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Preliminary communication

Diisopropylaminomethylidyne complexes of iron, chromium, molybdenum and tungsten *

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Abstract

Treatment of $[M(CO)_n]$ ($n = 6$, M = Cr, Mo, W; $n = 5$, M = Fe) successively with LiN^iPr_2, $(CF_3CO)_2O$, and PPh_3 leads to the thermally stable diisopropylaminomethylidyne complexes $[M(\equiv CN^iPr_2)(O_2CCF_3)(CO)_3(PPh_3)]$ (M = Cr, Mo, W) and $[Fe(\equiv CN^iPr_2)(O_2CCF_3)(CO)_2(PPh_3)]$ in high yield. The latter is the first neutral mononuclear carbyne complex of iron.

The chemistry of terminal alkylidyne metal complexes $[L_nM(\equiv CR)]$ has developed rapidly in recent years, especially because of the realisation that these complexes are versatile precursors for the systematic assembly of polymetallic ensembles [1]. The growth in this field has, however, been limited to metals from Groups 5–7 and the heavier members of Group 8. Fischer has prepared and structurally characterised a cationic aminomethylidyne complex $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]^+$ obtained via alkoxide abstraction from the carbene complex $[Fe\{=C(N^iPr_2)OEt\}(CO)_3(PPh_3)]$ [2], and arylmethylidyne complexes of ruthenium and osmium are accessible via the reaction of aryl lithiums with the dichlorocarbene complexes $[MCl_2(CO)(=CCl_2)(PPh_3)_2]$ (M = Ru, Os) [3], but the absence to date of synthetic routes to the corresponding iron complex $[FeCl_2(CO)(=CCl_2)(PPh_3)_2]$ precludes the extension of this method to iron. We report here an expedient one-pot procedure for the synthesis of a range of diisopropylaminomethylidyne complexes of the form $[M(\equiv CN^iPr_2)(O_2CCF_3)(CO)_n(PPh_3)]$ (M = Cr, Mo, W, $n = 3$; M = Fe, $n = 2$).

Following its introduction by Mayr and co-workers [4], trifluoroacetic anhydride has proved to be a useful reagent for the conversion of Group 6 metal acylates into alkylidyne complexes [4]. We find that a similar strategy provides a route to dialkylaminomethylidyne complexes if suitable ligands are introduced to stabilise

* Dedicated to Professor F.G.A. Stone with best wishes on the occasion of his 65th birthday.

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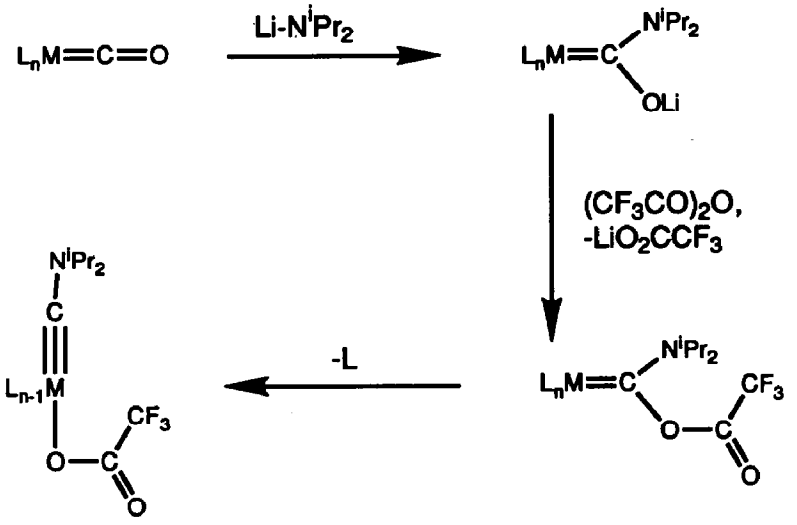
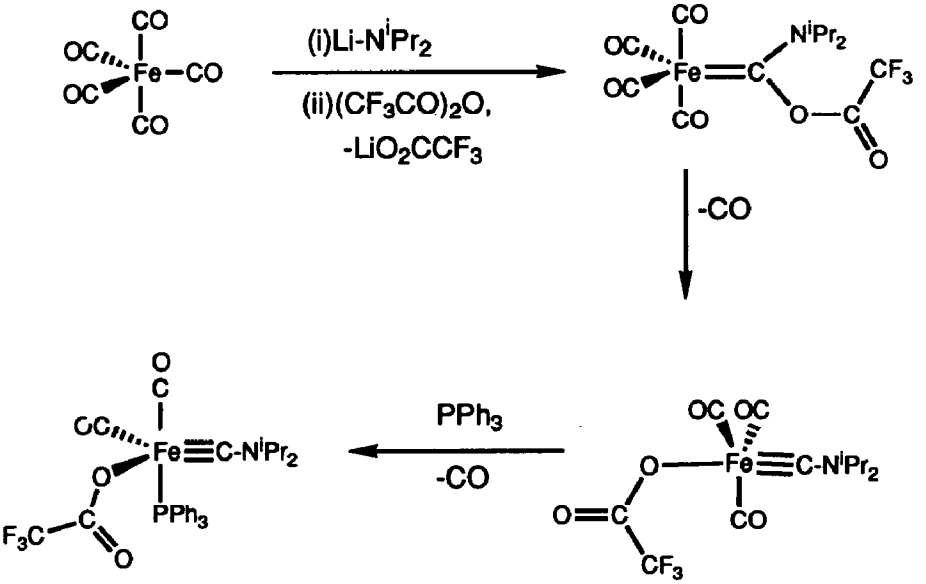


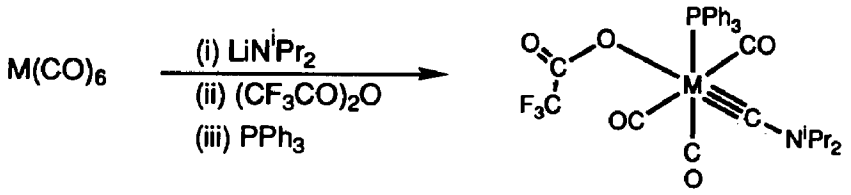
Scheme 1. Diisopropylaminomethylidyne synthesis via oxide abstraction.

the labile intermediate (Scheme 1). Reaction of iron pentacarbonyl with lithium diisopropylamide (LDA) in diethyl ether solution gives the acylate complex $[Fe\{C(O)N^iPr_2\}(CO)_4]Li$, which is subsequently treated with one equivalent of trifluoroacetic anhydride ($-78°C$) to give a solution of a species we assume to be $[Fe(\equiv CN^iPr_2)(O_2CCF_3)(CO)_3]$ [IR(CH_2Cl_2): $\nu(CO)_{max}$ 2086, 2034, 1996 cm^{-1}]. Addition of an excess of triphenylphosphine and slow warming to room temperature affords a precipitate of the yellow complex $[Fe(\equiv CN^iPr_2)(O_2CCF_3)(CO)_2(PPh_3)]$ (**1**) [5*] (Scheme 2), the first neutral mononuclear carbyne complex of



Scheme 2. Synthesis of a diisopropylaminomethylidyne complex of iron.

* Reference number with asterisk indicates a note in the list of references.



Scheme 3. Synthesis of diisopropylaminomethylidyne complexes of Group 6 metals (M = Cr, Mo, W).

iron. Spectroscopic data for **1** include three doublet resonances in the ^{13}C-{^1H} NMR to low field at δ 217.4, 210.8 and 196.2 ppm, with couplings to phosphorus of 18, 16, and 18 Hz, respectively. It is not possible to unequivocally assign these resonances, which are due to the methylidyne and two chemically distinct carbonyl carbon nuclei, but that at lower field is presumably due to the alkylidyne carbon. The signals may be compared to the corresponding signals observed at δ 264.7 (Fe≡C) and 203.8 ppm (FeCO) for the cationic complex $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]^+$ [2].

Analogous treatment of the Group 6 metal hexacarbonyls gives the mono(phosphine) complexes *mer*-$[M(\equiv CN^iPr_2)(O_2CCF_3)(CO)_3(PPh_3)]$ [M = Cr(**2a**), Mo (**2b**), W (**2c**)] [6*] (Scheme 3) in high yield. The diisopropylamino group was chosen because of the expected hyperconjugative and steric stabilising effects that this class of substituent displays in alkylidyne chemistry [7*]. This proved a good choice, and the diisopropylaminomethylidyne complexes of iron and the Group 6 metals are thermally stable at room temperature in dichloromethane solution. We are currently investigating the extension of this work to hydrocarbylmethylidyne complexes of iron.

References and notes

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3 (a) G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Am. Chem. Soc., 102 (1980) 6570; (b) G.R. Clark, N.R. Edmonds, R.A. Pauptit, W.R. Roper and A.H. Wright, J. Organomet. Chem., 244 (1983) C57; (c) W.R. Roper, J. Organomet. Chem., 300 (1986) 167; (d) M.A. Gallop and W.R. Roper, Adv. Organomet. Chem., 25 (1986) 121.

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5 Spectroscopic data for **1** (yellow): IR (CH_2Cl_2) 2021, 1951 cm^{-1} [ν(CO)]; ^1H NMR ($CDCl_3$), δ 1.13 (m, 12 H, NCHMe_2), 3.30 (m, 2 H, NCHMe$_2$), 7.35 (m, 15 H, PC_6H_5); ^{13}C-{^1H} NMR ($CDCl_3$), δ 217.4 [d, J(PC) 18 Hz, Fe≡C], 210.8 [d, J(PC) 16 Hz, CO], 196.2 [d, J(PC) 18 Hz, CO], 136.5, 132.6, 132.5, 129.8, 129.2, 128.0, 127.8 [PPh_3], 54.0, 47.0 [s×2, NCHMe$_2$], 19.8, 19.5, 19.2, 19.0 [s×4, NCHMe_2]; ^{31}P NMR ($CDCl_3$) 49.8 [q, J(PF) 27.2 Hz]; FAB-MS: m/z 337 $[M-PPh_3]^+$.

6 Spectroscopic data for *mer*-**2a** (yellow): IR (CH_2Cl_2) 2048, 1973, 1931 [ν(CO)]; ^1H NMR ($CDCl_3$), δ 1.10 (d, 12 H, J(HH) 7 Hz, NCHMe_2), 2.96 (m, 2 H, NCH Me$_2$), 7.44, 7.68 (m×2, 15 H, PC_6H_5); ^{13}C-{^1H} NMR ($CDCl_3$), δ 238.2 [d, J(PC) 7.2 Hz, W≡C], 204.7 [d, J(PC) 39.5 Hz, CO *trans* to P], 200.6 [d, J(PC) 7.2 Hz, CO *cis* to P], 135.1, 134.2, 134.0, 130.2, 128.4, 128.2 [PPh_3], 49.1 [s, NCHMe$_2$], 22.7, 22.0 [s×2, NCHMe_2]; FAB-MS:. m/z 667 $[M-2^iPr]^+$, 641 $[M-2^iPr-CO]^+$, 612 $[M-2^iPr-2CO]$.

7 A resonance contribution from $[^-M{=}C{=}NR_2{}^+]$ must be considered in addition to the alkylidyne $[M{\equiv}CNR_2]$ representation, and accordingly these ligands may be also be viewed as alkylated isonitriles; e.g., see H.P. Kim and R.J. Angelici, Adv. Organomet. Chem., 27 (1987) 51.