Two Counterintuitive Routes to an Iron Alkylidyne Complex

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Summary: The cationic aminomethylidyne complex $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]^+$ *has been prepared by two unexpected routes: (i) Iodination of the carbamoyl complex* $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ *and (ii) O-trifluoroacetylation of the carbamoylate* $[Fe\{C(=O)N^iPr_2\}(CO)_4]Li$*, a reaction which shows an unusual solvent dependence.*

Alkylidyne complexes of group 8[1] remain very rare, with only one example known for iron.[2] Recent advances in the chemistry of osmium[3] in addition to Roper's studies on the complexes $[M(\equiv CR)Cl(CO)(PPh_3)_2]$[4,5] would however suggest that there is nothing inherently unstable about late transition metal alkylidynes, merely that many of the synthetic routes used for groups 5–7 are not *generally* applicable to the later transition metals. We have been concerned recently with the preparation of alkylidyne complexes of iron. These efforts are based on the realization that if alkylidyne complexes are to have the extensive application to stoichiometric organic synthesis enjoyed by alkylidene complexes, economic and expedient synthetic strategies are required. We have previously attempted, unsuccessfully, to adapt Mayr's oxide-abstraction approach[6] to iron(0) acylates.[7] Our failure resulted from a generally encountered problem with the *O*-alkylation of acylate complexes of the form $[Fe\{C(=O)R\}(CO)_4]^-$, this being that the metal center offers an alternative site for electrophilic attack by any but the hardest of electrophiles. Thus the sequential treatment of $[Fe(CO)_5]$ with LiN^iPr_2, $(CF_3CO)_2O$, and PPh_3 in diethyl ether provides $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1**)[7] rather than the desired alkylidyne complex $[Fe(\equiv CN^iPr_2)(O_2CCF_3)(CO)_2(PPh_3)]$. Semmelhack has discussed the effect of solvent on the *O*- vs *Fe*-alkylation of acyl complexes of iron and shown that very hard electrophiles and strongly solvating solvents (thf, HMPA) favor attack at the oxygen atom of the acyl ligand and the formation of alkylidene complexes.[8] In applying these ideas to the reaction of $[Fe\{C(=O)N^iPr_2\}(CO)_4]^-$ (**2**) with $(CF_3CO)_2O/PPh_3$, we have met with comprehensive failure. For a variety of thf, Et_2O, and HMPA solvent combinations the only products observed were $[Fe(CO)_3(PPh_3)_2]$ and $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1**). It was therefore with some surprise that we find that if the carbamoylate (**2**) (preformed in diethyl ether) is dissolved in dichloromethane and treated with $(CF_3CO)_2O$ and PPh_3, the product isolated in moderate yield is the salt $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)](O_2CCF_3)$ (**3a**) (13% based on 15 mmol of $[Fe(CO)_5]$)[9a] in addition to $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2](O_2CCF_3)$ (**4a**) (3%).[10] The latter complex may be prepared independently, and in high yield, as the BF_4^- salt (**4b**) from the reaction of $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1**) with HBF_4 to provide $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_3(PPh_3)](BF_4)$ (**5**)[11] followed by treatment with PPh_3 which results in substitution of one carbonyl ligand. Alternatively reaction of **2** with iodine and triphenylphosphine provides the iodo complex $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ (**6**)[12] and the halide of this complex may be abstracted with $AgBF_4$ in the presence of CO to provide **5**. The ultimate retention of the η^2-

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[1] Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. For a recent review of group 8 alkylidyne complexes, see: Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 7.

[2] Fischer, E. O.; Schneider J.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1820.

[3] Hodges, L. H.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 37. Lapointe, A. M.; Schrock, R. R. *Organometallics* **1993**, *12*, 3379.

[4] Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167.

[5] Roper, W. R. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; pp 155–168.

[6] Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 458.

[7] Anderson, S.; Hill, A. F.; Clark, G. R. *Organometallics* **1992**, *11*, 2323.

[8] Semmelhack, M. F.; Tamura, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

[9] (a) $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]O_2CCF_3$ (**3a**): $[Fe(CO)_5]$ (3.0 g, 15 mmol) was diluted in diethyl ether (50 cm^3) under nitrogen and LiN^iPr_2 (10.2 cm^3, 1.5 mol dm^{-3} in hexane, 15 mmol) added dropwise. The ether was removed in vacuo, the residue was redissolved in dry CH_2Cl_2, the solution was cooled (dry ice/acetone), and a solution of $(CF_3CO)_2O$ (2.4 cm^3, 17 mmol) in ether (20 cm^3) was added dropwise. After the solution was stirred for 15 min, PPh_3 (6.0 g, 23 mmol) was added and the mixture allowed to warm slowly to room temperature to provide an oily precipitate. Petroleum ether (40–60) (25 cm^3) was added and the reaction mixture filtered through Celite. The filtrate was concentrated and cooled to −30 °C to provide **4** [Yield: 0.24 g (2.5%)].[10] The yellow precipitate remaining on the Celite was then eluted through with THF, diluted with petroleum ether, and cooled (−30 °C) to provide **3a**. Yield: 1.2 g (13%). (b) $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]I$ (**3c**): Iodine (0.17 g, 0.68 mmol) and **1** (0.39 g, 0.68 mmol) were combined under nitrogen. Diethyl ether (30 cm^3) was then added and the mixture stirred for 3 h. The gray precipitate which formed was isolated and extracted into CH_2Cl_2/petrol (2:1), and the extracts were filtered through Celite. On concentration of the solution under vacuum, the product crystallized. Yield: 0.16 g (36%). (c) Data for $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]X$ [X = CF_3CO_2, (**3a**), I (**3c**)] are as follows. IR: CH_2Cl_2, 2083, 2034, 2012 (CO), 1664 cm^{-1} (CN); Nujol, 2079, 2041, 1992 (CO), 1642 (CN) cm^{-1}. NMR [$(CD_3)_2CO$, 25 °C]: ^1H, δ 1.17 [d, 12 H, $CHMe_2$, $J(HH)$ 6.3 Hz], 3.96 [h, 2 H, CH Me$_2$], 7.58–7.76 [m, 15 H, C_6H_5] ppm; $^{13}C\{^1H\}$, 266.5 [d, Fe$\equiv$C, J (PC) 42.8 Hz], 206.5 [d, FeCO, J(PC) not resolved], 134.4–130.3 [C_6H_5], 58.5 [s, $CHMe_2$], 22.0 [s, $CHMe_2$,] ppm; $^{31}P\{^1H\}$, 58.4 ppm. These data are essentially identical to those reported[2] for **3b**. FAB-MS (nba matrix, correct isotope patterns): m/z = 514, [M]$^-$, 486 [M − CO]$^+$, 458 [M − 2(CO)]$^+$, 318 $[FePPh_3]^+$ (M refers to the cationic complex).

[10] $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2]BF_4$ (**4**): PPh_3 (0.13 g, 0.5 mmol) and **5**[11] (0.20 g, 0.30 mmol) were heated in refluent THF (20 cm^3) for 1 h, and then the THF was removed under vacuum. The residue was titurated ultrasonically with diethyl ether (30 cm^3) and the resulting yellow solid recrystallized from CH_2Cl_2/petroleum ether. Yield: 0.16 g (58%). IR: CH_2Cl_2, 2039, 1968 (CO), 1605 cm^{-1} (NCO); Nujol, 2026, 1960 (CO), 1612 (NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 0.08, 1.03 [d × 2, 12 H, $CHMe_2$], 3.06, 5.16 [h × 2, 2 H, $CHMe_2$], 7.33–7.53 [m, 30 H, C_6H_5] ppm; $^{13}C\{^1H\}$, 214.0 [t, FeCO, J(PC) 30.1 Hz], 211.4 [t, FeCO, J(PC) 21.3 Hz], 184.0 [t, OCN, J(PC) 23.0 Hz], 133.6–129.4 [C_6 H$_5$, virtual triplicity of $C^1(C_6H_5)$ confirms *trans* FeP_2], 56.2, 49.6 [$CHMe_2$], 21.5, 19.2 [$CHMe_2$] ppm; $^{31}P\{^1H\}$, 54.6 ppm. FAB-MS (nba matrix, correct isotope patterns): m/z = 764[M]$^+$, 708 [M − 2(CO)]$^+$, 580 $[Fe(PPh_3)_2]^+$ [M refers to complex cation].

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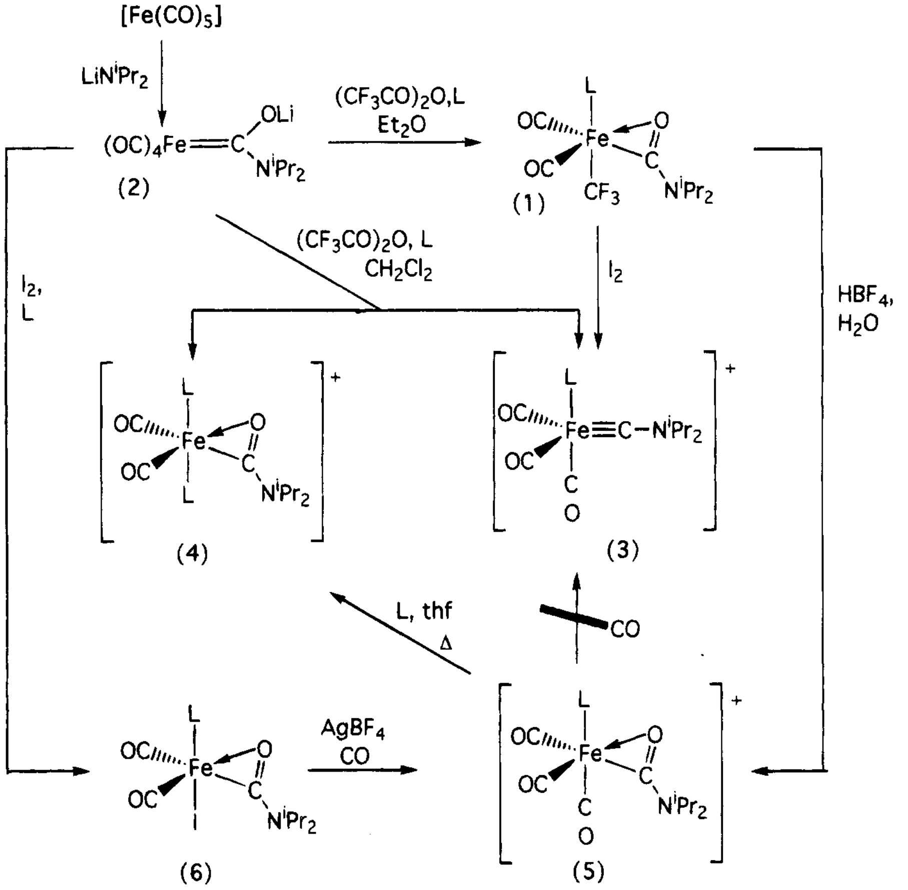
Scheme 1. Synthesis and Interconversion of Carbamoyl and Aminomethylidyne Complexes of Iron (L = PPh$_3$)



carbamoyl coordination mode in these transformations is noteworthy, although η^1 intermediates cannot yet be excluded.

The salt $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)](BCl_4)$ (**3b**) has been reported by Fischer[2] as resulting from the reaction of $[Fe\{=C(OEt)N^iPr_2\}(CO)_3(PPh_3)]$ with BCl_3. Fischer's multistep procedure requires comparatively sophisticated synthetic techniques. Clearly the procedure described here offers considerable economy and expedience; however, we have subsequently found an even more convenient if somewhat more curious route to this complex. The carbamoyl complex $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1**) reacts cleanly with iodine to produce $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]I$ (**3c**) (Scheme 1)[9b] (36% nonoptimized yield based on 0.68 mmol of precursor). If the somewhat arbitrary description of an alkylidyne ligand as $[CR]^+$ (isolobal with $[NO]^+$) is accepted, we are faced with a situation where iodine has acted *formally* as a reductant [Fe(II) → Fe(0)].[13] The nature of the salt **3c** was not initially appreciated, and so we can confidently say that it is stable in the solid state for up to 3 years.

We are still investigating and somewhat equivocal about the actual mechanism by which this unusual transformation takes place; however, the following observations should be noted: The trifluoromethyl group is of critical importance, since no **3c** is obtained from the reaction of $[Fe\{C(=O)N^iPr_2\}(CO)_4]^-$ (**2**) with I_2 and PPh_3, or preformed I_2PPh_3, the sole product being the new complex $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ (**6**).[12] This is also the product of the reaction of $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)]$[7] with iodine.[14] Furthermore,

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(11) $[Fe\{\eta^2\text{-}OCN^iPr_2\}(CO)_3(PPh_3)]BF_4$ (**5**): To **1** (1.00 g, 1.75 mmol) in diethyl ether (50 cm^3) was added $HBF_4(aq)$ (0.12 mL {wt/mL = 1.31 g}, 1.75 mmol). A bright yellow precipitate slowly formed which was isolated and then recrystallized from CH_2Cl_2/petroleum ether. Yield: 0.89 g (82%). IR: CH_2Cl_2, 2102, 2058, 2023 cm^{-1} (CO): 1650 cm^{-1} (NCO); Nujol, 2099, 2053, 2011 cm^{-1} (CO); 1652 cm^{-1} (NCO). NMR ($CDCl_3$, 25 °C): ^1H, δ 0.55, 1.24, 1.36, 1.45 [4 × d (br), 12H, $CH\mathit{Me}_2$], 3.64, 4.68 [2 × h, 2H, $C\mathit{H}Me_2$], 7.30, 7.53 [2 × m, 15H, $C_6\mathit{H}_5$]; $^{13}C\{^1H\}$, 206.6 [d, Fe*C*O, *J*(PC) 31.4 Hz], 202.2 [d, Fe*C*O, *J*(PC) 26.5 Hz], 197.1 [d, Fe*C*O, *J*(PC) 51.0 Hz], 185.9 [d, O*C*N, *J*(PC) = 18.8 Hz], 133.2–127.5 [C_6H_5], 56.7, 50.3 [2 × s, *C*HMe$_2$], 21.8, 19.7, 19.4, 19.1 ppm [4 × s, $CH\mathit{Me}_2$]; $^{31}P\{^1H\}$, 22.4 ppm. FAB-MS: $m/z = 530\ [M]^+$, 502 $[M' - CO]^+$, 474 $[M' - 2CO]^+$, 446 $[M' - 3CO]^+$, 318 $[FePPh_3]^+$ [M refers to complex cation].

(12) $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ (**6**): To $[Fe(CO)_5]$ (3.0 g, 15 mmol) in diethyl ether (50 cm^3) was added LiN^iPr_2 (1.5 mol dm^{-3} in hexane, 10.2 cm^3, 15 mmol) dropwise. The reaction mixture was cooled (dry ice/acetone) and I_2 (3.88 g, 15 mmol) added. When all the iodine had dissolved, PPh_3 (6.0 g, 23 mmol) was added, and the reaction was left to warm slowly to room temperature. The resulting purple precipitate was isolated and extracted with CH_2Cl_2/petroleum ether (2:1). The combined extracts were filtered through Celite and chromatographed (silica gel, −40 °C). Concentration and cooling of the purple band eluted with CH_2Cl_2 provided **6**. Yield: 6.9 g (72%). Yield: 8.5 g (88%) using preformed I_2PPh_3. IR: CH_2Cl_2, 2017, 1958 (CO), 1634, 1614 cm^{-1} (NCO); Nujol, 2012, 1964 (CO), 1634 (NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 1.28, 1.41, 1.46, 1.53 [d × 4, 12 H, $CH\mathit{Me}_2$], 3.87, 4.67 [h × 2, 2H, $C\mathit{H}Me_2$], 7.34–7.69 [m, 15 H, $C_6\mathit{H}_5$] ppm; $^{13}C\{^1H\}$, 218.6 [d, Fe*C*O, *J*(PC) 26.8 Hz], 210.4 [d, Fe*C*O, *J*(PC) 21.4 Hz], 197.4, O*C*N, *J*(PC) 19.7 Hz], 134.2–127.4 [C_6H_5], 53.8, 49.5 [*C*HMe$_2$], 21.7, 21.4, 20.9, 20.7 [$CH\mathit{Me}_2$] ppm; $^{31}P\{^1H\}$, 78.5 ppm. FAB-MS (nba matrix, correct isotope patterns): $m/z = 629\ [M]^+$, 573 $[M - 2(CO)]^+$, 445 $[FeI(PPh_3)]^+$.

(13) The assignment of formal oxidation states for alkylidyne–carbyne complexes offers more debate than utility, with both extremes $[\equiv CR]^{3-}$ and $[\equiv CR]^+$ having their proponents. If infrared data of carbonyl coligands are taken as indicative of metal electron density, then the effect of an alkylidyne ligand on a metal center is most comparable to that of a linear nitrosyl, *i.e.*, $[CR]^+$ isolobal with $[NO]^+$, *e.g.*, see ref 5. The alternative trianionic formulation would make the compound **3** a somewhat implausible tricarbonyl derivative of tetravalent iron.

as the complexes **5** and **6** are isolable and indefinitely stable, they may be excluded as intermediates.

The two approaches to the synthesis of thermally stable iron alkylidyne complexes presented here, while surprising, do further illustrate that late transition metal alkylidynes can be easily prepared if suitable synthetic strategies can be found, which need not have precedent in the chemistry of groups 5–7. Furthermore, the expedient methods described do not require sophisticated preparative techniques, are economic, and may be carried out on large scales using commercially available starting materials. We hope that these factors will facilitate the study of these complexes as synthons in organic synthesis, and we are currently exploring this avenue, in particular with respect to C–C bond-forming processes.

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(14) Anderson, S.; Berridge, T.; Hill, A. F. Unpublished observations.