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Dihapto Carbamoyl (Carboxamide) Complexes of Iron(II)

Stephen Anderson,† Timothy E. Berridge,‡ Anthony F. Hill,*,‡,§ Ying Thong Ng,‡
Andrew J. P. White,‡ and David J. Williams‡

*School of Theoretical and Applied Sciences, Ramapo College, Mahwah, New Jersey 07430,
Department of Chemistry, Imperial College London, South Kensington London, U.K., and
Research School of Chemistry, Institute of Advanced Studies, Australian National University,
Canberra ACT, Australia*

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The carbamoyl ferrate $\mathrm{Li[Fe\{C(=O)N^{i}Pr_2\}(CO)_4]}$ reacts in diethyl ether with $\mathrm{Br_2PPh_3}$, $\mathrm{I_2PPh_3}$, or $\mathrm{I_2}$ followed by triphenylphosphine to provide the complexes $\mathrm{[Fe(\eta^2\text{-}OCN^{i}Pr_2)X(CO)_2(PPh_3)]}$ [X = I *trans* to $\mathrm{PPh_3}$ (**1a**); Br (**1b**) two isomers], each of which feature *dihapto-C,O* carbamoyl coordination. The reactions of **1a** or **1b** with $\mathrm{AgBF_4}$ in the presence of CO provide $\mathrm{[Fe(\eta^2\text{-}OCN^{i}Pr_2)(CO)_3(PPh_3)]BF_4}$ (**2a**·$\mathrm{BF_4}$), one carbonyl ligand of which is labile and readily replaced by $\mathrm{I^-}$, $\mathrm{Br^-}$, or $\mathrm{PPh_3}$ to provide **1a**, **1b**, or $\mathrm{[Fe\{\eta^2\text{-}OCN^{i}Pr_2\}(CO)_2(PPh_3)_2]BF_4}$ (**2b**·$\mathrm{BF_4}$). The reaction of **1a** with dppe leads to a separable mixture of the salt $\mathrm{[Fe\{\eta^2\text{-}OCN^{i}Pr_2\}(CO)_2(dppe)]I}$ (**3**·I) and $\mathrm{[Fe\{\eta^2\text{-}OCN^{i}Pr_2\}I(CO)(dppe)]}$ (**4**). Successive treatment of $\mathrm{Li[Fe\{C(=O)N^{i}Pr_2\}(CO)_4]}$ with $\mathrm{ClSnPh_3}$ and $\mathrm{PPh_3}$ provides the stannyl complex $\mathrm{[Fe(\eta^2\text{-}OCNiPr_2)(SnPh_3)(CO)_2(PPh_3)]}$ (**1d**). Treating **1d** with iodine leads to Sn−Fe rather than Sn−C cleavage and formation of **1a**. In all the above transformations the integrity of the dihapto carbamoyl coordination is *ultimately* retained. The crystal structures of **1d** and **2b**·$\mathrm{PF_6}$ are reported.

Introduction

Carbamoyl (carboxamido) complexes $\mathrm{L_nMC(=O)NR_2}$ (Chart 1) have received considerably less attention than their acyl analogues $\mathrm{L_nMC(=O)R'}$. Comparatively little novel ligand-based chemistry has been added in the interim to that reviewed by Angelici[1] in 1972. Principal foci of carbamoyl coordination chemistry have included (i) their use, particularly anionic examples, as intermediates in the synthesis of aminomethylidene[2] and aminomethylidyne complexes;[3] (ii) their implication in the metal-mediated (often catalytic) formation of urea derivatives;[4] (iii) their formation by carbonylation of metal amido complexes;[5] (v) implicit formamide C−H activation processes,[6] and (vi) the reactions of coordinated CO with amines.[7] By far the bulk of this chemistry has involved monodentate coordination of the carbamoyl ligand through carbon.

We have attempted to employ iron carbamoyls as precursors to aminomethylidyne complexes of iron[8] but have to date found that, with one exception,[9] this approach does not readily lead to alkylidyne complexes. Rather, access is provided to a wealth of unanticipated chemistry that almost exclusively involves the surprisingly stable carbamoyl ligand adopting a purely spectatorial role.[10] We report herein the synthesis of a range of carbamoyl complexes of divalent iron, all of which feature the apparently favorable bidentate coordination

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* Corresponding author. E-mail: a.hill@anu.edu.au.

† Ramapo College.

‡ Imperial College London.

§ Australian National University.

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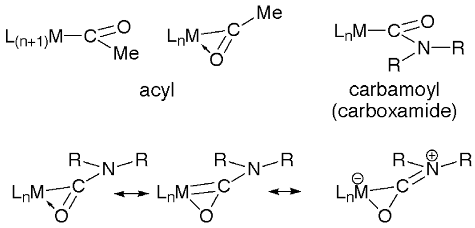
Chart 1. Acyl and Carbamoyl (carboxamido) Coordination



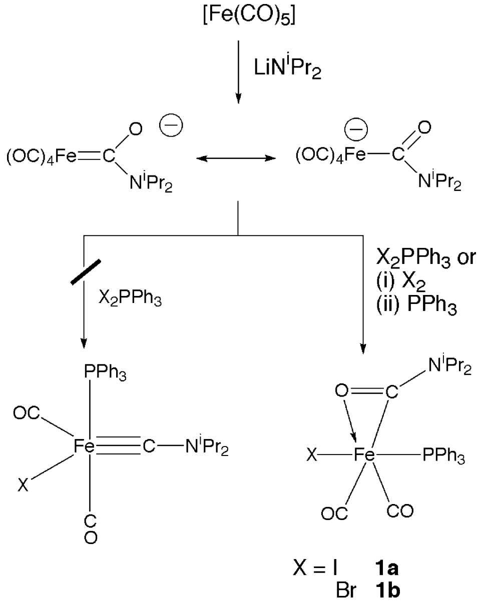
of the carbamoyl ligand. This prevalence of bidentate coordination, indicated by spectroscopic data, has prompted us to investigate the crystal structures of two examples, $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2]PF_6$ and $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)]$.

Results and Discussion

Fischer has reported the in situ preparation of the iron carbamoylate salt $Li[Fe\{C({=}O)N^iPr_2\}(CO)_4]$ from the reaction of $[Fe(CO)_5]$ and lithium diisopropylamide (hereafter LDA).[11] Petz has described a related and isolated salt, $[Fe\{C({=}O)NMe_2\}(CO)_4][C(NMe_2)_3]$,[12] from the reaction of $[Fe(CO)_5]$ and $C(NMe_2)_4$. Indeed, the general class of compounds $[Fe\{C({=}O)NR_2\}(CO)_4][NR_2H_2]$ has a long history, resulting from their facile equilibrium with $[Fe(CO)_5]$ and secondary amines (HNR_2).[1] The complex $[Fe\{C(O)N^iPr_2\}(CO)_4]^-$ is readily alkylated by the "hard" electrophile $[Et_3O]BF_4$ to provide the neutral carbene complex $[Fe\{{=}C(OEt)N^iPr_2\}(CO)_4]$.[11]

Mayr has previously introduced an oxalyl chloride- or trifluoroacetic anhydride-mediated oxide-abstraction protocol as a convenient route to alkylidynes of group 6.[13] However, in the case of $Li[Fe^0\{C({=}O)N^nPr_2\}(CO)_4]$, oxalyl chloride apparently induces a redox disproportionation process to generate the bis(carbamoylate) $[Fe^{II}\{C({=}O)N^nPr_2\}_2(CO)_4]$, which rearranges to the carbene complex $[Fe^0\{\kappa^2\text{-}C(N^nPr_2)OC(N^nPr_2)O\}(CO)_3]$.[14] In contrast, with $Li[Fe\{C({=}O)N^iPr_2)(CO)_4]$ and $HgCl_2$ as the oxidant in the presence of PPh_3, the binuclear complex $[Fe_2(\mu\text{-}OCN^iPr_2)_2(CO)_5(PPh_3)]$ is obtained.[15] Phosphine dihalides have been previously employed as reagents for the conversion of anionic aroylates and carbamoylates into alkylidyne complexes of group 6 metals,[16,17] and we were eager to extend this to group 8 metals, given the scarcity of general synthetic routes for alkylidyne complexes of iron.[10b,18]

Scheme 1. Synthesis of $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ (1a)



Treating a solution of $[Fe(CO)_5]$ in diethyl ether with LDA, followed by cooling (dry ice/propanone) and addition of triphenylphosphine diiodide, leads to a smooth reaction to provide a carbamoyl derivative of iron(II), viz., $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ (**1a**) (88%, Scheme 1) rather than the desired aminomethylidyne complex $[Fe({\equiv}CN^iPr_2)I(CO)_2(PPh_3)]$. The same complex is also obtained, in comparable yields (72%), if the carbamoyl ferrate is treated sequentially with 1 equiv of iodine followed by triphenylphosphine. The formulation follows from spectroscopic data: In addition to metal−carbonyl infrared absorptions at 2012 and 1948 cm^{-1} (Nujol), a peak at 1615 cm^{-1} is characteristic of an iron-bound bidentate carbamoyl ligand; for example, the structurally characterized complex $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1c**) has absorptions at 2020, 1949, and 1606 cm^{-1} (Nujol).[8] The diisopropylamino group of **1a** features chemically inequivalent methyl groups evident as four doublets in the ^1H NMR spectrum. The carbamoyl carbon gives rise to a $^{13}C\{^1H\}$ NMR resonance at 197.4 ppm, slightly to higher field of the two chemically inequivalent terminal carbonyl resonances at δ 220.5 and 212.4. The FAB mass spectrum shows a molecular ion (m/z = 629), and substantially abundant isotope patterns are also observed for fragmentations involving loss of carbonyl, iodide, and/or carbamoyl ligands.

A slightly more complicated situation arises for the corresponding bromide derivative: A complex formulated as $[Fe(\eta^2\text{-}OCN^iPr_2)Br(CO)_2(PPh_3)]$ (**1b**) (on the basis of elemental microanalytical and FAB-MS data) appears to be obtained by treating $Li[Fe\{C({=}O)N^iPr_2\}(CO)_4]$ either with preformed Br_2PPh_3 or alternatively by sequential addition of bromine and triphenylphosphine, and the complex may be isolated in a yield comparable to **1a**. Furthermore, the same species may also be obtained by treating $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_3(PPh_3)]BF_4$ (vide infra) with $[^nBu_4N]Br$ (Scheme 2). Following cryostatic chromatographic purification (−30 °C), spectroscopic data acquired for the complex **1b** suggest that in the solid state it is isostructural with **1a** and **1c**, whereas in solution two species coexist in proportions that are solvent dependent. Thus the infrared spectrum of **1b** obtained from a Nujol mull

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Scheme 2. Synthesis and Isomerism of $[\mathrm{Fe(OCN^iPr_2)Br(CO)_2(PPh_3)}]$ (1b)

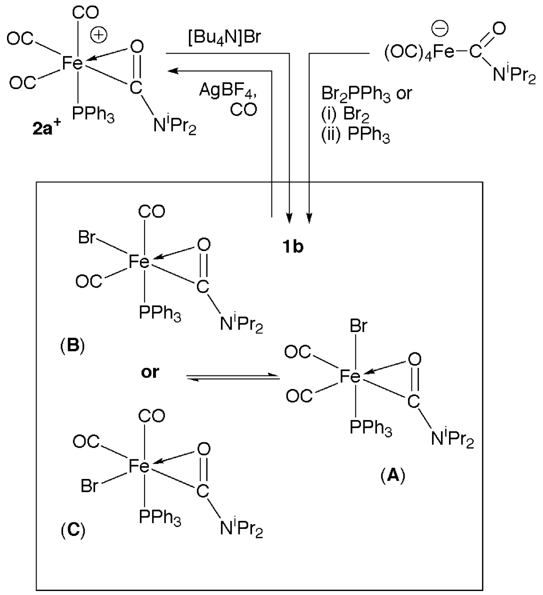


Table 1. Selected ^{13}C and ^{31}P NMR Data for Bidentate Carbamoyl and Related Complexes of Iron[a]

complex	$\delta(\mathrm{O^{13}CN})$ (ppm)	^2J(PC) (Hz)	$\delta(^{31}\mathrm{P})$ (ppm)
$[\mathrm{Fe(OCN^iPr_2)I(CO)_2(PPh_3)}]$	197.4	19.4	78.5
$[\mathrm{Fe(OCN^iPr_2)Br(CO)_2(PPh_3)}]$ major	194.9	28.6	38.0
$[\mathrm{Fe(OCN^iPr_2)Br(CO)_2(PPh_3)}]$ minor	198.4	19.7	74.6
$[\mathrm{Fe(OCN^iPr_2)(CF_3)(CO)_2(PPh_3)}]$[10b,b]	197.1	n.r.[c]	49.6
$[\mathrm{Fe(OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)}]$[b]	196.7	12.9	53.8
$[\mathrm{Fe(OCN^iPr_2)(CO)_3(PPh_3)}]^+$[b]	185.9	18.8	22.4
$[\mathrm{Fe(OCN^iPr_2)(CO)_2(PPh_3)_2}]^+$	184.0	23.0	54.6
$[\mathrm{Fe(OCN^iPr_2)(CO)(dppe)I}]$	204.9	37.5,	105.5,
		21.4	68.2
$[\mathrm{Fe(OCN^iPr_2)(CF_3)(CO)(dppe)}]$[10b]	205.4	50.0	74.4
		28.0	71.1
$[\mathrm{Fe(OCC_6H_2Me_3)Br(CO)(dppe)}]$[19]	260	32.5	114.7[d]
		17.7	81.8

[a] Data obtained from saturated solutions in $\mathrm{CDCl_3}$ at 25 °C. Chemical shifts given relative to internal $\mathrm{CDCl_3} = 77.0$ (^{13}C) or external $\mathrm{H_3PO_4} = 0.0$ (^{31}P). [b] Characterized by X-ray crystallography. [c] n.r. = not resolved. [d] $J(\mathrm{P_AP_B}) = 17.3$ Hz.

reveals two Fe–CO absorptions and one carbamoyl-associated absorption at 2012, 1964, and 1637 cm^{-1}, respectively. However, a spectrum measured in dichloromethane solution shows two carbamoyl-associated absorptions at 1634 and 1624 cm^{-1}. Furthermore, in addition to the bands due to the terminal carbonyl ligands at 2017 and 1958 cm^{-1}, a shoulder at ca. 2034 cm^{-1} was discernible. A spectrum of a solution of **1b** in toluene also showed two major carbonyl peaks at 2012 and 1954 cm^{-1} and a carbamoyl absorption at 1632 cm^{-1}; however peaks at 2032 and 1615 cm^{-1} were also clearly resolved in this solvent. Data from ^{31}P{^{1}H}, ^{1}H, and ^{13}C{^{1}H} NMR measurements also confirm that two species are present in solution and that they do not interconvert on the NMR time scales. The ^{31}P{^{1}H} NMR spectrum of **1b** in $\mathrm{CDCl_3}$ shows two singlet resonances at δ 74.6 and 38.0, in an approximate ratio of 1:2. In toluene-d_8 or benzene-d_6 at 30 °C, however, the peak at δ 75.3 represents approximately 5% of the total phosphorus, the remainder giving rise to a singlet at δ 37.6. The relative proportions of the two species are invariant from 30 to 65 °C, and above this temperature range decomposition ensues rapidly. The type of isomerism occurring remains equivocal; however it can be noted that the position of the ^{31}P NMR resonance for the minor species ($\delta = 74.6$) corresponds most closely with that for **1a** ($\delta = 78.5$) and presumably corresponds to **A** (Scheme 2). In a similar manner the methine ^{1}H resonances for the minor isomer (δ 5.19, 3.47) correspond well with those for **1a** (δ 5.09, 3.35), while those for the major isomer show a less dramatic difference in chemical shift (δ 4.67, 3.87). Table 1 collects selected ^{13}C and ^{31}P NMR data for related carbamoyl complexes of iron(II), including three examples that have been structurally characterized (vide infra). From these data it is clear that typical *cis*-^2J(PC) couplings for the carbamoyl ligand lie in the range 13–28 Hz, while the two examples of *trans*-^2J(PC) couplings are larger at 37.8 and 50.0 Hz. Thus it appears that both isomers have a *cis* arrangement of carbamoyl and phosphine ligands. Furthermore, similar analysis of ^2J(PC) couplings for carbonyl ligands in these complexes suggests that the minor isomer has a *facial* $\mathrm{Fe(CO)_2(PPh_3)}$ disposition. The ^{13}C carbonyl resonances due to the major isomer are broad, and this precludes identification of ^2J(PC); however it is most likely that the major isomer is either **B** or **C**. The two atoms of the carbamoyl ligand have complimentary π-interactions with the metal center in that the oxygen is π-basic and the carbon is π-acidic. It therefore seems most likely that the major isomer is that with bromide *trans* to the carbamoyl carbon, i.e., **B** (Scheme 2).

The iodide ligand in **1a** and the bromide ligand in **1b** are both labile and readily removed by $\mathrm{Ag[BF_4]}$ in the presence of CO to provide the yellow salt $[\mathrm{Fe(\eta^2\text{-}OCN^iPr_2)(CO)_3(PPh_3)}]\mathrm{BF_4}$ (**2a**·$\mathrm{BF_4}$) in high yield. The same complex results from the reaction of $[\mathrm{Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)}]$ with aqueous $\mathrm{HBF_4}$, notably in the absence of added CO, the third carbonyl ligand arising from hydrolysis of a putative difluorocarbene intermediate. Spectroscopic data indicate that the $\mathrm{Fe(CO)_3}$ unit adopts a *facial* geometry and that the bidentate carbamoyl coordination is retained: Carbon-13 NMR signals for the carbonyl ligands show distinct *cis* (31.4, 26.5) and *trans* (51.0 Hz) couplings to phosphorus, while the signal due to the carbamoyl carbon once again appears to higher field (δ 185.9, $^2J(\mathrm{PC}) = 18.8$ Hz) of those due to the carbonyls. Consistent with the cationic charge and comparatively high ν(CO) values ($\mathrm{CH_2Cl_2}$: 2102, 2058, 2023 cm^{-1}), one carbonyl ligand is labile and readily replaced by triphenylphosphine to provide *trans*-$[\mathrm{Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2}]\mathrm{BF_4}$ (**2b**·$\mathrm{BF_4}$). Phosphorus-31 NMR data indicate that the two phosphine ligands are mutually *trans* (δ 54.6), and this is confirmed by the triplet multiplicity of the ^{13}C resonances due to the carbonyl (δ 214.0 $^2J(\mathrm{PC}) = 30.1$; 211.4 $^2J(\mathrm{PC}) = 21.3$) and carbamoyl (δ 184.0, $^2J(\mathrm{PC}) = 23.0$ Hz) carbons and the virtual triplicity of the aryl resonances of the phosphine ligands. The molecular geometry was confirmed by a crystallographic study of the **2b**·$\mathrm{PF_6}$ salt, which provided crystals suitable for analysis. The results of this study are summarized in Table 2 and Figure 1 and are discussed below. Neither the carbonyl ligands nor the bidentate carbamoyl in **2b**·$\mathrm{BF_4}$ is labile. Thus no reaction is observed with the potential ligands or pro-ligands KI, 1,2-bis(diphenyl-

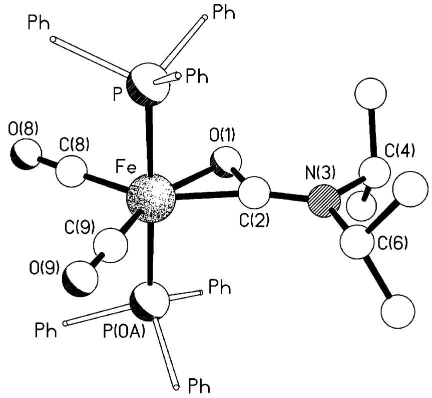


Figure 1. Molecular structure of the cation ($2b^+$) of $[Fe(OCN^iPr_2)(CO)_2(PPh_3)_2]PF_6$. Phenyl groups omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $2b^+$

Fe−P	2.3106(12)	Fe−P(0A)	2.3106(12)
Fe−C(8)	1.823(7)	Fe−C(9)	1.764(7)
Fe−O(1)	1.985(4)	Fe−C(2)	1.920(6)
C(2)−O(1)	1.271(7)	C(8)−O(8)	1.136(7)
C(9)−O(9)	1.151(7)	C(2)−N(3)	1.305(7)
N(3)−C(6)	1.485(8)	N(3)−C(4)	1.515(8)
P−Fe−P(0A)	177.95(7)	C(8)−Fe−C(9)	100.6(3)
C(9)−Fe−C(2)	119.2(3)	C(8)−Fe−O(1)	102.2(2)
O(1)−Fe−C(2)	37.9(2)	Fe−C(2)−N(3)	160.4(5)
O(1)−C(2)−N(3)	125.8(6)	Fe−O(1)−C(2)	68.3(3)
O(1)−C(2)−Fe	73.8(3)	C(6)−N(3)−C(4)	117.8(5)
C(4)−N(3)−C(2)	121.5(5)	C(6)−N(3)−C(2)	120.7(6)

phosphino)ethane, $Na[S_2CNMe_2]$, $CNC_6H_3Me_2$-2,6, or excess PPh_3 over a period of 24 h in dichloromethane at room temperature. Complex and intractable mixtures were obtained for the same combinations of reagents in refluxing tetrahydrofuran.

The complex $\mathbf{2b}^+$ can also be obtained as the trifluoroacetate salt $\mathbf{2b}\cdot O_2CCF_3$ from the reaction of $Li[Fe\{C(=O)N^iPr_2\}(CO)_4]$ with trifluoroacetic anhydride and triphenylphosphine at low temperature. In this synthesis, the time delay between the successive addition of $(CF_3CO)_2O$ and PPh_3 is crucial. As the delay increases, so does the proportion of $[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$ (**1c**)[8] at the expense of $\mathbf{2b}\cdot O_2CCF_3$. This behavior might be a consequence of slow (at −78 °C) decarboxylation of an intermediate of the form $[Fe\{C(=O)CF_3\}\{C(=O)N^iPr_2\}(CO)_n]$ (n = 3, 4, ?) to provide $[Fe\{C(=O)N^iPr_2\}(CF_3)(CO)_n]$. The extensive chemistry of **1c** has been discussed elswhere.[10b]

The reaction of $\mathbf{2a}\cdot BF_4$ with dppe [1,2-bis(diphenylphosphino)ethane] leads to substitution of one carbonyl and the triphenylphosphine ligand to provide $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(dppe)]BF_4$ ($\mathbf{3}\cdot BF_4$) (Scheme 3). The gross formulation follows from the FAB mass spectrum, which features a molecular ion and peaks due to the loss of one and two carbonyl ligands. The yellow salt shows two terminal carbonyl-associated absorptions in the infrared (CH_2Cl_2) spectrum, at 2043 and 1978 cm^{-1}, consistent with the ionic formulation and a *cis*-dicarbonyl arrangement. The $^{31}P\{^1H\}$ NMR spectrum, however, shows only one resonance (δ 74.0), which is inconsistent with an octahedral arrangement of the six ligating atoms. These data are consistent with a trigonal prismatic arrangement (**D**, Chart 2) or perhaps, more likely, a fluxional process involving a symmetrical intermediate (**E**, Chart 2), possibly arising from monodentate coordination of the carbamoyl ligand. This latter interpretation is further supported by the broad nature of the ^1H NMR spectra of recrystallized material, which nevertheless allow identification of four doublets due to the isopropyl methyl groups in addition to the multiplet due to the ethylene chain of the dppe ligand, which is also broadened. Furthermore, only one broad ^{13}C resonance is observed for the carbonyl ligands.

Scheme 3. Ligand Exchange Reactions of the Complex 1a

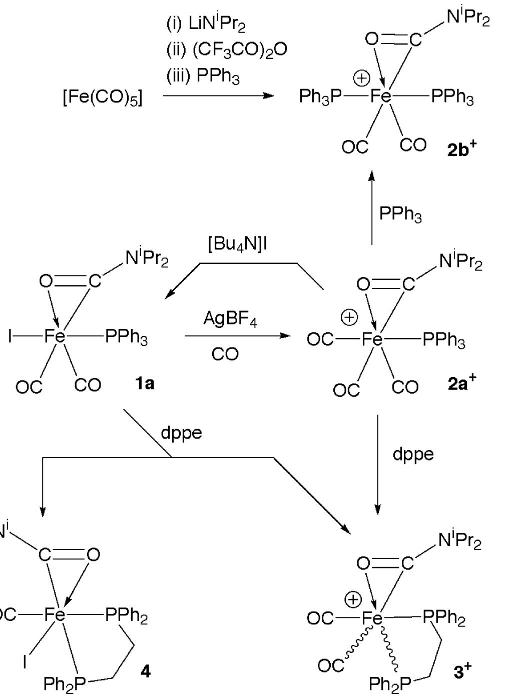
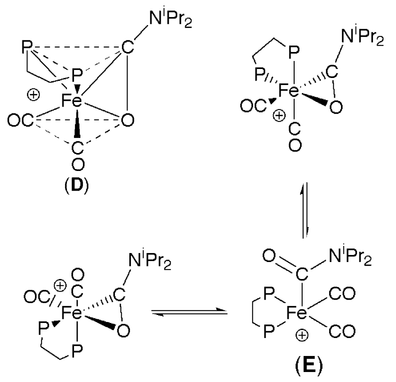
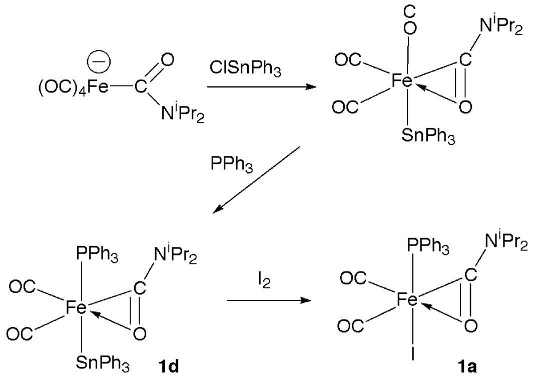


Chart 2. Proposed Fluxionality in the Cationic Complex 3^+ (P = PPh_2)



The complex $\mathbf{3}^+$ is also formed as an iodide salt directly from **1a** and dppe in tetrahydrofuran, although the neutral complex $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)(dppe)]$ (**4**) is also formed as a side product. The two compounds are readily separable, as the salt $\mathbf{3}\cdot I$ is only sparingly soluble in thf and precipitates from the reaction mixture. The various spectroscopic data for **4** indicate a considerably more π-basic iron center than in **1b** including a decrease in the frequency of the carbamoyl-associated infrared peak observed at 1584 cm^{-1} and the terminal carbonyl absorption at 1922 cm^{-1}. The geometry at iron, as shown in Scheme 3, follows from the ^{31}P and ^{13}C NMR data. The chemically inequivalent

Scheme 4



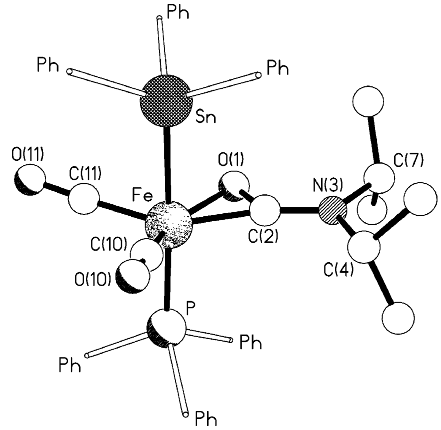


Figure 2. Molecular structure of the complex [Fe(OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_2$(PPh$_3$)$_2$] (**1d**). Phenyl groups omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex 1d

Fe−P	2.205(3)	Fe−Sn	2.5632(13)
Fe−C(10)	1.722(6)	Fe−C(11)	1.787(6)
Fe−O(1)	2.051(4)	Fe−C(2)	1.885(5)
C(2)−O(1)	1.296(6)	C(10)−O(10)	1.166(7)
C(11)−O(11)	1.169(7)	C(2)−N(3)	1.302(6)
N(3)−C(4)	1.496(7)	N(3)−C(7)	1.478(7)
P−Fe−Sn	176.53(7)	C(10)−Fe−C(11)	99.0(3)
C(10)−Fe−C(2)	116.2(3)	C(11)−Fe−O(1)	104.7(2)
O(1)−Fe−C(2)	38.1(2)	Fe−C(2)−N(3)	157.9(4)
O(1)−C(2)−N(3)	124.2(5)	Fe−O(1)−C(2)	64.0(3)
O(1)−C(2)−Fe	77.9(3)	C(7)−N(3)−C(4)	119.7(4)
C(4)−N(3)−C(2)	117.1(4)	C(7)−N(3)−C(2)	123.2(5)

phosphorus nuclei give rise to an **AB** system [δ 68.2, 105.5, ^2J(AB) = 22.0 Hz] in the ^{31}P NMR spectrum, while the carbamoyl ^{13}C resonance is evident as a double-doublet [δ 204.9] with quite distinct couplings to *trans* (37.5) and *cis* (21.4 Hz) phosphorus nuclei. These data may be compared with those for the related aroyl complex [Fe(η^2-OCC$_6$H$_2$Me$_3$)(CO)(dippe)Br] (Table 1),[19] which has been structurally characterized and is obtained by the facile carbonylation of [Fe(C$_6$H$_2$Me$_3$)Br(dippe)] (dippe = 1,2 bis(diisopropylphosphino)ethane).

Treatment of a solution of Li[Fe{C(=O)N^{i}Pr$_2$}(CO)$_4$] with triphenylchlorostannane provides a thermally sensitive intermediate presumably of the form [Fe(η^2-OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_3$], which can be converted to the thermally stable derivative **1d** by treatment with triphenylphosphine (Scheme 4). In addition, varying amounts of [Fe(CO)$_3$(PPh$_3$)$_2$] are obtained, which may be removed by column chromatography or recrystallization from dichloromethane and ethanol. Spectroscopic data suggest the formulation of the compound as a stannyl-carbamoyl complex of iron(II) [Fe(η^2-OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_2$(PPh$_3$)] (**1d**), and this was confirmed crystallographically (Figure 2, Table 3, vide infra). Variable-temperature ^{1}H NMR spectroscopy in the range 225−335 K failed to provide completely resolved spectra due to fluxional processes. The static molecular geometry as depicted in Scheme 4 and Figure 2 has no element of symmetry, and at no temperature within this range do the isopropyl substituents become equivalent. At the hot extreme (335 K), before decomposition ensues, two methine multiplets and a four-line pattern in the methyl region are apparent. At the cold extreme (225 K), when precipitation occurs, two unresolved methine and three methyl resonances (ratio ca. 1:1:2) are observed. Among the various conceivable fluxional processes the two most plausible are (i) dissociation of the bidentate carbamoyl coordination followed by rotation about the iron−carbon bond, allowing exchange of methyl sites but retaining the independence of methine sites, or (ii) rotation about the C−N bond. The former appears the most plausible and accounts for the persisting inequivalence of the methine resonances and the facility of ligand exchange reactions via the presumed five-coordinate intermediate (vide infra). The ^{31}P NMR spectrum consists of a singlet showing coupling to tin, consistent with a *trans* disposition of the PPh$_3$ and SnPh$_3$ groups. The infrared data for the Fe(CO)$_2$ unit (1979, 1908 cm^{-1}) suggest that the iron center is more π-basic than in the previously reported and related complex [Fe(η^2-OCN^{i}Pr$_2$)(CF$_3$)(CO)$_2$(PPh$_3$)] (2020, 1953 cm^{-1}),[8] reflecting the relative electronegativies of the CF$_3$ and SnPh$_3$ groups.

The complex [Fe(η^2-OCN^{i}Pr$_2$)(CF$_3$)(CO)$_2$(PPh$_3$)] reacts with K[HB(pz)$_3$] (pz = pyrazol-1-yl) to provide the ferraoxetene [Fe(κ^2-CF$_2$OCN^{i}Pr$_2$)(CO){HB(pz)$_3$}] presumably via the coupling of the carbamoyl ligand with a putative difluorocarbene complex.[10] One motivation for developing synthetic routes to stannyl-carbamoyl complexes was to establish whether it might be possible to generate an electrophilic stannylene ligand which would be similarly trapped intramolecularly by the carbamoyl ligand to provide a stannaferraoxetene. Accordingly, the reaction of the complex **1d** with iodine was investigated as a means of cleaving one or more Sn−Ph linkages to generate cationic stannylene or neutral iodostannyl complexes. Such processes have been implicated in the chemistry of ruthenium stannyl complexes.[20] Reaction of [Fe(η^2-OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_2$(PPh$_3$)] with iodine however leads to cleavage of the Sn−Fe bond and formation of [Fe(η^2-OCN^{i}Pr$_2$)I(CO)$_2$(PPh$_3$)] (**1a**), the alternative preparation of which was described above.

Crystal and Molecular Structure of [Fe(η^2-OCN^{i}Pr$_2$)(CO)$_2$(PPh$_3$)$_2$]PF$_6$ (2b·PF$_6$). The molecular structure of the complex cation [Fe(η^2-OCN^{i}Pr$_2$)(CO)$_2$(PPh$_3$)$_2$]$^+$ (**2b**$^+$) is shown in Figure 1, and selected geometrical parameters are given in Table 2. The complex and counterion interact only weakly via a pair

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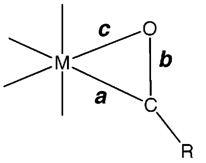
Table 4. Structural Data (Å) for Bidentate Acyl, Aroyl, and Carbamoyl Complexes of Group 8 Metals



complex	*a*	*b*	*c*
M = Fe			
$[Fe(\eta^2\text{-}OCMe)I(CO)(PMePh_2)_2]$[24]	1.83	1.23	2.25
$[Fe(\eta^2\text{-}OC^iPr)I(CO)(PEt_3)_2]$[25c]	1.81	1.24	2.19
$[Fe(\eta^2\text{-}OCC_6H_2Me_3)I(CO)(dippe)]$[19]	1.86	1.28	1.99
$[Fe(\eta^2\text{-}OCN^iPr_2)(CF_3)(CO)_2(PPh_3)]$[8]	1.87	1.25	2.04
$[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)]$	1.89	1.30	2.05
$[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)_2]^+$	1.92	1.27	1.99
M = Ru, Os			
$[Ru(\eta^2\text{-}OCMe)I(CO)(PPh_3)_2]$[26]	1.88	1.33	2.47
$[Ru(\eta^2\text{-}OCC_6H_4Me)Cl(CO)(PPh_3)_2]$[26]	1.92	1.21	2.36
$[Ru(\eta^2\text{-}OCNMe_2)H_2Cl(P^iPr_3)_2]$[6b]	1.96	1.25	2.34
$[Ru(\eta^2\text{-}OCC_6H_4NH_2)Cl(CO)(PPh_3)_2]$[27]	1.96	1.25	2.38
$[Os(\eta^2\text{-}OCC_6H_4Me)Cl(CH_2)(PPh_3)_2]$[28]	2.01	1.22	2.42
$[Fe^0(\eta^2\text{-}OCHPh)(CO)_2(PEt_3)_2]$[a,29]	2.04	1.29	1.96
$[Fe^0(\eta^2\text{-}OC{=}CPh_2)(CO)_2(PEt_3)_2]$[a,30]	1.92	1.28	1.98
$[Fe^0(\eta^2\text{-}OC{=}CHCO_2Et)(CO)_2(PEt_3)_2]$[a,31]	1.92	1.28	2.01

[a] Included as a benchmarks for aldehyde and ketene coordination; however the iron center is formally zerovalent.

of C−H···F hydrogen bonds involving a meta-C−H group on one of the phenyl rings of each PPh_3 unit; [C···F], [H···F] 3.36, 2.14 Å, [C−H···F] 164°. The complex has crystallographic C_s symmetry about the plane containing the iron atom, the two CO groups, and the OCN^iPr_2 ligand. The "$Fe(CO)_2(PPh_3)_2$" unit is unremarkable, with the equatorial C(8)−Fe−C(9) angle of 100.6(3)° lying between trigonal and octahedral norms. The two Fe−CO distances differ significantly, with that *trans* to the carbamoyl carbon [Fe−C(8) 1.832(7) Å] being longer than that *trans* to oxygen [Fe−C(9) 1.764(7) Å]. Here the difference in bond lengths probably reflects the π-acceptor and π-donor roles of the *trans* carbamoyl carbon and oxygen atoms. The two phosphines are mutually *trans*, and the two Fe−P vectors are almost collinear [P(1)−Fe-P(2) 177.95(7)°].

The main interest in this structure centers on the iron-carbamoyl interaction, given that the chemistry outlined above suggests that this may be strong. The Fe−C(2) separation of 1.920(6) Å clearly suggests some limited degree of multiple bonding, while the iron oxygen separation of 1.985(4) Å is somewhat shorter than that observed for the complex **1c** [2.030(2Å][8] and the acyl complexes collected in Table 4. However, since **2b**$^+$ is the only cationic complex in this series, the stronger binding of the oxygen donor is consistent with the more electrophilic iron center. The trigonally coordinated nitrogen atom of the carbamoyl ligand is separated by 1.305(7) Å from the carbamoyl carbon, which clearly indicates a considerable amount of multiple bonding (cf. N(3)−C(4) 1.515(8), N(3)−C(6) 1.485(8) Å]. Thus it appears that each of the canonical forms in Chart 1 contributes appreciably to the overall bonding. The positions of the isopropyl methyl groups are such as to minimize nonbonding interactions with each other and with the phosphine ligands. Alternative rotational isomers would lead to substantial and unfavorable steric conflict between these groups.

Crystal and Molecular Structure of $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)]$ (1d). The molecular geometry of the complex is shown in Figure 2, and selected geometrical parameters are given in Table 3. The complex exhibits mirror disorder with in ca. 10% of the molecules the positions of the PPh_3 and $SnPh_3$ groups being reversed. Figure 2 illustrates the major occupancy conformer and confirms (i) the *trans* disposition of stannyl and phosphine groups; (ii) the *cis* dicarbonyl arrangement [C(10)−Fe−C(11) 99.0(3)°] with both carbonyls more strongly bound to the neutral iron center [Fe−C(10) 1.722(10), Fe−C(11) 1.787(6) Å] than in the cationic complex **2b**$^+$, and (iii) the bidentate carbamoyl mode of coordination. The iron−phosphorus separation [2.205(3) Å] compared with that observed in **1c** [2.291(4) Å][8] and **2b**$^+$ [2.3106(12) Å] suggests that the coordination of the electropositive stannyl group *trans* to the phosphine strengthens the binding relative to the electronegative CF_3 group or the PPh_3 group in the cation **2b**$^+$. The iron−tin separation of 2.5632(13) Å is within the range previously observed for Fe−$SnPh_3$ bond lengths, e.g., $[Fe(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ [2.533, 2.540 Å][21] and *cis*-$[Fe(SnPh_3)_2(CO)_4]$ [2.661(1) Å],[22] although longer than observed for the tribromo derivative $[Fe(SnBr_3)(CO)_2(\eta\text{-}C_5H_5)]$ [2.462(2) Å].[2323−31]

As with **2b**$^+$ above, interest centers on the $FeOCN^iPr_2$ unit, and pertinent structural features for this group are summarized in Table 4 along with those for **1c** and bidentate acyl/aroyl complexes of iron. The nitrogen is clearly trigonal planar, although in contrast to **2b**$^+$, here this is not a crystallographic requirement. Accordingly, pπ−pπ overlap between N(3) and C(2) [N(3)−C(2) 1.302(6) Å] is a factor that should bear on the dimensions of the FeO(1),C(2) metallacycle. Of the valence bond descriptions contributing to the bonding descriptions (Chart 1) it is the zwitterionic (hyperconjugative) contributor that is peculiar to carbamoyls as distinct from acyl and aroyl complexes. This should lead to a lengthening of the bonds within the metallacycle, and this is clearly evident, with Fe−O(1) at 2.051(4) Å and C(2)−O(1) at 1.296(6) Å. The bond between iron and the carbamoyl carbon at 1.885(5) Å is *shorter* than in **2b**$^+$ and comparable to that in **1c**,

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consistent with a π-acceptor role for this carbon accommodating the increased metal π-basicity of neutral complexes.

Concluding Remarks. A convenient entry into the chemistry of carbamoyl complexes of divalent iron has been established. A feature of the reactivity described is the apparent tenacity of the bidentate mode of carbamoyl coordination, at least in ground-state structures. Nevertheless, the facility of ligand exchange reactions, the facile isomerism, and the fluxionality of some of the complexes might be taken to suggest that monodentate carbamoyl complexes play a role in the solution chemistry. The importance of bidentate versus monodentate carbamoyl coordination in preactivation toward ligand substitution is further supported by the observation that of all the carbamoyl complexes studied, the one that is substitution inert, i.e., $\mathbf{2b}^+$, has a significantly shorter iron−oxygen bond length.

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).

^1H, $^{13}C\{^1H\}$, 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 ("M" refers to the cationic complex for salts). 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. Solvent of crystallization was confirmed by ^1H NMR integration where appropriate and by X-ray crystallography in the case of $\mathbf{2b}\cdot PF_6$.

Synthesis of [Fe(η^2-OCN^{i}Pr$_2$)I(CO)$_2$(PPh$_3$)] (1a). (a) $[Fe(CO)_5]$ (3.00 g, 15 mmol) was placed in a Schlenk tube with diethyl ether (50 mL), and a solution of LDA was then added dropwise (Aldrich: 1.5 mol dm^{-3}, 10.2 mL, 15 mmol). On completion, the reaction mixture was cooled (dry ice/propanone) and iodine (3.88 g, 15 mmol) added. The iodine eventually reacted as the reaction mixture was warmed to ca. −30 °C. When all had dissolved, triphenylphosphine (6.0 g, 23 mmol) was added, and the reaction mixture allowed to warm slowly to room temperature, causing a purple precipitate to form, which was isolated by decantation. Lithium iodide was removed by extraction of the solid with CH_2Cl_2/light petroleum (2:1) and filtration of the extracts through diatomaceous earth. The filtrate was concentrated and chromatographed (silica gel, CH_2Cl_2 eluant). The purple fraction was collected, concentrated, and diluted with petrol. On cooling (−30 °C), purple crystals of the product formed. Yield: 6.92 g (72%). (b) The product can also be prepared using a suspension of preformed I_2PPh_3 (15 mmol, obtained by combining I_2 (3.88 g) and PPh_3 (4.00 g)) in diethyl ether (50 mL). Yield: 8.51 g (88%). (c) To a solution of [Fe(η^2-OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_2$(PPh$_3$)] (**1d**, 0.30 g, 0.35 mmol) in dichloromethane (50 mL) was added solid iodine (0.10 g, 0.40 mmol). The mixture was stirred for 4 h and then freed of volatiles in vacuo. The residue was washed with light petroleum and then crystallized from a mixture of dichloromethane and petroleum ether. Yield: 0.11 g (48%). (d) A suspension of [Fe(η^2-OCN^{i}Pr$_2$)(SnPh$_3$)(CO)$_2$(PPh$_3$)] (**1d**, 0.30 g, 0.35 mmol) and iodine (0.10 g, 0.40 mmol) in diethyl ether (20 mL) was stirred for 1 h. The precipitate that formed was isolated and recrystallized from dichloromethane and light petroleum. Yield: 0.17 g (76%). IR (CH_2Cl_2): 2021, 1953 ν(CO) 1610 ν(NCO) cm^{-1}. IR (Nujol): 2012, 1948 ν(CO), 1615 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.55, 1.15, 1.19, 1.52 [d × 4, CH$_3$, ^3J(HH) = 6.6], 3.35, 5.09 [h × 2, 2 H, NCH, ^3J(HH) = 6.6 Hz], 7.19−7.67 [m × 2, 15 H, C$_6$H$_5$]. $^{13}C\{^1H\}$ (67.5 MHz): δ 220.5 [d, FeCO, ^2J(PC) = 25.0], 212.4 [d, FeCO, ^2J(PC) = 20.8], 197.4 [d, NCO, ^2J(PC) = 19.4 Hz], 134.2−128.3 [C$_6$H$_5$], 55.5, 47.9 (NCH), 21.6, 21.3, 20.4, 19.7 (CH$_3$). $^{31}P\{^1H\}$ (109 MHz): δ 78.5. FAB-MS: *m/z* 629[M]$^+$, 573[M − 2CO]$^+$, 445[FePPh$_3$I]$^+$, 318[FePPh$_3$]$^+$. Anal. Found: C, 51.1; H, 4.6; N, 2.0. Calcd for $C_{27}H_{29}FeINO_3P$: C, 51.5; H, 4.7; N, 2.2.

Synthesis of [Fe(η^2-OCN^{i}Pr$_2$)Br(CO)$_2$(PPh$_3$)] (1b). Bromine (0.79 mL, 15 mmol) was diluted in diethyl ether (100 mL), and the solution placed in an ice-bath. Triphenylphosphine (10.2 g, 38 mmol) was then added slowly, and the resulting PPh_3Br_2/PPh_3 suspension stirred at room temperature for 15 min. $[Fe(CO)_5]$ (3.00 g, 15 mmol) was placed in a second Schlenk tube with diethyl ether (50 mL), and a solution of LDA added dropwise (1.5 mol dm^{-3}, 10.0 mL, 15 mmol). On completion of the addition, the reaction mixture was cooled (dry ice/propanone) and the PPh_3Br_2/PPh_3 suspension added dropwise via a pressure-equalized dropping funnel. The reaction was then left to warm slowly to room temperature. A yellow precipitate eventually formed, which was isolated by decanting off the ethereal supernatant. Lithium bromide was removed by extracting the residue with a mixture of dichloromethane and light petroleum (2:1) and filtering the combined extracts through diatomaceous earth. On removing the solvent from the filtrate, the product was isolated and further purified by chromatography (silica gel, CH_2Cl_2 eluant, −30 °C), followed by crystallization from a mixture of dichloromethane and light petroleum. Yield: 7.06 g (79%). NB: Solution data are complicated by the presence of two isomers, designated **A** (minor) and **B** (major) according to Scheme 2. IR (CH_2Cl_2): 2034(sh) 2017, 1958 ν(CO), 1634, 1614 ν(NCO) cm^{-1}. IR (toluene): 2032, 2012, 1954 ν(CO), 1632, 1615 ν(NCO) cm^{-1}. IR (Nujol): 2012, 1964 ν(CO), 1637 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.65, 1.19, 1.14, 12.9 [d × 4, **A**-CH$_3$, ^3J(HH) = 6.6], 1.28, 1.41, 1.46, 1.53 [d × 4, **B**-CH$_3$, ^3J(HH) = 6.6], 3.43, 5.19 [h × 2, **A**-NCH, ^3J(HH) = 6.6], 3.87, 4.67 [h × 2, **B**-NCH, ^3J(HH) = 6.6 Hz], 7.34−7.69 [m, 15 H, C$_6$H$_6$]. $^{13}C\{^1H\}$ (67.5 MHz): 218.6 [d, **A**-FeCO, ^2J(PC) = 26.8], 215.2, 212.4 [br × 2, **B**-FeCO], 210.3 [d, **A**-FeCO, ^2J(PC) = 21.4], 198.4 [d, **A**-NCO, ^2J(PC) = 19.7], 194.9 [d, **B**-NCO, ^2J(PC) = 28.6 Hz], 134.2−127.4 [C$_6$H$_5$], 55.5, 47.8 [**A**-NCH], 53.8, 49.5 [**B**-NCH], 21.9, 20.3, 20.2, 20.1 [**A**-CH$_3$], 21.7, 21.4, 20.9, 20.7 [**B**-CH$_3$]. $^{31}P\{^1H\}$ (109 MHz): δ 74.6 (**A**), 38.0 (**B**). FAB-MS: *m/z* 525 [M − 2CO]$^+$, 474 [M − CO,Br]$^+$, 446 [M − 2CO,Br]$^+$, 398 [FePPh$_3$Br]$^+$. Anal. Found: C, 54.1; H, 4.9; N, 2.3. Calcd for $C_{27}H_{29}BrFeNO_3P(0.25CH_2Cl_2)$: C, 54.2; H, 4.9; N, 2.3.

Synthesis of [Fe(η^2-OCN^{i}Pr$_2$)(CO)$_2$(PPh$_3$)$_2$]X (2b·X). (a) X = BF$_4$. [Fe(η^2-OCN^{i}Pr$_2$}(CO)$_2$(PPh$_3$)]BF$_4$ (**2a**·BF$_4$, 0.20 g, 0.30 mmol)[10b] was dissolved in thf (20 mL) and triphenylphosphine added (0.13 g, 0.50 mmol). The reaction mixture was then heated under reflux for 1 h, and on completion the thf was removed under reduced pressure. Diethyl ether (30 mL) was added to the residue, and upon ultrasonic trituration, a yellow precipitate was produced, which was isolated by decantation. This crude product was then recrystallized from a mixture of dichloromethane and light petroleum (−30 °C). Yield: 0.16 g (58%). (b) X = PF$_6$. A solution of [Fe(η^2-OCN^{i}Pr$_2$)(CO)$_2$(PPh$_3$)$_2$](CF$_3$CO$_2$) (**2b**·O$_2$CCF$_3$) (1.00 g, 1.14 mmol)[10b] in dichloromethane (15 mL) was treated with concentrated aqueous HPF$_6$ (0.34 g, 0.46 mL, 2.4 mmol) followed by light petroleum (8 mL). The mixture was stirred for 15 min and then left to stand without stirring overnight. The well-formed yellow crystals were isolated by filtration, washed with diethyl ether, and dried in vacuo. IR (CH_2Cl_2): 2039, 1968 ν(CO) 1605 ν(NCO) cm^{-1}. IR (Nujol): 2026, 1960 ν(CO), 1612 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.09, 1.00 [d × 2, 12 H, CH$_3$], 3.06, 5.16 [h × 2, 2 H, NCH], 7.33−7.53 [m, 30 H,C_6H_5]. $^{13}C\{^1H\}$ (67.5 MHz): δ 214.0 [t, FeCO, $^2J(P_2C) = 30.1$], 211.4 [t, FeCO, $^2J(P_2C) = 21.3$], 184.0 [t, OCN, $^2J(P_2C) = 23.0$ Hz], 133.6−129.4 (C_6H_5), 56.2, 49.6 (NCH), 21.3, 19.2 (CH_3). $^{31}P\{^1H\}$ (109 MHz): δ 54.6. FAB-MS: *m*/*z* 764 $[M]^+$, 708 $[M - 2CO]^+$, 580 $[Fe(PPh_3)_2]^+$. Anal. Found C, 53.0; H, 4.4; N, 1.3. $C_{45}H_{44}F_6FeNO_3P_3{\cdot}(2CH_2Cl_2)$ requires C, 52.3; H, 4.5; N, 1.3. Dichloromethane solvate confirmed by ^1H NMR and X-ray diffraction. Crystal data for **2b**·PF_6: $[C_{45}H_{44}NO_3P_2Fe](PF_6){\cdot}2CH_2Cl_2$, $M = 1079.42$, monoclinic, $P2_1/m$ (no. 11), $a = 9.349(2)$ Å, $b = 24.347(3)$ Å, $c = 10.980(2)$ Å, $\beta = 96.467(14)°$, $V = 2483.4(6)$ Å^3, $Z = 2$ (C_s symmetry), $D_c = 1.444$ g cm^{-3}, μ(Mo Kα) = 0.68 mm^{-1}, $T = 223$ K, yellow plates; 3134 independent measured reflections, F^2 refinement, $R_1 = 0.049$, $wR_2 = 0.105$, 2267 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 45°$], 277 parameters. CCDC 232296.

Reaction of $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)_2(PPh_3)]$ with dppe: Synthesis of (a) $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(dppe)]I$ (3·I) and (b) $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)(dppe)]$ (4). $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)I]$ (**1a**, 0.20 g, 0.31 mmol) and 1,2-bis(diphenylphosphino)ethane (0.13 g, 0.31 mmol) were placed in a Schlenk tube, and the tube was evacuated and refilled with nitrogen. Tetrahydrofuran (30 mL) was added and the reaction mixture stirred at room temperature overnight, resulting in a yellow precipitate and a purple supernatant. On allowing the precipitate to settle, the thf liquor was decanted off, the residue washed with thf (5 mL), and the product $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(dppe)]I$ isolated. Yield: 0.09 g (37%). IR (CH_2Cl_2): 2043, 1978 ν(CO), 1626 ν(NCO) cm^{-1}. IR (Nujol): 2030, 1969 ν(CO), 1627 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.96, 1.41, 1.55, 1.84 [d × 4, 12 H, CH_3, $^3J(HH) = 6.6$], 2.98, 3.39 [m(br) × 2, 4 H, PCH_2], 3.63, 4.79 [h × 2, 2 H, NCH, $^3J(HH) = 6.6$ Hz], 7.02, 7.57 [m × 2, 20 H, C_6H_5]. $^{13}C\{^1H\}$ (67.5 MHz): δ 208.5 [br, FeCO], 193.4 [d, OCN, $^2J(PC) = 14.3$ Hz], 133.3−129.4 (C_6H_5), 55.2, 49.6 (NCH), 29.5 [m(br), PCH_2], 21.0, 20.1 (CH_3). $^{31}P\{^1H\}$ (109 MHz): δ 74.1. FAB-MS: *m*/*z* 638 $[M]^+$, 610 $[M - CO]^+$, 582 $[M - 2CO]^+$, 453 $[Fe(dppe)]^+$. Anal: Found C, 52.4; H, 4.6; N. 1.7. Calcd for $C_{35}H_{38}FeINO_3P_2{\cdot}0.5CH_2Cl_2$: C, 52.8, H 4.9; N 1.7. (b) The solvent was removed from the thf supernatant above, under vacuum, and diethyl ether (30 mL) added to the residue. On ultrasonic trituration, a precipitate was formed, and after decanting off the diethyl ether, the product $[Fe(\eta^2\text{-}OCN^iPr_2)I(CO)(dppe)]$ was isolated. Yield: 0.08 g (34%). IR (CH_2Cl_2): 1917 ν(CO) 1593 ν(NCO) cm^{-1}. IR (Nujol): 1922 ν(CO), 1584 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.77, 1.19, 1.37, 1.57 [d × 4, 12 H, CH_3, $^3J(HH) = 6.6$], 2.40, 2.71 [m(br) × 2, 4 H, PCH_2], 3.49, 5.30 [h × 2, 2 H, NCH, $^3J(HH) = 6.6$ Hz], 7.02, 7.57 [m × 2, 20 H, C_6H_6]. $^{13}C\{^1H\}$ (67.5 MHz): δ 223.9 [d, FeCO, $^2J(PC) = 28.5$], 204.9 [dd, OCN, $^2J(PC) = 37.5$, 21.4 Hz], 135.2−127.7 (C_6H_5), 54.9, 47.4 (NCH), 32.2, 28.5 (dd × 2, PCH_2), 21.6, 21.1, 20.8, 20.2 (CH_3). $^{31}P\{^1H\}$ (109 MHz): δ 68.2, 105.5 [**AB**, ^2J(**AB**) = 22.0 Hz]. FAB-MS: *m*/*z* 709 $[M - CO]^+$, 610 $[M - I]^+$, 582 $[M - CO,I]^+$, 453$[Fe(dppe)]^+$. Anal. Found: C, 51.7; H, 4.6; N. 1.4. Calcd for $C_{34}H_{38}FeINO_2P_2{\cdot}CH_2Cl_2$: C, 51.8; H, 4.8; N, 1.7.

Preparation of $[Fe(\eta^2\text{-}OCN^iPr_2)(SnPh_3)(CO)_2(PPh_3)]$ (1d). To a solution of $[Fe(CO)_5]$ (3.00 g, 15 mmol) in diethyl ether (50 mL) was added LiN^iPr_2 (1.5 mol dm^{-3}, 10.2 mL, 15 mmol). The mixture was then cooled (dry ice/propanone) and treated with $ClSnPh_3$ (5.90 g, 15 mmol) and the mixture allowed to warm with stirring until the $ClSnPh_3$ had dissolved, after which time PPh_3 (6.00 g, 23 mmol) was added The mixture was stirred at room temperature for 12 h, after which time the supernatant liquor was decanted from the red-orange precipitate and discarded. Lithium chloride was removed by extracting the residue with a mixture of CH_2Cl_2 and petroleum ether (2:1). The combined extracts were filtered through diatomaceous earth and concentrated in vacuo to effect crystallization of the product. In the occasional event that the crude product was contaminated with $[Fe(CO)_3(PPh_3)_2]$ [ν(CO) 1880 cm^{-1}], the material could be further purified by chromatography [silica gel, ethyl ethanoate as eluant] or recrystallization from a mixture of dichloromethane and ethanol. Yield: 4.81 g (37%). IR (CH_2Cl_2): 1979, 1908 ν(CO) 1585 ν(NCO) cm^{-1}. IR (Nujol): 1973, 1907 ν(CO), 1586 ν(NCO) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H (270 MHz): δ 0.60 [br, 12 H, CH_3], 2.93, 4.70 [h × 2, 2 H, NCH], 7.10−7.60 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ (67.5 MHz): δ 218.0 [d, FeCO, ^2J(PC) not resolved], 196.7 [d, OCN, $^2J(PC) = 12.9$], 145.7 [C^1(SnPh), $^3J(PC) = 5.1$, $^1J(^{119}SnC) = 258$], 137.2 [$C^{2,6}$(SnPh), $^2J(^{119}SnC) = 32.9$], 133.8−128.2 [$PC_6H_5 + C^4(SnC_6H_5)$], 127.4 [$C^{3,5}(SnC_6H_5)$, $^3J(^{119}SnC) = 37.5$ Hz], 54.4, 47.5 (NCH), 20.7, 20.1 (CH_3). $^{31}P\{^1H\}$ (109 MHz): δ 53.8 [$^2J(^{119}SnP) = 637$ Hz]. FAB-MS: *m*/*z* 851 $[M]^+$, 795 $[M - 2CO]^+$, 720 $[M - 2CO - Ph]^+$, 668 $[Fe(SnPh_3)(PPh_3)]^+$, 563 $[M - CO - PPh_3]^+$, 535 $[M - 2CO - PPh_3]^+$, 351 $[SnPh_3]^+$, 318 $[FePPh_3]^+$. Anal. Found: C, 63.5; H, 4.9; N. 1.5. Calcd for $C_{45}H_{44}FeNO_3PSn$: C, 63.4; H, 5.2; N, 1.6. Crystal data for **1d**: $C_{45}H_{44}NO_3PSnFe{\cdot}CH_2Cl_2$, $M = 937.25$, monoclinic, $P2_1/n$ (no. 14), $a = 10.527(7)$ Å, $b = 19.299(11)$ Å, $c = 21.567(7)$ Å, $\beta = 93.97(3)°$, $V = 4371(4)$ Å^3, $Z = 4$, $D_c = 1.424$ g cm^{-3}, μ(Mo Kα) = 1.10 mm^{-1}, $T = 293$ K, orange-yellow blocks; 5689 independent measured reflections, F^2 refinement, $R_1 = 0.044$, $wR_2 = 0.123$, 4454 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 45°$], 445 parameters. CCDC 232295.

Supporting Information Available: Full details of the crystal structure determinations and ORTEP representations for **2b**·**PF_6** and **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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