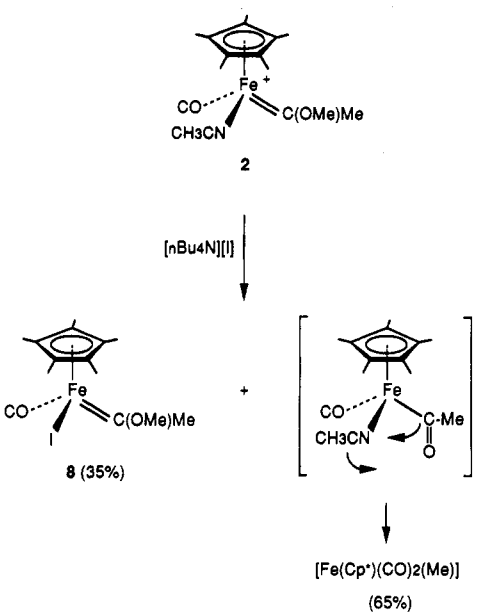
broadened, indicating a slow exchange of CH_3CN/CD_3CN in the NMR time scale.

Treatment of **3** with PMe_3 and PPh_3 in CH_3CN at room temperature gives the di- and monophosphine complexes, respectively, $[Fe(Cp^*)(L)(L')(=C(OMe)Me)][CF_3SO_3]$ (**4**, L = L' = PMe_3; **5**, L = CH_3CN, L' = PPh_3). The formation of the bis(triphenylphosphine) complex is not observed whatever the amount of ligand added, suggesting that steric hindrance of the bulky triphenylphosphine inhibits a second coordination. An attempt to prepare the mixed complex (L = PMe_3, L' = PPh_3) by addition of PMe_3 to **5** gives in fact compound **4**, the formation of which results from displacement of both PPh_3 and CH_3CN. As expected, the chiral mono(phosphine) complex $[Fe(Cp^*)(CO)(PPh_3)(=C(OMe)Me)][CF_3SO_3]$ (**6**) is obtained directly by irradiation of **1** with 1 equiv of PPh_3; in this case the optimum yield is obtained by using CH_2Cl_2 as solvent. All the new complexes **2**–**6** exhibit ^1H and ^{13}C resonance patterns characteristic of the methoxycarbene ligand. The yield of these above syntheses are good to excellent (75–95%).

Preliminary studies on the reactivity of these complexes illustrate their synthetic potential. The PPh_3-substituted complex **6** upon treatment with $[^nBu_4N][I]$ affords, *via* an O-demethylation reaction,[1,8] the acetyl complex $[Fe(Cp^*)(CO)(PPh_3)(C(O)Me)]$ (**7**) in 98% yield. This constitutes a route to substituted acyl complexes: Me^+ acts as a protecting group toward the acyl function allowing the photochemical substitution step. Reaction of $[Fe(Cp^*)(CH_3CN)(CO)(=C(OMe)Me)][CF_3SO_3]$ (**2**) with $[^nBu_4N][I]$ leads to the formation of the known methyl derivative $[Fe(Cp^*)(CO)_2(Me)]$ and the new neutral iodo complex $[Fe(Cp^*)(CO)(I)(=C(OMe)Me)]$ (**8**) in a 65:35 ratio (Scheme II). Compound **2**, which possesses two reactive sites, namely the labile acetonitrile ligand and the carbene fragment, undergoes competitive processes. We assume that the formation of the methyl complex results from dealkylation of the carbene ligand to give the acetyl intermediate $[Fe(Cp^*)(CH_3CN)(CO)(C(O)Me)]$ and that subsequent desinsertion/migration of the carbonyl of the acetyl group is then induced by facile dissociation of the CH_3CN ligand. Substitution of CH_3CN by the iodide leads to the formation of a neutral carbene complex

(8) Such a dealkylation pathway is well-known: (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

Scheme II



containing a halide ligand.[9] Alkoxy(alkyl)carbene complexes can be converted into either the corresponding (α-alkoxy)alkyl or alkyl derivatives, depending on the hydride reagent used.[1] For example, we have found that reduction of $[Fe(Cp^*)(PMe_3)_2(=C(OMe)Me)][CF_3SO_3]$ (**4**) with $NaBH_4$ yields the ethyl complex $[Fe(Cp^*)(PMe_3)_2(CH_2CH_3)]$ (**9**), which is not directly available by photolysis; it was previously obtained from $Fe(C_6H_6)(PMe_3)_2$ generated by metal vapor synthesis.[4b]

In summary, we have developed synthetic procedures for the preparation of new substituted iron–carbene complexes. The access to different ligands at the metal center should allow better control of reactivity, and in particular the presence of a labile ligand should provide a new field for investigation.

Experimental Section

General Data. All manipulations were carried out under an argon atmosphere with Schlenk or glovebox techniques. Solvents were dried and distilled under nitrogen before use by standard methods. Photolysis experiments were carried out by using a Hanovia 450-W Hg lamp. NMR spectra (^1H, ^{13}C, ^{31}P) were recorded on Bruker WP-80 or AC 3000 spectrometers by S. Sinbandhit (CRMPO, Rennes). Infrared spectra were obtained with a Nicolet 205 FT-IR spectrometer. Microanalyses were performed by the "Centre de Microanalyse du CNRS" at Vernaison, France. $[Fe(Cp^*)(CO)_2(=C(OMe)Me)][CF_3SO_3]$ was prepared by the literature procedure.[2d]

Preparation of $[Fe(Cp^*)(CH_3CN)(CO)(=C(OMe)Me)][CF_3SO_3]$ (2). In a Schlenk tube, a CH_3CN (10 mL) solution of 454 mg (1 mmol) of $[Fe(Cp^*)(CO)_2(=C(OMe)Me)][CF_3SO_3]$ (**1**) was irradiated under stirring for 6 h. The initial yellow solution became orange. The solvent was concentrated, and compound **2** was precipitated out and washed with diethyl ether (3 × 30 mL). Recrystallization from CH_2Cl_2/diethyl ether provided 373 mg (80%) of compound **2**. ^1H NMR ($CDCl_3$): δ 4.58 (s, 3H, OMe), 2.89 (s, 3H, Me), 2.45 (s, 3H, CH_3CN), 1.62 (s, 15H, C_5Me_5). $^{13}C[^1H]$ NMR ($CDCl_3$): δ 343.9 (=C), 217.0 (CO), 131.6 (CN), 96.3 (C_5Me_5), 65.7 (OMe), 42.4 (Me), 9.2 (C_5Me_5), 4.8 (CH_3-

(9) Adams, H.; Bailey, N. A.; Bentley, G. W.; Hough, G.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1991**, 749. Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349. Bailey, N. A.; Dunn, D. A.; Foxcroft, C. N.; Harrison, G. R.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1988**, 1449.

CN). IR (CH_2Cl_2): 1976 (s, ν_{CO}), 2293 (m, ν_{CN}) cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_5FeNSF_3$: C, 43.70; H, 5.18. Found: C, 43.31; H, 5.04.

Preparation of [Fe(Cp*)(CH_3CN)$_2$(=C(OMe)Me)][CF_3SO_3] (3). A CH_3CN solution of 1.59 g (3.5 mmol) of [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF_3SO_3] (1) was photolyzed for 4 h. The solvent was removed by a trap to trap procedure, and the residue was washed with diethyl ether (3 × 30 mL). Compound 3 was recovered as a brown powder (1.60 g, 95%). ^1H NMR (CD_3CN): δ 4.71 (s, 3H, OMe), 2.86 (s, 3H, Me), 2.03 (br s, CH_3CN/CD_3CN), 1.42 (s, 15H, C_5Me_5). $^{13}C[^1H]$ NMR (CD_3CN): δ 360.8 (=C), 138.8 (broad s, CH_3CN/CD_3CN), 88.4 (C_5Me_5), 66.0 (OMe), 43.5 (Me), 9.3 (C_5Me_5), 2.7 (CH_3CN/CD_3CN). IR (Nujol): 2267.5 (m, ν_{CN}) cm^{-1}. Anal. Calcd for $C_{18}H_{27}O_4FeN_2SF_3$: C, 45.01; H, 5.67. Found: C, 45.08; H, 5.58.

Preparation of Phosphine-Substituted Complexes [Fe(Cp*)(L)(L')(=C(OMe)Me)][CF_3SO_3] (4, L = L' = PMe_3; 5, L = CH_3CN, L' = PPh_3). The appropriate phosphine (PMe_3 in excess or 263 mg (1 mmol) of PPh_3) was added to a CH_3CN solution of 480 mg (1 mmol) of the carbene complex 3 and the mixture stirred at room temperature for 1 h. The solvent was evaporated to dryness, and the resulting solid residue was washed with ether. The orange powder was then crystallized in a CH_2Cl_2/diethyl ether mixture.

[Fe(Cp*)(PMe_3)$_2$(=C(OMe)Me)][CF_3SO_3] (4): orange microcrystals; yield, 85%; ^1H NMR (CD_2Cl_2) δ 4.09 (s, 3H, OMe), 2.58 (s, 3H, Me), 1.64 (s, 15H, C_5Me_5), 1.30 (virtual t, $^2J_{P-H}$ 4 Hz, 18H, PMe_3); $^{13}C[^1H]$ NMR (CD_2Cl_2) δ 329.4 (t, $^2J_{P-C}$ 28 Hz, =C), 94.7 (C_5Me_5), 60.8 (OMe), 41.8 (Me), 21.0 (t, $^1J_{P-C}$ 13 Hz, PMe_3), 11.5 (C_5Me_5); $^{31}P[^1H]$ NMR (CD_2Cl_2/H_3PO_4 ext) δ 26.5 (PMe_3). Partial decomplexation of PMe_3 precludes a satisfactory analysis of 4.

[Fe(Cp*)(CH_3CN)(PPh_3)(=C(OMe)Me)][CF_3SO_3] (5): orange microcrystals; yield, 75%; ^1H NMR (CD_2Cl_2) δ 7.41–7.23 (2 × m, 15H, Ph), 4.07 (s, 3H, OMe), 2.26 (s, 6H, Me and CH_3CN), 1.27 (s, 15H, C_5Me_5); $^{13}C[^1H]$ NMR (CD_2Cl_2) δ 354.1 (d, $^2J_{P-C}$ 32.6 Hz, =C), 134.0 (d, $^1J_{P-C}$ 39 Hz, C_{ipso} Ph), 133.8 (d, $^2J_{P-C}$ 10 Hz, C_{ortho} Ph), 132.5 (CH_3CN), 130.7 (C_{para} Ph), 128.8 (d, $^3J_{P-C}$ 9 Hz, C_{meta} Ph), 90.8 (C_5Me_5), 63.9 (OMe), 39.5 (Me), 9.5 (C_5Me_5), 5.3 (CH_3CN); $^{31}P[^1H]$ NMR (CD_2Cl_2/H_3PO_4 ext) δ 64.2 (PPh_3); IR (Nujol) 2251 (m, ν_{CN}) cm^{-1}. Anal. Calcd for $C_{34}H_{39}O_4FePNSF_3$: C, 58.21; H, 5.60. Found: C, 58.10; H, 5.75.

Preparation of [Fe(Cp*)(CO)(PPh_3)(=C(OMe)Me)][CF_3SO_3] (6). Near-UV photolysis of 1.36 g (3 mmol) of 1 with 1.00 g (3.3 mmol) of PPh_3 in CH_2Cl_2 was carried out for 2 h. After evaporation of the solvent in vacuo, the residue was recrystallized from CH_2Cl_2/diethyl ether. Yellow microcrystals were collected (1.86 g, 90%). ^1H NMR ($CDCl_3$): δ 7.49–7.31 (2 × m, 15H, Ph), 4.25 (s, 3H, OMe), 2.38 (s, 3H, Me), 1.55 (s, 15H, C_5Me_5). $^{13}C[^1H]$ NMR ($CDCl_3$): δ 347.2 (d, $^2J_{P-C}$ 24 Hz, =C), 218.6 (d, $^2J_{P-C}$ 24 Hz, CO), 135.3 (d, $^4J_{P-C}$ 3 Hz, C_{para} Ph), 133.1 (d, $^3J_{P-C}$ 11 Hz, C_{meta} Ph), 130.6 (d, $^2J_{P-C}$ 13 Hz, C_{ortho} Ph), 128.9 (d, $^1J_{P-C}$ 9.9 Hz, C_{ipso} Ph), 97.3 (C_5Me_5), 67.0 (OMe), 44.8 (Me), 9.5 (C_5Me_5). $^{31}P[^1H]$ NMR ($CDCl_3/H_3PO_4$ ext): δ 62.6 (PPh_3). IR (CH_2Cl_2): 1953 (s, ν_{CO}) cm^{-1}. Anal. Calcd for $C_{33}H_{36}O_5FePSF_3$: C, 57.57; H, 5.27. Found: C, 57.72; H, 5.23.

Preparation of [Fe(Cp*)(CO)(PPh_3)(C(O)Me)] (7). A solution of 689 mg (1 mmol) of 6 in CH_2Cl_2 (10 mL) with 369 mg (1 mmol) of [$^nBu_4N$][I] was stirred at room temperature for 10 min. After evaporation of the solvent, the residue was extracted with pentane. A yellow solid was recovered: 514 mg (98%). ^1H NMR ($CDCl_3$): δ 7.32–7.10 (2 × m, 15H, Ph), 1.95 (s, 3H, Me), 1.39 (s, 15H, C_5Me_5). IR (CH_2Cl_2): 1896 (s, ν_{CO}), 1590 (s, ν_{C-O}) cm^{-1}.

Reaction of [Fe(Cp*)(CH_3CN)(CO)(=C(OMe)Me)][CF_3SO_3] (2) with [$^nBu_4N$][I]: Characterization of [Fe(Cp*)(I)(CO)(=C(OMe)Me)] (8). In a Schlenk tube containing 467 mg (1 mmol) of 2 and 406 mg (1.1 mmol) of [$^nBu_4N$][I] was added, at −80 °C, 10 mL of CH_2Cl_2. The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane. ^1H NMR analysis of the crude product indicated that 8 and [Fe(Cp*)(CO)$_2$Me] were formed in a 35:65 ratio. Sublimation (30 °C, 10^{-2} mmHg) of the resulting mixture allowed the separation of these two compounds. The nonvolatile fraction was then extracted with pentane, and concentration gave pure compound 8. The methyl derivative was identified by comparison of its spectral properties with those of an authentic sample.[6]

[Fe(Cp*)(I)(CO)(=C(OMe)Me)] (8). ^1H NMR ($CDCl_3$): δ 4.38 (s, 3H, OMe), 3.18 (s, 3H, Me), 1.80 (s, 15H, C_5Me_5). $^{13}C[^1H]$ NMR ($CDCl_3$): δ 343.5 (=C), 222.5 (CO), 95.6 (C_5Me_5), 63.2 (OMe), 46.2 (Me), 10.4 (C_5Me_5). IR (Nujol): 1942 (s, ν_{CO}) cm^{-1}. Anal. Calcd for $C_{14}H_{21}O_2IFe$: C, 41.62; H, 5.24. Found: C, 41.62; H, 5.23.

Preparation of [Fe(Cp*)(PMe_3)$_2$(CH_2CH_3)] (9). In a Schlenk tube containing 550 mg (1 mmol) of [Fe(Cp*)(PMe_3)$_2$(=C(OMe)Me)][CF_3SO_3] (4) and 57 mg (1.5 mmol) of $NaBH_4$ was added, at −80 °C, 10 mL of THF. The resulting mixture was stirred for 3 h; the solvent was removed, and the reaction product was extracted with pentane (3 × 10 mL). Evaporation of the solvent gave 250 mg (67%) of an oil of which ^1H and ^{13}C NMR data are identical to those described in the literature for [Fe(Cp*)(PMe_3)$_2$(CH_2CH_3)].[4b]

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