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Carbamoyl (Carboxamido) Complexes as Precursors for Metallaoxetene, Isonitrile, and Aminomethylidyne Complexes of Iron

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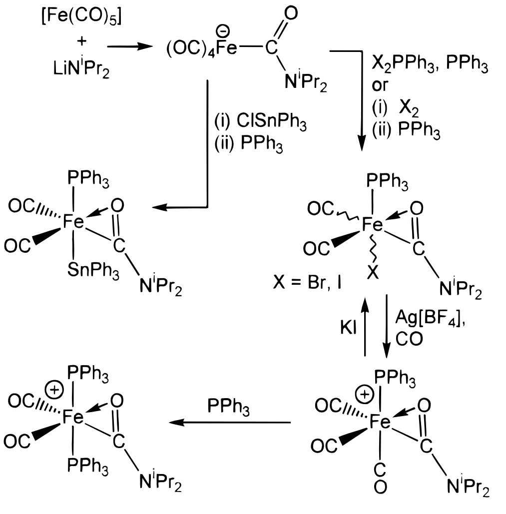
The reaction of $[Fe\{C(=O)N^iPr_2\}(CO)_4]Li$ with $(CF_3CO)_2O$ in diethyl ether followed by triphenylphosphine provides carbamoyl complexes $[Fe\{\eta^2\text{-}OCN^iPr_2\}(CF_3)(CO)_2(PPh_3)]$ (**1**) or $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2](O_2CCF_3)$ (**2a·O₂CCF₃**) depending on the reaction conditions. The same procedure performed in dichloromethane provides the aminomethylidyne complex $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)](O_2CCF_3)$ (**5·O₂CCF₃**) as well as traces of $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2](O_2CCF_3)$ (**2a·O₂CCF₃**). The reactions of **1** with moist $AgBF_4$ or HBF_4 provide $[Fe\{\eta^2\text{-}OCN^iPr_2\}(CO)_3(PPh_3)]BF_4$ (**2b·BF₄**), via a putative difluorocarbene intermediate, $[Fe\{\eta^2\text{-}OCN^iPr_2\}(=CF_2)(CO)_2(PPh_3)]BF_4$. In a similar manner, $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)(dppe)]$ (**3**) (obtained from **1** and dppe) reacts with $HBF_4(aq)$ to provide $[Fe\{\eta^2\text{-}OCN^iPr_2\}(CO)_2(dppe)]BF_4$ (**4·BF₄**). A difluorocarbene complex is also implicated in the formation of the ferraoxetene $[Fe\{\kappa^2\text{-}C(N^iPr_2)OCF_2\}(CO)\{HB(pz)_3\}]$ (**6**) (pz = pyrazol-1-yl), which results from treatment of **1** with $K[HB(pz)_3]$ under high dilution. Under more concentrated conditions $[Fe\{HB(pz)_3\}_2]$ is obtained. The ferraoxetene undergoes an unusual acid hydrolysis with $HBF_4(aq)/CO$ to provide the isonitrile salt $[Fe(CN^iPr)(CO)_2\{HB(pz)_3\}]PF_6$ (**7·PF₆**). The salt $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]I$ (**5·I**) is the product of the reaction of **1** with iodine, via an as yet obscure mechanism, which may however also involve ferraoxetene intermediates.

Introduction

We have previously described, in brief, the synthesis of a range of bidentate carbamoyl (carboxamide) complexes of iron which are co-ligated by halide, phosphine, stannyl, and carbonyl ligands.[1] These complexes are readily obtained by the electrophilic halogenation or stannylation of $[Fe\{C(=O)N^iPr_2\}(CO)_4]Li$. The subsequent chemistry is dominated by ligand substitution reactions, which leave the bidentate mode of coordination for the carbamoyl ligand *ultimately* unchanged (Scheme 1). In this report we describe full details of the preparation of the trifluoromethyl derivative $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1**) and show that the chemistry of this species is dominated by reactions that intimately involve the carbamoyl and/or trifluoromethyl ligands, such that the carbamoyl ligand is converted into aminomethylidyne, ferraoxetene, and isonitrile groups. Aspects of the results described herein have formed the basis of preliminary reports.[1,2]

Scheme 1



Results and Discussion

The reactions of iron acylates $[Fe\{C(=O)R\}(CO)_4]^-$ with electrophiles have been studied in considerable detail.[3] Of particular relevance are the studies of Semmelhack which show that HSAB considerations may be useful in determining the preference of O- vs Fe-alkylation in reactions with carbon-based electrophiles.[4] The reactivity of the corresponding carbamoylates $[Fe\{C(=O)NR_2\}(CO)_4]^-$ has received less attention;[5,6] however Fischer has reported the in situ preparation of the iron carbamoylate salt [Fe{C(O)-

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[1] (a) Anderson, S.; Clark, G. R.: Hill, A. F. *Organometallics* **1992**, *11*, 1988. (b) Anderson, S.; Hill, A. F.; Slawin, A. M. Z.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1998**, *37*, 594.

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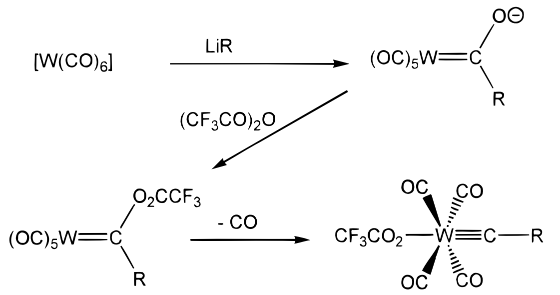
10.1021/om990385y CCC: $19.00

Scheme 2. The Mayr Alkylidyne Synthesis[8] (R = CH_3, C_6H_5)

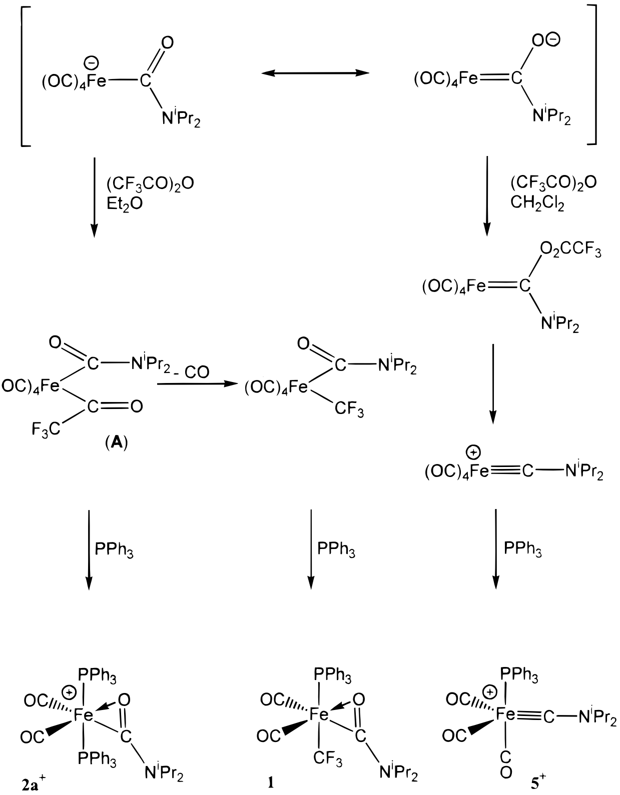


$N^iPr_2\}(CO)_4]Li$ from the reaction of $[Fe(CO)_5]$ and lithium diisopropylamide (hereafter LDA) and its reaction with $[Et_3O]BF_4$ to provide a neutral carbene complex $[Fe\{{=}C(OEt)N^iPr_2\}(CO)_4]$.[7]

Our initial studies sought to establish whether the Mayr alkylidyne synthesis (Scheme 2)[8] might be extended to group 8 metals with aminomethylidyne substituents. In Mayr's synthetic approach, oxide is formally abstracted from an anionic pentacarbonyl acyl or aroyl carbonylmetallate of group 6 metals to produce an alkylidyne complex. We have been able to successfully extend this synthesis to include aminomethylidyne,[9] ferrocenebis(methylidyne),[10] cymatrenylmethylidyne,[11] and alkynylmethylidyne[12] complexes of chromium, molybdenum, and tungsten. Furthermore the use of phosphine dihalides in place of $(CF_3CO)_2O$ provides convenient access to amino-, aryl-, and thienyl alkylidynes of tungsten and molybdenum.[13] It therefore appeared reasonable and desirable to extend this chemistry to other metal centers and in particular later transition metals. Comparatively fewer alkylidyne complexes are known for these metals, and the synthetic routes typically lack generality.[14]

Treating a diethyl ether solution of $[Fe\{C({=}O)N^iPr_2\}(CO)_4]Li$ (prepared in situ) with trifluoroacetic anhydride followed by triphenylphosphine does not in fact lead to the anticipated aminomethylidyne complex $[Fe({\equiv}CN^iPr_2)(O_2CCF_3)(CO)_2(PPh_3)]$ but rather a trifluoromethyl(carbamoyl) derivative formulated as $[Fe\{\eta^2\text{-}OCN^iPr_2\}(CF_3)(CO)_2(PPh_3)]$ (**1**) on the basis of spectroscopic and analytical data and a single-crystal X-ray diffraction study.[1a] The bidentate carbamoyl ligand gives rise to a characteristic infrared absorption at 1610 cm^{-1} (CH_2Cl_2) in addition to two terminal carbonyl associated absorptions at 2027, 1953 cm^{-1}, which indicate a *cis*-dicarbonyl arrangement. The ^{31}P NMR spectrum consists of a poorly resolved quartet showing $^3J(PF)$ coupling (27 Hz) also evident in the ^{19}F NMR spectrum, which shows a doublet, consistent with the trans disposition of CF_3 and PPh_3 ligands. The ^1H and ^{13}C NMR data associated with the carbamoyl methyl groups indicate that these are all chemically distinct.

Scheme 3



The failure of this approach to provide the desired aminomethylidyne complex may be interpreted with reference to Scheme 3. Electrophilic attack at a metal acyl complex may occur at either the acyl oxygen or the metal center, and the factors that control such reactions are still emerging. Those relevant to the present group 6/group 8 dichotomy presumably include 6 vs 5 metal coordination number, d^6 vs d^8 electron configuration, HSAB character of the electrophile, and possible steric bulk of the acyl substituent. The HSAB aspects of iron acylate alkylation have been thoroughly investigated by Semmelhack.[4] The conclusions of the study, i.e., that strongly solvating solvents (HMPA, Et_2O) and hard electrophiles ($R{-}O_3SF$, $R{-}O_3SC_6H_4Me\text{-}4$) favor O-alkylation over Fe-alkylation, were shown to be reminiscent of those for isolobal enolate anions.[15] The remaining factors pertain to the steric accessibility and nucleophilicity of the metal centers involved.

HSAB considerations usefully rationalize the regioselectivity of aryl and aroyl ferrate alkylation allowing the optimization of yields of alkoxy carbene complexes. Unfortunately, employing a range of solvent combinations with the carbamoyl ferrate analogue (thf, HMPA, and Et_2O) including the optimum conditions devised by Semmelhack (ether/HMPA, 1:4) led only to mixtures of **1** and $[Fe(CO)_3(PPh_3)_2]$. The formation in many of these

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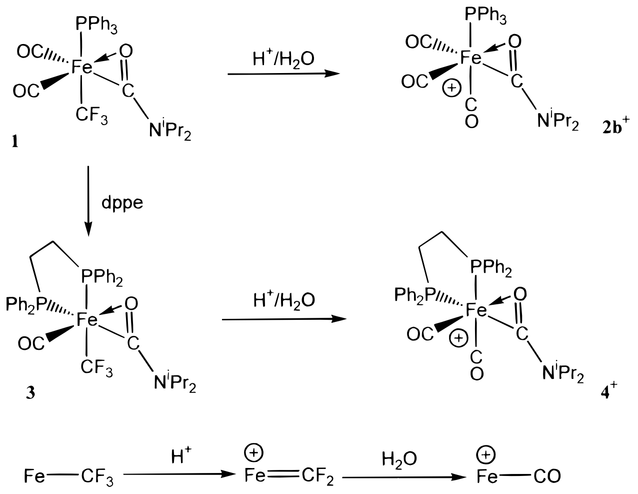
[14] Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. For a review of group 8 alkylidyne complexes see: Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Eds. Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 7.

[15] House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: New York; pp 522–529.

reactions of large amounts of $[Fe(CO)_3(PPh_3)_2]$ is perhaps surprising given that reductive elimination reactions involving trifluoroacyl and trifluoromethyl ligands are generally not facile, especially in the latter case due to the characteristically strong metal−carbon bond. The complex **1** is very stable toward addition of excess phosphine (vide infra), and so the point of mechanistic divergence leading to $[Fe(CO)_3(PPh_3)_2]$ is presumably not later than the initial product of electrophilic attack at the metal by $(CF_3CO)_2O$. A further noteworthy aspect of the sequence leading to **1** is the extremely facile decarbonylation of the presumed trifluoroacyl intermediate (**A**, Scheme 2). This occurs at subambient temperatures, while the closely related complex $[Fe\{C(=O)CF_3\}_2(CO)_4]$ requires considerably more elevated temperatures (refluxing heptane, 2 h).[16] Indeed, it appears that low-temperature decarbonylation of the presumed intermediate $[Fe\{C(=O)CF_3\}\{C(=O)N^iPr_2\}(CO)_n]$ (**A**, $n = 3, 4, ?$) is crucial to the progress of the reaction in that the addition of PPh_3 immediately following trifluoroacetylation (within 10−15 min, −78 °C) leads to almost exclusive formation of $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2](O_2CCF_3)$ (**2a·O₂CCF₃**), while the formation of **1** is maximized by a delay of over an hour (at −78 °C). The presence of trifluoroacetate in the reaction mixture may be a significant factor, given that acetate salts have been used as catalysts for the decarbonylation and ligand substitution reactions of group 8 metal carbonyls.[17]

The apparently robust nature of the bidentate carbamoyl coordination is perhaps surprising given the typically soft nature of low-valent iron centers, although this feature has also emerged in our study of related halide/carbamoyl complexes of divalent iron.[1] Furthermore, related bidentate aroyl complexes of iron have been described by Girolami,[18] and these readily coordinate CO under comparatively mild conditions with the assumption of monodentate aroyl coordination. This behavior is in direct contrast to the complexes $[Ru(\eta^2\text{-}OCR)X(CO)(PPh_3)_2]$ (R = Me, Ph, C_6H_4Me; X = Cl, Br, I),[19] which do not readily carbonylate to form $[Ru\{\sigma\text{-}C(=O)R\}X(CO)_2(PPh_3)_2]$. In an attempt to induce monodentate carbamoyl coordination **1** was treated with dppe. A reaction slowly ensues in refluxing thf; however the product is $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)(dppe)]$ (**3**) rather than the anticipated $[Fe\{\sigma\text{-}C(=O)N^iPr_2\}(CF_3)(CO)_2(dppe)]$. Spectroscopic data for **3** suggest that the stereochemistry adopted is most likely that indicated in Scheme 4. In particular, the ^{31}P NMR spectrum consists of two multiplets [74.4, 71.1 ppm], indicating chemical inequivalence. The ^{13}C NMR resonance attributable to the carbamoyl carbon appears as a double doublet (205.4 ppm), showing distinct couplings to cis (28 Hz) and trans (50 Hz) coordinated phosphorus nuclei.

Scheme 4. Acid Hydrolysis of Trifluoromethyl Ligands (dppe = 1,2-bis(diphenylphosphino)ethane)



Reactions of the Trifluoromethyl Ligand. The nucleofugicity of fluoride substituents in metal−CF_3 complexes has been a key observation in the renaissance of metal perfluoroalkyl chemistry.[20] Thus for example trifluoromethyl complexes of ruthenium have been used extensively by Roper as precursors for dihalocarbene complexes.[20,21] Shriver has illustrated that fluoride abstracting agents can also be employed with iron−CF_3 complexes.[22] Thus, for example, treating $[Fe(CF_3)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ with BCl_3 leads to the trichloromethyl derivative $[Fe(CCl_3)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ via a difluorocarbene intermediate, $[Fe(=CF_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$. The fluoride substituents of **1** are also nucleofugic; for example, treatment with aqueous HBF_4 leads to the tricarbonyl salt $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_3(PPh_3)]BF_4$ (**2b·BF₄**). The yields obtained are too high for the third carbonyl ligand to have originated from decomposition and CO scavenging (Scheme 3). The product is also obtained using $AgBF_4$ in place of HBF_4, and it therefore appears that the carbonyl ligand results from hydrolysis of a putative difluorocarbene complex $[Fe(\eta^2\text{-}OCN^iPr_2)(=CF_2)(CO)_2(PPh_3)]BF_4$. This possibility was also investigated using the complex **3**, which is also hydrolyzed by aqueous acid $[HBF_{4(aq)}]$ to provide $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(dppe)]BF_4$ (**4·BF₄**) presumably via the carbene complex $[Fe(\eta^2\text{-}OCN^iPr_2)(=CF_2)(CO)(dppe)]^+$. That this reaction is facile is also indicated by the absence of a molecular ion in the FAB-mass spectrum (protic nba matrix) of **3** in favor of an intense peak corresponding to $\mathbf{4}^+$.

Acyl and carbamoyl ligands are typically nucleophilic at the carbonyl oxygen, and difluorocarbene ligands are strongly oxophilic electrophiles. It is therefore somewhat surprising that the proposed intermediate carbamoyl−difluorocarbene complexes do not rearrange with coupling of the two mutually compatible sites of reactivity. The question of electrophilic attack at monodentate acyls is less well documented; however it appears plausible that the bidentate coordination of the carbamoyl ligand in the present situation leads to a lowering

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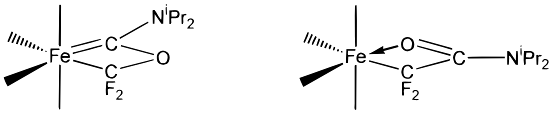
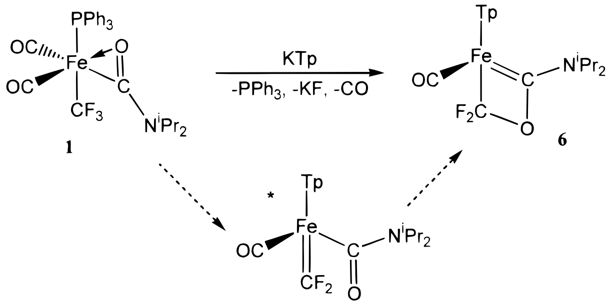
Chart 1. Ferraoxetene Connectivities



(**A**) (**B**)

Scheme 5. Ferraoxetene Formation (Tp = κ^3-HB(pyrazol-1-yl)$_3$; * = proposed intermediate)



of the nucleophilicity of the acyl oxygen atom, enabling the ligand to act as a potent donor to the metal center. Accordingly, the reactions of **1** with strongly chelating ligands were investigated in an attempt to open up the FeCO metallacycle: Treating **1** with NaC_5H_5·dme (dme = 1,2-dimethoxyethane) provided $[Fe(CO)_3(PPh_3)_2)]$ as the only isolable organometallic product. The use of potassium hydrotris(pyrazolyl)borate (K[HB(pz)$_3$]; pz = pyrazol-1-yl) however proved more informative. In refluxing thf a smooth and high-yielding reaction ensued under comparatively high dilution; however neither of the anticipated products $[Fe\{\eta^1\text{-}C({=}O)N^iPr_2\}(CO)({=}CF_2)\{HB(pz)_3\}]$ nor $K[Fe\{\eta^1\text{-}C({=}O)N^iPr_2\}(CO)(CF_3)\{HB(pz)_3\}]$ were obtained. Rather, a novel ferraoxetene was obtained, $[Fe\{\kappa^2{=}C(N^iPr_2)OCF_2\}(CO)\{HB(pz)_3\}]$ (**6**). Under more concentrated conditions $[Fe\{HB(pz)_3\}_2]$ was the only iron-containing product isolated. Spectroscopic data did not unambiguously distinguish the possible coupling arrangements of the carbamoyl and difluorocarbene components of the metallacycle (Chart 1), although NOE data suggested a close proximity of one isopropyl substituent to a pyrazol ring favoring connectivity **A**. The connectivity (**A**) within the metallacycle could however be confirmed by X-ray crystallography[2a] as that shown in Scheme 4. The formation of the ferraoxetene complex supports the plausibility of $[Fe\{\eta^1\text{-}C({=}O)N^iPr_2\}(CO)({=}CF_2)\{HB(pz)_3\}]$ as an intermediate which under the thermal conditions of the reaction undergoes intramolecular attack at the difluorocarbene ligand by the monodentate (and accordingly nucleophilic) carbamoyl oxygen (Scheme 5). 1,3-Metallaoxetenes remain a very rare class of complex, with the only other examples being $[Ru(\kappa^2{=}CPhOCH_2)(CA)_2(PPh_3)_2]^+$ (A = O, NC_6H_4Me-4), which result from the π-acid (CA) induced coupling of benzoyl and methylene ligands in the complex $[Ru(\eta^2\text{-}OCPh)Cl({=}CH_2)(PPh_3)_2]$,[23] a reaction with parallels to that proposed to account for the formation of **6**.

Aminomethylidyne Formation. The motivation for the results described so far was the synthesis of alkylidyne complexes of iron. Alkylidyne complexes of the later transition metals remain rare, and the routes applied sucessfully to date tend to be without precedent in early transition metal chemistry.[14] It was also noted above that the "sensible" solvent combinations chosen to favor O-trifluoroacetylation of the carbamoylate $[Fe\{\sigma\text{-}C({=}O)N^iPr_2\}(CO)_4]Li$ failed comprehensively. We were therefore somewhat surprised and gratified to find that $[Fe\{\sigma\text{-}C({=}O)N^iPr_2\}(CO)_4]Li$ (preformed in diethyl ether and isolated) when treated with $(CF_3CO)_2O$ and PPh_3 in dichloromethane led to two compounds, the carbamoyl salt **2a·O$_2$CCF$_3$** described above and the aminomethylidyne salt $[Fe({\equiv}CN^iPr_2)(CO)_3(PPh_3)](O_2CCF_3)$ (**5·O$_2$CCF$_3$**). The tetrachloroborate salt of this complex has been described by Fischer[24] and remains the only isolable mononuclear alkylidyne complex of iron. Fischer's preparation of **5·BCl$_4$** follows his now classical approach of alkoxide abstraction from an alkoxy carbene complex $[Fe\{{=}C(OEt)N^iPr_2\}(CO)_3(PPh_3)]$ using BCl_3. The present ("one-pot") method offers considerable practical advantage and economy, notwithstanding the unexpected and unusual solvent dependence.

An alternative preparation of the complex **5**$^+$ was subsequently discovered: Reaction of **1** with iodine provides the iodide salt **5·I** via a most unusual and as yet obscure mechanism. The yield (36%), while synthetically useful, is not sufficient to exclude CO scavenging as the source of the third carbonyl ligand. Nevertheless we are inclined to suspect that the CF_3 ligand is intimately involved in the ultimate reduction of the carbamoyl ligand to an aminomethylidyne, since no **5·I** is obtained from the treatment of any of the complexes $[Fe(\eta^2\text{-}OCN^iPr_2)X(CO)_2(PPh_3)]$ (X = Br, I, $SnPh_3$), $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)(dppe)]$, $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)(dppm)]$, **2a**$^+$, or **2b**$^+$ with iodine. One possibility (suggested by the formation of a ferraoxetene discussed above) involves the formation of a ferraoxetene of the form $[Fe\{\kappa^2{=}C(N^iPr_2)OCF_2\}I(CO)_2(PPh_3)]$ (**A**, Scheme 6). Hydrolysis of the metallacyclic difluoroalkyl group could provide a ferraoxetenone $[Fe\{\kappa^2{=}C(N^iPr_2)OC({=}O)\}I(CO)_2(PPh_3)]$ (**B**, Scheme 6), which extrudes CO_2 to provide the complex $[Fe({\equiv}CN^iPr_2)(CO)_2(PPh_3)]^+$. Capture of adventitious CO could then provide the final product. The reluctance of iodide to occupy the free coordination site is perhaps surprising; however it should be noted that ruthenium alkylidyne complexes $[Ru({\equiv}CAr)Cl(CO)(PPh_3)_2]$ (Ar = Ph, C_6H_4Me-4) are readily carbonylated under 1 atm of CO to provide cationic complexes $[Ru({\equiv}CAr)(CO)_2(PPh_3)_2]^+$, indicating that the electron-rich metal center is better stabilized by cation formation and π-acid ligation.[14] In further support of the ferraoxetenone intermediacy, we refer to our recent isolation of a ruthenaoxetenone from the addition of carbon dioxide to the alkylidyne complex $[Ru({\equiv}CPh)Cl(CO)(PPh_3)_2]$.[25]

The possibility that hydrolysis of a difluoroferraoxetene might be involved in the formation of **5·I** was investigated by treating **6** with aqueous HPF_6. The product of this reaction is however the isonitrile salt

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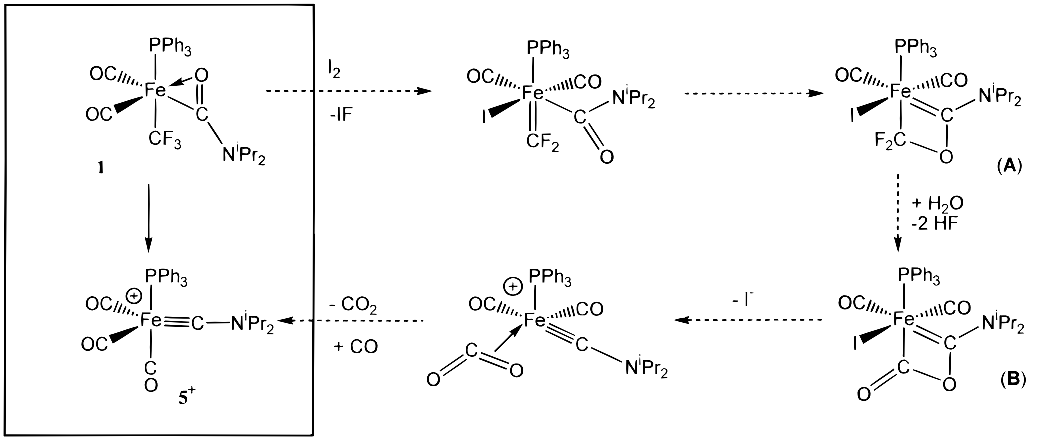
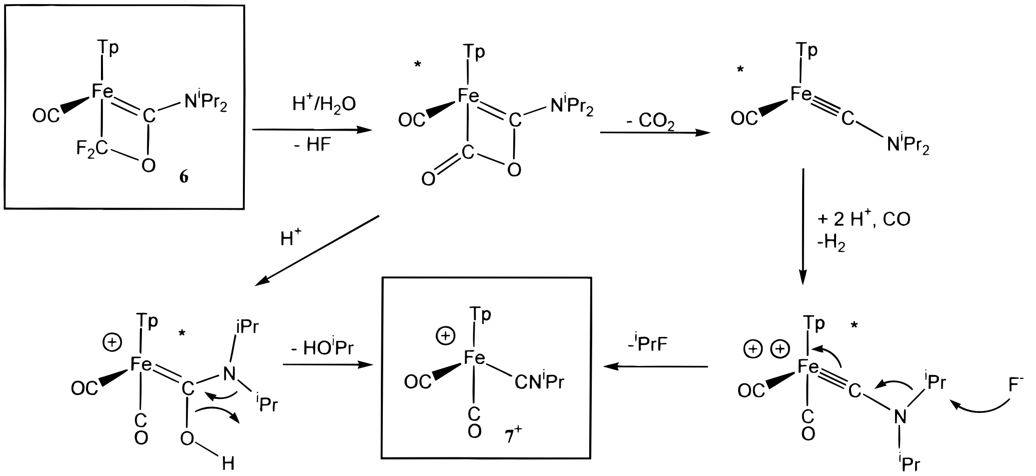
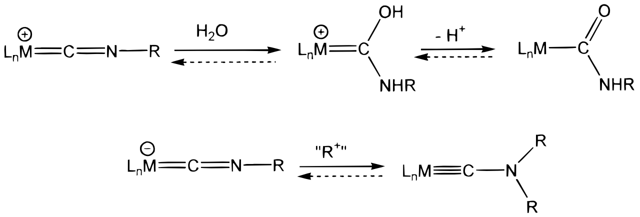
Scheme 6. Proposed Mechanism for the Formation of 5·I by Carbamoyl Iodination



Scheme 7. Mechanistic Proposals for the Ferraoxetene/Isonitrile Interconversion (Tp = κ^3-HB(pyrazol-1-yl)$_3$; * = proposed intermediates)



Scheme 8. Isonitrile Conversions



$[\mathrm{Fe(CN^iPr)(CO)_2\{HB(pz)_3\}]PF_6}$ (**7·PF$_6$**). Notably, reasonable yields (60%) are only obtained if the reaction is carried out under an atmosphere of carbon monoxide. The mechanism of isonitrile formation has not been established; however those shown in Scheme 7 are at least plausible. We have recently had occasion[25] to implicate the metallacycle $[\mathrm{Ru\{\kappa^2{=}CPhSC({=}S)\}Cl(CO)(PPh_3)_2}]$ in the formation of $[\mathrm{Ru(\eta^2\text{-}SCPh)Cl(CS)(PPh_3)_2}]$ from $[\mathrm{Ru({\equiv}CPh)Cl(CO)(PPh_3)_2}]$ and carbon disulfide. The metallacycle $[\mathrm{Fe\{\kappa^2{=}C(N^iPr_2)OC({=}O)\}(CO)\{HB(pz)_3\}}]$ is therefore a reasonable intermediate. Protonation of the endocyclic oxygen could then provide the alkylidene complex $[\mathrm{Fe\{{=}C(N^iPr_2)OH\}(CO)_2\{HB(pz)_3\}}]^+$, which subsequently eliminates 2-propanol to provide the isonitrile ligand. While this transformation is unprecedented, the dehydration of primary carbamoyl ligands to form isonitrile complexes has some precedent in late transition metal chemistry[5] and represents the reverse of isonitrile hydration as a means of carbamoyl synthesis (Scheme 8). An alternative route for the conversion of "$[\mathrm{Fe\{C(N^iPr_2)OC({=}O)\}(CO)\{HB(pz)_3\}}]$" to **7·PF$_6$** might involve loss of CO$_2$ from the metallacycle to provide the formally zerovalent alkylidyne complex $[\mathrm{Fe({\equiv}CN^iPr_2)(CO)\{HB(pz)_3\}}]$. This complex would be prone to acid oxidation to provide $[\mathrm{Fe({\equiv}CN^iPr_2)(L)(CO)\{HB(pz)_3\}}]^{2+}$ (L = OH$_2$, CO), which due to the high positive charge might be expected to undergo nucleophilic (HO$^-$, F$^-$?) dealkylation of the aminomethylidyne ligand. This last step is the reverse of isonitrile alkylation as a route to aminomethylidyne complexes, a process only favored for very electron-rich precursors.[26] This latter mechanism is perhaps more attractive given the yield enhancement resulting from an external source of CO.

Concluding Remarks. The formation of stable carbamoyl complexes of iron is surprisingly facile if the ligand can be stabilized by bidentate coordination. Once this has occurred, the bidentate mode of coordination appears to be favored and *ultimately* preserved in many reactions. The role of the carbamoyl ligand is however not exclusively spectatorial, as illustrated by its conversion to metallaoxetene, aminomethylidyne, and isonitrile groups. The mechanisms of these transformations

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(25) Bedford, R.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 95.

(26) Mayr, A.; Hoffmeister. H. *Adv. Organomet. Chem.* **1991**, *32*, 227. Angelici, R. J.; Kim, H. S. *Adv. Organomet. Chem.* **1987**, *27*, 51.

remain speculative and require further study. The alkylidyne-forming reaction does however further illustrate that in designing synthetic approaches to alkylidyne complexes of the later transition metals, one should not necessarily look to precedents from earlier triads.

Experimental Section

General Procedures. All manipulations were routinely carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent [ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH_2]. All reagents were commercially available (Aldrich) and used as received.

^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL GNM EX270 NMR spectrometer and calibrated against internal Me_4Si (^1H), $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. FAB mass spectrometry was carried out with an Autospec Q mass spectrometer using nitrobenzyl alcohol as matrix. For salts, "M" refers to the cationic complex. Light petroleum refers to that fraction of bp 40−60 °C. Elemental microanalyses were carried out by Medac Ltd, Middlesex, or by the Imperial College Microanalytical Laboratory.

Synthesis of $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (1). $[Fe(CO)_5]$ (3.00 g, 15 mmol) was placed in a Schlenk tube with diethyl ether (50 mL), and then LDA was added dropwise (1.5 mol dm^{-3}, 10.2 mL, 15 mmol). On completion of the addition, the reaction mixture was cooled (dry ice/propanone) and trifluoroacetic anhydride (2.4 mL, 17 mmol) diluted in ether (20 mL), added dropwise. After stirring at low temperature for 90 min, triphenylphosphine (6.00 g, 23 mmol) was added and the reaction allowed to warm slowly to room temperature overnight. A bright yellow precipitate formed, which was isolated by decanting off the supernantant. Lithium trifluoroacetate was removed by extraction of the residue with a mixture of dichloromethane and light petroleum (2:1) and filtration of the combined extracts through a plug of diatomaceous earth. On removing the solvent, the isolated product was further purified by column chromatography. Yield: 4.92 g (56%). The preparation may be carried out on a larger scale (15.0 g $[Fe(CO)_5]$) without compromising the yield. IR (CH_2Cl_2): 2027, 1953 ν(CO); 1610 ν(NCO) cm^{-1}. (Nujol): 2020, 1949 ν(CO), 1606 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C), ^1H: δ 0.53, 1.04, 1.16, 1.29 [d × 4, 12 H, CH_3, $J(HH) = 6.6$ Hz], 3.28, 4.79 [h × 2, 2 H, NCH], 7.18−7.41 [m, 15 H, C_6H_5] ppm. $^{13}C\{^1H\}$: 218.3 [d, FeCO, J(PC) not resolved], 211.6 [d, FeCO, J(PC) not resolved], 197.1 [d, OCN, J(PC) not resolved], 133.6−128.5 [C_6H_5], 54.7, 48.5, [2 × s, NCH], 21.2, 20.5, 20.2, 19.9 [4 × s, CH_3] ppm. $^{31}P\{^1H\}$: 49.6 ppm [q, $J(PF) = 27.2$ Hz]. ^{19}F: −7.15 ppm [d, $J(PF) = 29.3$ Hz]. FAB-MS: $m/z = 543$ $[M - CO]^+$, 515 $[M - 2CO]^+$, 465 $[M - 2CO - CF_3]^+$, 318 $[FePPh_3]^+$. Anal. Found: C, 58.8; H, 5.2; N, 2.4. Calcd for $C_{28}H_{29}F_3FeNO_3P$: C, 58.9; H, 5.1; N, 2.5. The complex was also characterized by an X-ray diffraction analysis.[1]

Synthesis of $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2](O_2CCF_3)$ (2a·O$_2$CCF$_3$). A solution of $[Fe(CO)_5]$ (3.00 g, 2.0 mL, 15 mmol) in diethyl ether (50 mL) was treated with a solution of LDA (10.2 mL, 1.50 mol dm^{-3}, 15 mmol) and then cooled in a dry ice/propanone bath. Trifluoroacetic anhydride (2.40 mL, 17 mmol) was added dropwise, and the mixture stirred for 15 min. Triphenylphosphine (6.00 g, 23 mmol) was then added, and the mixture allowed to warm to room temperature overnight. The small amount of precipitate that formed was removed by filtration, and then all volatiles were removed from the filtrate under reduced pressure. The residue was extracted with a mixture of propanone and light petroleum (2:1), and the combined extracts were concentrated under reduced pressure and cooled (−30 °C) to provide yellow crystals of the product, which were dried in vacuo. Yield: 7.60 g (58%). IR (CH_2Cl_2): 2039, 1968 ν(CO) 1605 cm^{-1} ν(NCO). (Nujol) 2026, 1960 ν(CO), 1612 cm^{-1} ν(NCO). NMR ($CDCl_3$, 25 °C), ^1H: δ 0.08, 1.03 [d × 2, 12 H, CH_3], 3.06, 5.16 [h × 2, 2 H, NCH], 7.33−7.53 ppm [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$: 214.0 [t, FeCO, $J(PC) = 30.7$ Hz], 211.3 [t, FeCO, $J(PC) = 21.5$ Hz], 184.3 [t, OCN, $J(PC) = 23.0$ Hz], 133.6−129.4 [C_6H_5], 56.1, 49.6 [NCH], 21.3, 19.2, ppm [CH_3]. $^{31}P\{^1H\}$: 53.9 ppm. FAB-MS: $m/z = 764$ $[M]^+$, 708$[M - 2CO]^+$, 580 $[Fe(PPh_3)_2]^+$. These data are essentially identical to those obtained for the crystallographically characterized salt **2a·PF$_6$** prepared via an alternative route.[27]

Synthesis of $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_3(PPh_3)]BF_4$ (2b·BF$_4$). $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)(CF_3)]$ (**1**; 1.00 g, 1.75 mmol) was dissolved in diethyl ether (50 mL) and $HBF_{4(aq)}$ (0.12 mL, {wt/mL = 1.31 g}, 1.75 mmol) added. On stirring at room temperature, a bright yellow precipitate eventually formed (2 h) from the ether liquor, which was then decanted off. The product was then recrystalized from a mixture of dichloromethane and light petroleum. Yield: 0.89 g (82%). IR (CH_2Cl_2): 2102, 2058, 2023 ν(CO) 1650 cm^{-1} ν(NCO). (Nujol) 2099, 2053, 2011 ν(CO), 1652 cm^{-1} ν(NCO). NMR ($CDCl_3$, 25 °C), ^1H: δ 0.55, 1.24, 1.36, 1.45 [d × 4 (br), 12 H, CH_3], 3.64, 4.68 [h × 2, 2 H, NCH], 7.30, 7.53 ppm [m, 15 H, C_6H_5]. $^{13}C\{^1H\}$: δ 206.6 [d, FeCO, $J(PC) = 31.4$ Hz], 202.2 [d, FeCO, $J(PC) = 26.5$ Hz], 197.1 [d, FeCO, $J(PC) = 51.0$ Hz], 185.9 [d, OCN, $J(PC) = 18.8$ Hz], 133.2−127.5 [C_6H_5], 56.7, 50.3 [NCH], 21.8, 19.7, 19.4, 19.1 ppm [CH_3]. $^{31}P\{^1H\}$: 22.4 ppm. FAB-MS: $m/z = 530$ $[M]^+$, 502 $[M' - CO]^+$, 474 $[M - 2CO]^+$, 446 $[M - 3CO]^+$, 318 $[FePPh_3]^+$. Anal. Found: C, 54.1; H, 4.7; N. 2.2. Calcd for $C_{28}H_{29}BF_4FeNO_4P$: C, 54.5; H, 4.7; N, 2.3.

Synthesis of $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)(dppe)(CF_3)]$ (3). $[Fe\{\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)(CF_3)]$ (**1**; 1.00 g, 1.75 mmol) and 1,2-bis (diphenylphosphino)ethane (dppe, 0.70 g, 1.75 mmol) were placed in a Schlenk tube under an atmosphere of nitrogen. Tetrahydrofuran (30 mL) was added and the mixture heated under reflux for 3 h. The thf was then removed under reduced pressure, and diethyl ether (30 mL) added to the oily residue to give a precipitate, which was washed with diethyl ether by decantation. The residue was then chromatographed (silica gel, CH_2Cl_2) and crystallized by addition of light petroleum, concentration, and cooling (−30 °C). Yield: 0.82 g (68%). IR (CH_2Cl_2): 1914 ν(CO) 1590, ν(NCO) cm^{-1}. (Nujol): 1912 ν(CO), 1564 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C), ^1H: 0.51, 1.05, 1.24, 1.31 [d × 4, 12 H, CH_3, $J(HH) = 6.6$ Hz], 1.91, 2.31 [m × 2, br, 4 H, PCH_2], 3.28, 5.04 [h × 2, 2 H, NCH], 6.74−8.07 [m, 20 H, C_6H_5] ppm. $^{13}C\{^1H\}$: 221.8 [d, FeCO, $J(PC) = 17.7$ Hz], 205.4 [dd, OCN, $J(PC) = 50.0$, 28.0 Hz], 137.9−127.6 [C_6H_5], 54.2, 47.1 [NCH], 30.3, 29.2 [m × 2, PCH_2], 22.5, 21.0, 20.5, 20.1 [CH_3]. $^{31}P\{^1H\}$: 74.4, 71.1 [m × 2]. FAB-MS $\{X = FeC(O)\text{-}N^iPr_2(dppe)(CO)_2\}$: $m/z = 638$ $[X]^+$, 610 $[X - CO]^+$, 582$[X - 2CO]^+$, 453 $[Fedppe]^+$, 183 $[FeOCN^iPr_2]^+$. Anal. Found: C, 57.5; H, 5.3; N, 1.8. Calcd for $C_{35}H_{38}F_3FeNO_2P_2.CH_2Cl_2$: C, 56.6; H, 5.3; N, 1.8. Dichloromethane of solvation confirmed by ^1H NMR integration.

Synthesis of $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]O_2CCF_3$ (5·O$_2$CCF$_3$) and $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2]O_2CCF_3$ (2a·O$_2$CCF$_3$). $[Fe(CO)_5]$ (3.00 g, 2.0 mL, 15 mmol) was diluted in diethyl ether (50 mL) in a Schlenk tube and LDA (10.2 mL, 1.5 mol dm^{-3}, 15 mmol) added. On completion of the addition, the ether and any unreacted $[Fe(CO)_5]$ was removed under reduced pressure and the residue redissolved in dichloromethane (50 mL). This was then cooled (dry ice/acetone), and a solution of trifluoroacetic anhydride (2.4 mL, 17 mmol) in diethyl ether (20 mL) was added dropwise. After stirring at low temperature for 15 min, triphenylphosphine (6.00 g, 23 mmol) was added and the reaction allowed to warm slowly to room temperature, during which time an oily precipitate

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(27) Anderson, S.; Hill, A. F.; Ng, Y. T.; White, A. J. P.; Williams, D. J., manuscript in preparation.

formed. Petrol (40−60) (25 mL) was added and the reaction mixture filtered through a plug of diatomaceous earth. The bright yellow precipitate that collected on the plug was then extracted into tetrahydrofuran, the extracts were filtered, and the solvent was removed from the filtrate under reduced pressure to provide **5·O$_2$CCF$_3$**. Yield: 1.20 g (12.5%). IR (CH$_2$Cl$_2$): 2083, 2034, 2012 ν(CO), 1664 cm^{-1} ν(CN). 2079, 2041, 1992 ν(CO), 1642 cm^{-1} ν(CN). NMR (CDCl$_3$, 25 °C), ^{1}H: δ 1.17 [d, 12 H, CH$_3$, J(HH) = 6.3 Hz], 3.96 [h, 2 H, NCH], 7.58−7.76 ppm [m, 15 H, C$_6$H$_5$]. ^{13}C{^{1}H}: δ 266.5 [d, Fe≡*C*, J(PC) = 42.8 Hz], 206.5 [d, FeCO], 134.4−130.3 [C$_6$H$_5$], 58.5 [NCH], 22.0 ppm [CH$_3$]. ^{31}P{^{1}H}: 58.4 ppm. FAB-MS: m/z = 514 [M]$^+$, 486 [M − CO]$^+$, 458 [M − 2CO]$^+$, 318 [FePPh$_3$]$^+$. These data correspond to those for the crystallographically characterized salt **5·BCl$_4$**.[24] The CH$_2$Cl$_2$/petrol liquor that initially passed through the diatomaceous earth plug was cooled (−30 °C), and eventually crystals formed. On decanting off the solvent and drying the crystals under nitrogen, the second product **2a·O$_2$CCF$_3$** was isolated. Yield (not optimized): 0.24 g (2.5%). Spectroscopic data were identical to those obtained above via an alternative procedure.

Synthesis of [Fe(≡CN^{i}Pr$_2$)(CO)$_3$(PPh$_3$)]I (5·I). [Fe(η^2-OCN^{i}Pr$_2$)(CO)$_2$(PPh$_3$)(CF$_3$)] (**1**; 0.39 g, 0.68 mmol) and iodine (0.17 g, 0.68 mmol) were placed in a Schlenk tube, which was then evacuated and refilled with nitrogen. Diethyl ether (30 mL) was then added and the mixture stirred at room temperature for 3 h. The residue which separated from the ether liquor was isolated by decanting off the supernatant and washed with diethyl ether. The residue was extracted with a mixture of dichloromethane and light petroleum (2:1), and the combined extracts were filtered through diatomaceous earth. On concentrating the filtrate under reduced pressure, the product crystallized out of the liquor and was isolated by decantion. Yield: 0.16 g (36%). Spectroscopic data associated with the cationic complex were identical to those for **5·O$_2$CCF$_3$** described above and **5·BCl$_4$**.[24]

Synthesis of [Fe{κ^2-CF$_2$OCN^{i}Pr$_2$}(CO){HB(pz)$_3$}] (6). [Fe(η^2-OCN^{i}Pr$_2$)CF$_3$(CO)$_2$(PPh$_3$)] (**1**; 1.00 g, 1.75 mmol) and potassium hydrotris(pyrazol-1-yl)borate (0.44 g, 1.75 mmol) were placed in a Schlenk tube, which was then evacuated and refilled with nitrogen. Tetrahydrofuran (30 mL) was then added and the mixture heated under reflux for 1 h. On completion, the thf was removed under reduced pressure and the residue chromatographed on silica gel, eluting with a mixture of dichloromethane and light petroleum (2:3). Yield: 0.61 g (73%). IR (CH$_2$Cl$_2$): 2485 ν(BH), 1959 ν(CO), 1557 ν(NCO) cm^{-1}. (Nujol) 2488 ν(BH), 1950 ν(CO), 1563 ν(NCO) cm^{-1}. NMR (CDCl$_3$, 25 °C), ^{1}H: δ 0.74, 1.20 1.38, 1.43 [d × 4, 12 H, CH$_3$], 3.42, 3.93 [h × 2, 2 H, NCH], 6.00, 6.03, 6.23 [t × 3, 3 H, H^4(pz)], 7.47, 7.51, 7.59, 7.64, 7.69, 7.92 [d × 6, 6 H, H^{3,5}(pz)] ppm. ^{13}C{^{1}H}: 225.0 [FeCO], 221.7 [q, OCN, J(FC) = 4.7 Hz], 138.4 [dd, FeCF$_2$, J(FC) = 352, 377 Hz], 143.7, 143.5, 142.8 [C^3(pz)], 135.0, 134.5 [C^5(pz)], 105.3, 104.9 [C^4(pz)], 54.7, 48.7 [NCH], 25.5, 21.3, 21.0, 20.3 [CH$_3$] ppm. ^{19}F: −33.5, −53.2 [**AB**, J(**AB**) = 97.6 Hz]. FAB-MS: m/z = 447 [M − CO]$^+$, 397 [M − CO − CF$_2$]$^+$, 269 [FeHB(pz)$_3$]$^+$. Anal. Found: C, 45.4; H, 5.1; N, 20.9. Calcd for C$_{18}$H$_{24}$BF$_2$FeN$_7$O$_2$: C, 45.5; H, 5.1; N, 20.6. The complex was also charaterized by an X-ray diffraction analysis.[2a]

Preparation of [Fe(CN^{i}Pr)(CO)$_2${HB(pz)$_3$}]PF$_6$ (7·PF$_6$). The complex [Fe(κ^2=C(N^{i}Pr$_2$)OCF$_2$}(CO){HB(pz)$_3$}] (**6**; 0.20 g, 0.42 mmol) was dissolved in diethyl ether (20 mL) and carbon monoxide passed through the solution for 5 min. The mixture was then treated with concentrated aqueous hexafluorophosphoric acid (0.12 g, 0.08 mL, 0.84 mmol). The mixture was stirred for 1 h, during which time a pale yellow solid precipitated, which was isolated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 0.10 g (60%). IR (CH$_2$Cl$_2$): 2222 ν(CN), 2104, 2068 cm^{-1} ν(CO) (Nujol) 2232 ν(CN), 2104, 2064 cm^{-1} ν(CO). NMR (CDCl$_3$, 25 °C), ^{1}H: δ 1.46 [d, 6 H, CH$_3$, J(HH) = 6.3 Hz], 4.50 [h, 1 H, NCH], 6.40, 6.45 [t × 2, 3 H, H^4(pz)], 7.80−7.96 [d × 4, 6 H, H^{3,5}(pz)] ppm. FAB-MS: m/z = 394 [M]$^+$, 338 [M − 2CO]$^+$, 269 [FeHB(pz)$_3$]$^+$. Anal. Found: C, 33.7; H, 3.1; N, 18.0. Calcd for C$_{15}$H$_{17}$BF$_6$FeN$_7$O$_2$P: C, 33.4; H, 3.2; N, 18.2.

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