

## Metallaometene Formation by Coupling of Carbamoyl and Difluorocarbene Ligands

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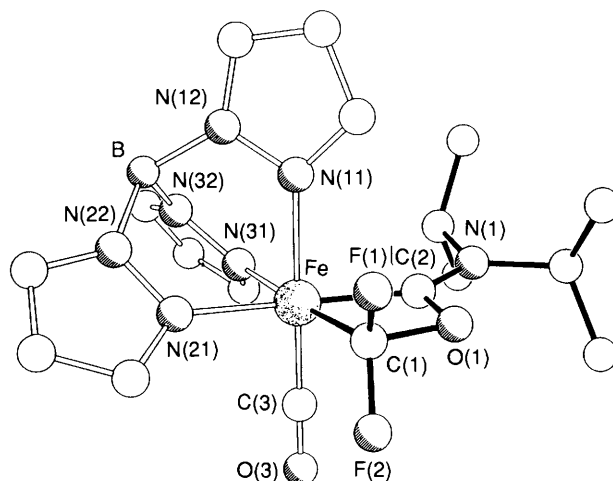
The reaction of the carbamoyl complex  $[\text{Fe}\{\eta^2\text{-C}(\text{=O})\text{NPr}_2\}\text{CF}_3(\text{CO})_2(\text{PPh}_3)]$  with potassium hydrotris(pyrazol-1-yl)borate provides the structurally characterised ferraometene  $[\text{Fe}\{\text{CF}_2\text{OC}(\text{NPr}_2)\}(\text{CO})\{\text{HB}(\text{pz})_3\}]$  (pz = pyrazol-1-yl), presumably *via* coupling of the carbamoyl ligand with a difluorocarbene intermediate.

Our understanding of the mechanisms whereby C<sub>1</sub> units couple during transition metal mediated Fischer–Tropsch processes has been greatly refined through studies of the coupling reactions of C<sub>1</sub> ligands on molecular organometallic species.<sup>1</sup> The origin of the oxygenate fraction of the Fischer–Tropsch product mixture has received less attention, and recently Roper has suggested that metallaometenes may be important intermediates, these being formed by the coupling of carbene and acyl ligands.<sup>2</sup> An alternative origin for this fraction has been suggested by Stone, based on the coupling of alkylidyne and acyl ligands on bimetallic systems.<sup>3</sup> We report herein the formation of an unusual ferraometene that results from the novel coupling of a carbamoyl and a difluorocarbene ligand.

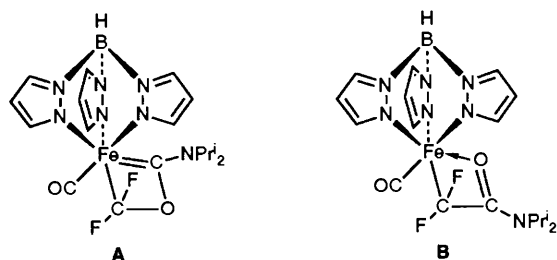
The carbamoyl–trifluoromethyl complex  $[\text{Fe}\{\eta^2\text{-C}(\text{=O})\text{NPr}_2\}\text{CF}_3(\text{CO})_2(\text{PPh}_3)]$  results from the successive treatment of iron pentacarbonyl with lithium diisopropylamide (LDA), trifluoroacetic anhydride and triphenyl phosphine.<sup>4</sup> The fluoro substituents of the CF<sub>3</sub> ligand are nucleofugic in nature, thus, for example, reaction with aqueous HBF<sub>4</sub> provides the tricarbonyl complex  $[\text{Fe}\{\eta^2\text{-C}(\text{=O})\text{NPr}_2\}(\text{CO})_3(\text{PPh}_3)]^+$ , the third carbonyl ligand being formed by hydrolysis of a putative cationic difluorocarbene intermediate  $[\text{Fe}\{\eta^2\text{-C}(\text{=O})\text{NPr}_2\}(\text{=CF}_2)(\text{CO})_2(\text{PPh}_3)]^+$ .<sup>5</sup> We were somewhat surprised that the carbamoyl ligand remained innocent during the course of this reaction, given the typically nucleophilic nature of acyl ligands and the oxophilic nature of difluorocarbene ligands. We now find that under suitable conditions the carbamoyl ligand may couple with a difluorocarbene ligand: Reaction of  $[\text{Fe}\{\eta^2\text{-C}(\text{=O})\text{NPr}_2\}\text{CF}_3(\text{CO})_2(\text{PPh}_3)]$  with potassium hydrotris(pyrazol-1-yl)borate,  $\text{K}\{\text{HB}(\text{pz})_3\}$  (pz = pyrazol-1-yl) leads to loss of KF and PPh<sub>3</sub> and the formation of a complex we formulate as a ferraometene on the basis of spectroscopic data, *viz*  $[\text{Fe}\{\text{C}(\text{NPr}_2)\text{OCF}_2\}(\text{CO})\{\text{HB}(\text{pz})_3\}]$  (A, Scheme 1).<sup>†</sup> The

alternative isomer involving C–C bond formation (B, Scheme 1) could be discounted on the basis of NOE-difference (nuclear Overhauser effect) experiments and the facile loss of the CF<sub>2</sub> group observed in the FAB mass spectrum (fast atom bombardment) of the product.

The ferraometene formulation was confirmed by a single crystal X-ray diffraction study (Fig. 1).<sup>‡</sup> Inter ligand angles for the  $[\text{Fe}(\text{CO})\{\text{HB}(\text{pz})_3\}]$  unit are between 86.5 and 95.5° and the primary distortion from ideal octahedral geometry derives from the small metallacycle bite  $[\text{C}(1)\text{–Fe–C}(2)]$  66.0° of the ferraometene. The strict planarity of the ferraometene unit enforces considerable contractions in the bond angles at C(1), O(1) and C(2) from ideal sp<sup>2</sup> and sp<sup>3</sup> values. The coplanarity of the metallacycle and the strictly trigonal diisopropylamido



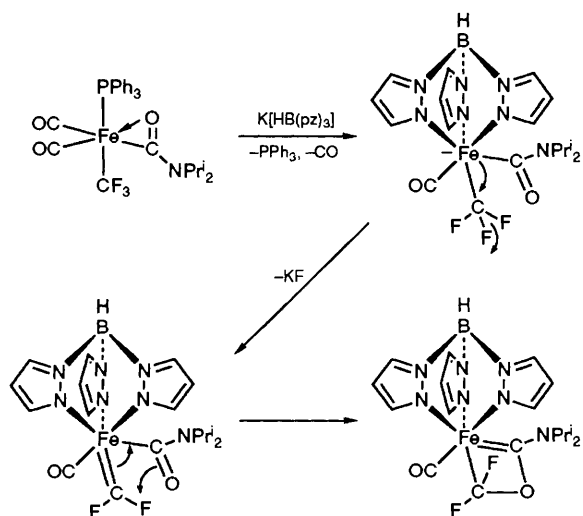
**Fig. 1** Molecular geometry for  $[\text{Fe}\{\text{C}(\text{NPr}_2)\text{OCF}_2\}(\text{CO})\{\text{HB}(\text{pz})_3\}]$ . Hydrogen atoms omitted. Selected structural features: Fe–C(1) 1.921(5), Fe–C(2) 1.908(5), C(1)–O(1) 1.443(5), C(2)–O(1) 1.362(5), N(1)–C(2) 1.308(5) Å. Fe–C(1)–O(1) 97.1(3), Fe–C(2)–O(1) 100.7(3), Fe–C(2)–N(1) 144.1(4), C(1)–O(1)–C(2) 96.1(3), C(1)–Fe–C(2) 66.0(2)°. Maximum deviation from Fe–C(1)–O(1)–C(2) least-squares plane: O(1) by 0.018 Å [N(1) by 0.12 Å].



**Scheme 1**

<sup>†</sup> Selected spectral data for  $[\text{Fe}\{\text{C}(\text{NPr}_2)\text{OCF}_2\}(\text{CO})\{\kappa^3\text{-HB}(\text{pz})_3\}]$ : Yield (2.0 mmol scale) 0.68 g (72%) [12% of  $[\text{Fe}\{\text{HB}(\text{pz})_3\}_2]$  also formed]. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu/\text{cm}^{-1}$  1959 (CO). NMR (CDCl<sub>3</sub>, 25 °C, SiMe<sub>4</sub>): <sup>1</sup>H δ 0.74, 1.20, 1.38, 1.43 (d × 4, 12 H, NCH Me<sub>2</sub>), 3.42, 3.93 (h × 2, 2 H, NCH Me<sub>2</sub>) 6.00, 6.03, 6.23 [t × 3, 3 H, H<sup>4</sup>(pz)], 7.47, 7.51, 7.59, 7.64, 7.69, 7.92 [d × 6, 6 H, H<sup>3,5</sup>(pz)]. <sup>13</sup>C-<sup>1</sup>H 225.0 [q(br) FeCO], 221.7 [q, <sup>3</sup>J (FC) 4.7 Hz, FeCNPr<sub>2</sub>], 138.4 [dd, J(CF) 352, 377 Hz, FeCF<sub>2</sub>O], 143.7, 143.5, 142.8, 135.0 (2 × C), 134.5, 105.3 (2 × C), 104.9 (BC<sub>3</sub>H<sub>3</sub>N<sub>2</sub>), 54.7, 48.7 (NCHMe<sub>2</sub>), 25.5, 21.3, 21.0, 20.3 (NCHMe<sub>2</sub>). FAB-MS *m/z* 447 (M<sup>+</sup> – CO, 37%), 397 (M<sup>+</sup> – CO – CF<sub>2</sub>, 73%), 269 [FeHB(pz)<sub>3</sub><sup>+</sup>, 100], satisfactory elemental analyses were obtained.

<sup>‡</sup> Crystal data for  $[\text{Fe}\{\text{C}(\text{NPr}_2)\text{OCF}_2\}(\text{CO})\{\text{HB}(\text{pz})_3\}]$ : C<sub>18</sub>H<sub>24</sub>BF<sub>2</sub>FeN<sub>7</sub>O<sub>2</sub>, *M* = 475.1, monoclinic, space group *P*2<sub>1</sub>/*n*, *Z* = 4, *a* = 9.308(4), *b* = 16.605(5), *c* = 14.878(5) Å, β = 100.02(3)°, *V* = 2264 Å<sup>3</sup>, *D*<sub>c</sub> = 1.39 g cm<sup>−3</sup>, *F*(000) = 984, μ(Cu-Kα) = 57 cm<sup>−1</sup>; 2θ ≤ 116° (Cu-Kα, λ = 1.54178 Å, graphite monochromator, ω scans, 291 K). The structure was solved by direct methods and refined anisotropically using absorption-corrected data to give *R* = 0.062 and *R*<sub>w</sub> 0.059 for 2722 independent observed reflections with  $[|F_o| > 3.0\sigma(|F_o|)]$ . Further details of the crystal structure investigation are available from the authors (D. J. W. and A. M. S. Z.). Also, the atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Scheme 2.** Mechanism for the formation of  $[\text{Fe}\{\text{=C}(\text{NPr}^i)_2\text{-OCF}_2\}(\text{CO})\{\text{HB}(\text{pz})_3\}]$

substituent is consistent with a short C(2)–N(1) distance (**B**, Fig. 2). The two metallacycle iron–carbon bond lengths are very similar [1.921 to C(1) and 1.908 Å to C(2)], in contrast to the known ruthenaoxetene  $[\text{Ru}\{\text{C}(\text{C}_6\text{H}_5)\text{OCH}_2\}(\text{CO})_2(\text{PPh}_3)_2]^+$ , which exhibits distinct single and double Ru–C bond lengths.<sup>2</sup> The ferraoxetene clearly shows considerable structural perturbation as a result of the conjugation of the diisopropylamino group, however, the bending of the difluoromethylene group away from iron [ $\text{Fe}-\text{C}(1)-\text{F}(1)$  121.9(3) and  $\text{Fe}-\text{C}(1)-\text{F}(2)$  123.5(3)°] towards a trigonal  $\text{CF}_2\text{Fe}$  arrangement suggests that a third canonical form (**C**,

Fig. 2) should also be considered to contribute to the metallacycle bonding.

A mechanism is proposed in Scheme 2 to account for the product formed and involves the intermediacy of a difluorocarbene complex  $[\text{Fe}\{\eta^1\text{-C}(\text{=O})\text{NPr}^i_2\}(\text{=CF}_2)(\text{CO})\{\kappa^3\text{-HB}(\text{pz})_3\}]$  which subsequently undergoes carbamoyl–carbene coupling. This process has precedent in the reactions of the ruthenium methylene complex  $[\text{Ru}(\text{C}_6\text{H}_5)\text{Cl}(\text{=CH}_2)(\text{CO})(\text{PPh}_3)_2]$  with CO or isocyanides to provide the metallaoxetenes  $[\text{Ru}(\text{=CPhOCH}_2)\text{L}_2(\text{PPh}_3)_2]^+$  ( $\text{L} = \text{CO}, \text{CNC}_6\text{H}_4\text{Me-4}$ ).<sup>2</sup> The elimination of fluoride from the trifluoromethyl precursor complex is surprisingly facile and we are currently investigating the synthetic utility of this feature.

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