Migratory insertion in N-heterocyclic carbene-containing Fe carbonyl complexes: an experimental and theoretical study

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The compound $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ reacts thermally with N-heterocyclic carbenes (L) to give both alkyl, $[Fe(\eta-C_{5}H_{5})(L)(CO)(Me)]$, and acyl, $[Fe(\eta-C_{5}H_{5})(L)(CO)(COMe)]$, derivatives. The reaction temperature has been shown to affect the product distribution. The alkyl and acyl derivatives exist in an equilibrium that is more easily perturbed than in the tertiary phosphine analogues. DFT studies on the reactivity of $[Fe(\eta-C_3H_3)(CO)_2(Me)]$ with PH₃ and dihydroimidazole-2-ylidene (IH) have shown that CO exchange is energetically favoured for IH, and energetically disfavoured for PH₃. The products of CO-induced migratory insertion, $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$, are more stable than the parent alkyl, $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$, compounds. This stabilisation is larger when L = IH than when L = PH₃. Stabilisation of the transition state by agostic interactions was seen in both instances, but this was significantly more pronounced for L = IH.

Introduction

Transition-metal complexes of N-heterocyclic carbenes NHCs have been synthesised by a number of different synthetic routes, including deprotonation of the imidazolium salt by metal anions,1,2 ligand displacement,3 oxidative addition,4 and silver carbene transmetallation.5 Transition-metal N-heterocyclic carbene compounds have also been synthesised by carbonyl group displacement. Thus the reaction of the simple carbonyl compounds $Fe(CO)_5$, $Ni(CO)_4$, $M(CO)_6$ (M = Cr, Mo, W) with N-heterocyclic carbenes gave the corresponding carbene complexes.³ Buchgraber et al. have synthesised Nheterocyclic carbene-containing iron piano-stool compounds, by treating the compound $[Fe(\eta-C_5H_5)(CO)_2(I)]$ with 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene, (IMes) and 1,3-bis(2,4,6trimethylphenyl)imidazolin-2-ylidene (H₂-IMes) to give the ionic compounds $[Fe(\eta-C_5H_5)(L)(CO)_2]^+[I]^-$, $(L = IMes, H_2-IMes)$. Subsequent light-induced decarbonylation afforded the neutral compounds [Fe(η -C₅H₅)(L)(CO)(I)] (L = IMes, H₂-IMes).⁶

Extensive work by Brown and Davies on systems of the type $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$ (L = tertiary phosphine)⁷ has demonstrated the application of such systems for alkyl homologation. Our interests focus on developing new templates for alkyl homologation,^{8,9} with a view to the development of homogeneous Fischer-Tropsch catalysts. In this paper we describe the synthesis and structure of new N-heterocyclic carbene derivatives of $[Fe(\eta-C_5H_5)(L)(CO)(R)]$ (R = Me, COMe), and their carbonylation/decarbonylation chemistry. A theoretical study at the DFT level has been conducted to explain the differences in behaviour of these systems when contrasted with their tertiary phosphine analogues.

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Synthesis

Results and discussion

IMes, to a solution of $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ in toluene gave the compound $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$, 1, after prolonged stirring at room temperature. Heating a solution of IMes with $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ in toluene at 60 °C gave the compound $[Fe(\eta - C_5H_5)(IMes)(CO)(COMe)]$, 2, after prolonged stirring. The compound 2 was observed to slowly decarbonylate in solution, forming 1. The compound 2 may also be synthesised by the carbonylation of 1 as described below. This reactivity is summarised in Scheme 1. The compound 1 is stable in solution. Both 1 and 2 are soluble in common polar organic solvents and essentially insoluble in non-polar organic solvents, such as pentane and hexane. Compounds 1 and 2 have been characterised by ¹H, $^{13}C{^{1}H}$ NMR and IR spectroscopies, by mass spectrometry and by elemental analysis. Compound 1 has also been characterised by X-ray crystal structure determination.

Addition of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene,

Crystallography

Crystals of [Fe(η-C₅H₅)(IMes)(CO)(Me)], 1, suitable for X-ray structure determination, were grown by slow diffusion of pentane into a saturated diethyl ether solution of 2 (presumably formed by decarbonylation in solution). An ORTEP representation of this structure is shown in Fig. 1. Selected bond lengths (Å) and angles (°) are given in Table 1. The asymmetric unit cell contains four crystallographically distinct molecules, all of which show similar conformations. These form two pairs, (Fe(1)-O(1)/Fe(2)-O(2) and Fe(3)-O(3)/Fe(4)-O(4), that are related by an approximate non-crystallographic centre of inversion. The crystal is formed by a stacking of alternate layers running perpendicular to the c axis, each set of which is composed entirely of one of these pairs. Despite the presence of both enantiomers, the crystal adopts a chiral space group, and refinement of the Flack enantiopole parameter¹⁰ gave



Scheme 1 Synthesis of Fe N-heterocyclic carbene complexes.

Table 1 Selected bond lengths (Å) and angles (°) for $[Fe(\eta - C_5H_5)-(IMes)(CO)(Me)]$ (average for four molecules)

Fe(1)-C(1) Fe(1)-C(22) Fe(1)-C(28) C(28)-O(1)	1.945(4) 2.034(4) 1.728(4) 1.162(5)	C(1)–N(1) C(1)–N(2) C(8)–C(9)	1.380(4) 1.376(5) 1.386(6)
C(22)-Fe(1)-C(28) C(1)-Fe(1)-C(22) C(1)-Fe(1)-C(28) C(1)-N(1)-C(4) C(1)-N(2)-C(13)	86.3(19) 91.4(15) 97.9(16) 128.9(3) 128.6(3)	Fe(1)-C(28)-O(1) Fe(1)-C(1)-N(1) Fe(1)-C(1)-N(2) N(1)-C(1)-N(2)	170.6(3) 130.1(3) 128.2(3) 101.6(3)

a value of 0.008(12), showing that the crystal as a whole consists of a single enantiomer.

Selected bond lengths (Å) for similar [Fe(η -C₅H₃)]-containing compounds are listed in Table 2. The Fe–C_{carbene} bond length in Fischer-carbene complexes of Fe are in the range 1.82– 1.97 Å.¹⁵ Thus, the 1.945(4) Å bond length found for **1**, lies at the higher end of this range, and is 0.035 Å shorter than that of the related compound [Fe(η -C₅H₅)(IMes)(CO)(I)]. The Fe–C_{methyl} bond length of 2.034(4) Å is significantly shorter than those reported in the related PPh₃-containing com-

Table 2	Comparison	of bond	lengths (A	Å)	
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Fig. 1 ORTEP view of **1**. Thermal ellipsoids are drawn at 40% probability. Hydrogen atoms have been omitted for clarity.

pounds $[Fe(\eta-C_3H_3)(PPh_2N(CH_3)CH(CH_3)Ph)(CO)(Me)]$ and $[Fe(\eta-C_3H_4I)(PPh_3)(CO)(Me)]$, which have reported bond lengths of 2.066(6) and 2.060 Å, respectively. The Fe–CO bond length of 1.728(4) Å lies in the range typical for Fe carbonyl alkyl complexes.

However, the C–O bond length, at 1.162(5) Å, is longer than is typical for Fe carbonyl alkyl compounds. Interestingly, the Fe(1)– C(28)–O(1) bond angle, in **1**, is 170.6° (average of four molecules). This represents a bend of the bond, away from the mesityl ligand. This may be due to a steric interaction between the carbonyl group and the IMes ligand. Both mesityl groups in the carbene ligand are twisted about the N–C bond with respect to metal–heterocycle plane, by 90.18 and 103.25°. This may be attributed to a steric interaction between the mesityl groups and the cyclopentadienyl ligand. A similar effect is observed in the crystal structure of [Fe(η -C₅H₅)(IMes)(CO)(I)].⁶

NMR Spectroscopy

The ¹H NMR spectra of the compounds **1** and **2** show three singlet resonances assignable to the methyl substituents of the mesityl groups. The chemical inequivalence of the 2,6 methyl groups may be attributed to the chirality of the molecule. The 3,5 aromatic hydrogen atoms are seen as two distinct resonances. Conversely, only a single resonance was observed for the heterocyclic ring protons (*HCN*). In the compound **1**, the Fe–CH₃ group is observed at δ 0.12, the high field value reflecting direct attachment to a metal atom. By contrast, in the compound **2** the methyl group, now an acyl, (COMe), is observed at δ 2.52, the large downfield shift being attributed to the electron withdrawing carbonyl group. The cyclopentadienyl resonances are observed at similar values in both

	Bond length				
Compound	Fe-C _{carbene}	Fe-C _{methyl}	$Fe-C_{carbonyl}$	C–O	Ref.
$[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$	1.945(4)	2.034(4)	1.728(4)	1.162(5)	This work
$[Fe(\eta-C_5H_5)(IMes)(CO)(I)]$	1.980(5)	_ ``	1.641(9)	1.077(8)	6
$[Fe(\eta-C_5H_5)(CO){\eta^2-C(OMe)-o-C_6H_4Cl}][OTf]$	1.857(6)		1.766(8)	_	11
$[Fe(\eta-C_5H_5)(CO){\eta^2-C(OMe)-o-C_6H_4OMe}][OTf]$	1.859(6)		1.769(7)	1.145(8)	12
$[Fe(\eta-C_5H_5)(PPh_2N(CH_3)CH(CH_3)Ph)(CO)(Me)]$		2.066(6)	1.684(9)	1.186(9)	13
$[Fe(n-C_{s}H_{4}I)(PPh_{3})(CO)(Me)]$		2.060 ^a	1.753ª	1.143ª	14

^{*a*} Esd not given.

compounds, at *ca*. δ 4.0. However, a slightly higher field value was recorded for **1**. The ¹³C{¹H} NMR spectra showed the carbene carbon resonances at δ 206.75 and 199.50 in the compounds **1** and **2**, respectively. Resonances attributable to the CO_{terminal} group were observed at *ca*. δ 220 in both instances. In compound **2**, a resonance attributable to CO_{acyl} was observed at δ 270.59.

Carbonylation/decarbonylation

A 30 mg sample of the compound $[Fe(\eta-C_5H_5)(IMes)-(CO)(COMe)]$, **2**, was dissolved in d₆-benzene, and the ensuing reaction was monitored by ¹H NMR spectroscopy. After 44 h in solution, 26% of the sample had decarbonylated to give $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$, **1**. This eventually equilibrated to give a 1 : 1 mixture of the compounds **1** : **2**. This was somewhat surprising, given that the related complex $[Fe(\eta-C_5H_5)(CO)(COMe)]$ is stable with respect to decarbonylation at temperatures of up to *ca*. 100 °C. This decarbonylation reaction was repeated, but this time the NMR tube was charged with a 1 atm pressure of carbon monoxide. Decarbonylation was observed again, but was retarded, equilibrating to a 0.4 : 1 (**1** : **2**) mixture after one week.

The carbonylation of 1 to give 2 was examined by dissolving 30 mg samples of $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$ in nitromethane or dichloromethane. These solutions were stirred under an atmosphere of CO. After removal of solvents under reduced pressure, the residues were then examined by ¹H NMR spectroscopy, to determine the amount of $[Fe(\eta-C_5H_5)(IMes)(CO)(COMe)]$ formed. The reaction conditions used for these carbonylations and the percent conversion are summarised in Table 3. Conversion yields were estimated by integration of the cyclopentadienyl and alkyl proton environments in the ¹H NMR spectrum.

The carbonylation of **1** at 1.5 atm of CO represents a facile carbonylation, when compared with $[Fe(\eta - C_5H_5)(PPh_3)(CO)(Me)]$. The formation of **2** from **1**, albeit in low yield, in dichloromethane is surprising, given that $[Fe(\eta - C_5H_5)(PPh_3)(CO)(Me)]$ is resistant to carbonylation in dichloromethane, even under a 5 bar pressure of carbon monoxide.¹⁶

Table 3 Reaction conditions and yields for the carbonylation of $[Fe(\eta - C_5H_5)(IMes)(CO)(Me)]$ to give $[Fe(\eta - C_5H_5)(IMes)(CO)(COMe)]$

Reaction conditions	Yield (%)
5 atm CO, rt, 12 h, nitromethane	92
1.5 atm CO, rt, 72 h, nitromethane	75
1.5 atm CO, rt, 24 h, dichloromethane	15

The chemical behaviour described above contrasts with the analogous reactivity of $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ with tertiary phosphines. These typically require elevated temperatures,17 affording acyl complexes of the form $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$ (L = tertiary phosphine), along with traces of the decarbonylation products of the type $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$ (L = tertiary phosphine). The acyl compounds $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$ (L = tertiary phosphine) are typically stable with respect to decarbonylation at temperatures of up to 80 °C. Experimental studies on the decarbonylation of the compound [Fe(η - $C_5H_5)(PPh_3)(CO)(COMe)$ have shown that this thermal decarbonylation process, that is observed at temperatures of 98 °C, occurs via the dissociation of PPh₃ to give $[Fe(\eta - C_5H_5)(CO)_2(Me)]$. The free PPh₃ subsequently displaces one CO group to give the product of decarbonylation, [Fe(η-C₅H₅)(PPh₃)(CO)(Me)].¹⁸ Carbonylation of $[Fe(\eta - C_5H_5)(PPh_3)(CO)(Me)]$ is known to require a combination of elevated CO pressures (5.5 atm), and very polar solvents such as nitromethane.¹⁶

Theoretical calculations

To understand the causes of the facile carbonylation/decarbonylation of the new NHC-containing compounds, when compared with the tertiary phosphine analogues, a series of DFT calculations was undertaken. For computational expediency, the bulky 1,3-bis(2,4,6,trimethylphenyl)imidazol-2-ylidene ligand was replaced with dihydroimidazol-2-ylidene (IH), and PPh₃ was replaced with PH₃.

Geometry optimisations

The molecular structures of $[Fe(\eta-C_5H_5)(IH)(CO)(Me)]$, I, $[Fe(\eta-C_5H_5)(IH)(CO)(COMe)]$, II, $[Fe(\eta-C_5H_5)(PH_3)(CO)(COMe)]$, III, and $[Fe(\eta-C_5H_5)(PH_3)(CO)(COMe)]$, IV, have been optimised. Selected data for the calculated bond distances are given in Table 4, along with experimentally derived values for similar compounds. Good agreement is seen between these calculated and experimentally derived values.

Migratory insertion

In order to model CO-induced migratory insertion, a series of Linear Transit (LT) calculations was performed in which the carbon atom of the methyl group was incrementally stepped towards the carbon atom of the terminal carbonyl group (Scheme 2). Maxima and minima on the LT energy surface were subsequently optimised

Table 4	Selected bond lengths	(Å	for calculated and experimentally derived structu	res
	Scherten bonn ingins	121	for calculated and experimentally derived structu	103

		Bond lengt	Bond length			
Compound		Fe–L	Fe-C _{acyl/alkyl}	Fe-C _{carbonyl}	C–O _{terminal}	Ref.
$[Fe(\eta - C_5H_5)(IM_5)]$	fes)(CO)(Me)] 1	1.945(4)	2.034(4)	1.728(4)	1.162(5)	This work
$[Fe(\eta-C_5H_5)(IH)]$	(CO)(Me) I	1.902	2.048	1.725	1.178	This work
$[Fe(\eta - C_5H_5)(IH)]$	()(CO)(COMe)] II	1.872	1.908	1.697	1.171	This work
$[Fe(\eta-C_5H_5)(PH)]$	I ₃)(CO)(Me)] III	2.092	2.007	1.703	1.167	This work
[Fe(n-C ₅ H ₅)(PH	H ₃)(CO)(COMe)] IV	2.113	1.925	1.711	1.166	This work
[Fe(C ₅ H ₄ I)(PPh	n ₃)(CO)(Me)]	2.195 ^a	2.060^{a}	1.753ª	1.143ª	14
Fe(C ₅ H ₅)(PPh)(CO)(COMe)]	2.187ª	1.939ª	1.805 ^a	1.134ª	19

" Values taken from CIF.



Scheme 2 Linear Transit trajectory.

to transition states and intermediates, respectively. Optimised geometries for the transition states (L = IH, **TS** and L = PH₃, **TS**') and intermediates (L = IH, **INT** and L = PH₃, **INT**'), are given in Fig. 2 and Fig. 3, and selected bond lengths are given in Table 5. Frequency calculations were performed to confirm these assignments. For **TS**, a single imaginary frequency was calculated at i170 cm⁻¹. This corresponded to a shortening of the CH₃ group to give bring the agostic-H closer to the metal. For **TS**', a single imaginary frequency also corresponded to a shortening of the CH₃-carbon to CO-carbon bond, and the rotation of the CH₃-carbon to CO-carbon bond, and the rotation of the CH₃ single imaginary frequency was calculated at i61 cm⁻¹. This frequency also corresponded to a shortening of the CH₃-carbon to CO-carbon bond. A shortening of the agostic H bond length also occurred.



Fig. 2 Geometry optimised structure of TS and INT.



Fig. 3 Geometry optimised structure of TS' and INT'.

Table 5 Selected bond lengths (Å) for TS, INT, TS' and INT'

For both species, the geometries of the calculated transition states and intermediates more closely resemble the product acyl, rather than the starting alkyl compounds, *i.e.* in both cases the transition states for methyl-migration are late.

This is particularly emphasised for the C_{alkyl} - C_{co} bond length. Short Fe–H (*ca.* 1.800 Å) bond distances and elongated C–H (*ca.* 1.155 Å) bonds were calculated for both **TS** and **INT**. These data are suggestive of agostic interactions between one hydrogen atom of the methyl group, and the metal centre. The results for **TS**' and **INT**' were similar, though the longest C–H bonds in **INT**' and **TS**' were longer, and the Fe–H bonds shorter than were calculated for **INT** and **TS** (see Table 5). This indicates that whilst agostic interactions were also important in **INT**' and **TS**', they are weaker than in **TS** and **INT**.

Energetics

The relative energies of I, II, INT and TS and III, IV, INT' and TS' are summarised in Table 6, and shown graphically on Fig. 4. In each series, the energies have been normalised to that of $[Fe(\eta-C_3H_3)(L)(CO)(Me)]$, *i.e.* I or III. Inspection of the values shows that the formation of the acyl compounds $[Fe(\eta-C_3H_3)(L)(CO)(COMe)]$ (L = IH, II, and L = PR₃, IV), from the parent alkyl compounds $[Fe(\eta-C_3H_3)(L)(CO)(Me)]$ (L = IH, I, and L = PR₃, III), is energetically favourable (-85 and -68 kJ mol⁻¹, respectively). This carbonylation reaction is a more favourable process for I than for III.

The activation energies for the carbonylation of $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$ were 75 kJ mol⁻¹ (L = PH₃) and 93 kJ mol⁻¹ (L = IH). Thus, the activation energy barrier is lower when L = PH₃ than when L = IH. This fails to explain the more facile carbonylation of $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$ compared with $[Fe(\eta-C_5H_5)(CO)(Me)]$, observed experimentally.

From the transition state calculations described, it is suggested that the more facile carbonylations when L = IH may be due to a

Table 6Relative energies (kJ mol⁻¹)

$[Fe(\eta - C_5H_5)(L)(CO)(Me)]$	Structure	Relative energy	Zero-point corrected relative energy
L = IH	I TS	0	0 93
	INT	86	94
	II	-117	-85
$L = PH_3$	III	0	0
	TS'	78	75
	INT'	78	76
	IV	-92	-68

		Bond length					
(Compound	Fe–L	$Fe-\!C_{acyl/alkyl}$	$Fe\!-\!C_{carbonyl}$	Fe–H	С–Н	C_{alkyl} – $C_{COterminal}$
[]	$Fe(\eta-C_sH_s)(IH)(CO)(Me)$] TS	1.861	2.131	1.753	1.790	1.159, 1.101, 1.099	1.524
. Ì	Fe(n-C ₅ H ₅)(IH)(CO)(Me)] INT	1.863	2.135	1.747	1.800	1.155, 1.100, 1.096	1.528
. Ì	$Fe(n-C_{5}H_{5})(IH)(CO)(Me)$] I	1.902	2.048	1.725		1.106, 1.101, 1.102	2.741
. Ì	Fe(n-C ₅ H ₅)(IH)(CO)(COMe)] II	1.872	1.908	1.697	3.029	1.102, 1.102, 1.104	1.497
. Ì	$Fe(n-C_{5}H_{5})(PH_{3})(CO)(Me)$] TS'	2.096	2.143	1.750	1.928	1.127, 1.096, 1.099	1.649
[$Fe(\eta - C_5H_5)(PH_3)(CO)(Me)$] INT'	2.096	2.139	1.759	1.880	1.135, 1.096, 1.099	1.620



Fig. 4 Energies for migratory insertion in I and III.

stronger agostic interaction in **TS** when compared with **TS**'. The steric differences between the model and experimental compounds may explain the discrepancy between the calculated activation energies, and the observed reactivity.

The relative energies of the complexes $[Fe(\eta-C_5H_5)(CO)_2(Me)]$, $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$ and $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$ are shown in Scheme 3 (L = IH) and Scheme 4 (L = PH₃). Inspection of these values shows that the energy change on replacement of a carbonyl ligand with the IH is -11 kJ mol⁻¹, and hence is energetically favoured.



Scheme 3 Energies of NHC complexes.

The magnitude of this stabilisation is small, but helps to rationalise the formation of $[Fe(\eta-C_3H_3)(IH)(CO)(Me)]$ in the room temperature reaction of IMes with $[Fe(\eta-C_3H_3)(CO)_2(Me)]$. By contrast, displacement of a CO ligand in $[Fe(\eta-C_3H_3)(CO)_2(Me)]$ by PH₃ requires an energy change of +76 kJ mol⁻¹, and is thus energetically disfavoured. This can be rationalised in terms of a stronger Fe–C_{carbene} bond with respect to Fe–P bond. This finding is consistent with those of Lee and Hu²⁰ who performed calculations on a series of transition-metal phosphine and Nheterocyclic carbene complexes and noted that NHC–metal bonds were significantly stronger than metal–phosphine bonds. They



Scheme 4 Energies of PH₃ complexes.

showed that, while CO exchange in $[Cr(CO)_6]$ was favourable for NHCs, it was unfavoured for tertiary phosphines.

The decarbonylation of acyl compounds of the form $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$ may proceed *via* one of two routes (see Scheme 5). This may occur *via* dissociation of L, so that after the reverse migratory insertion reaction, the compounds $[Fe(\eta-C_5H_5)(CO)_2(Me)]$, and non-coordinated L are formed. Displacement of CO by L would then lead to the observed product of decarbonylation, $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$.¹⁸ Alternatively, this may occur by loss of CO, followed by a reverse migratory insertion reaction. This represents the exact reverse of the migratory insertion mechanism that has been discussed above.



Scheme 5 Decarbonylation mechanisms.

The activation energy for the formation of $[Fe(\eta-C_5H_5)(CO)(COMe)] + L$ from $[Fe(\eta-C_5H_5)(L)(CO)(COMe)]$, was calculated as 86 kJ mol⁻¹ for L = PH₃. This compares well with a study by Cao *et al.*,²¹ on PH₃-induced migratory insertion in $[Fe(\eta-C_5H_5)(CO)_2(Me)]$, (*i.e.* the reverse process), who reported a rate-determining step of 74 kJ mol⁻¹. Cao *et al.* used the Gaussian 94 program. The activation energy for this decarbonylation process when L = IH is much higher, at 195 kJ mol⁻¹. This higher energy may be attributed to the greater Fe–carbene bond strength when compared with the Fe–phosphine bond strength.

Thus in the complex $[Fe(\eta-C_3H_3)(IH)(CO)(COMe)]$ the activation energy barrier to decarbonylation is similar *ca*. 200 kJ mol⁻¹, for both the CO dissociation and carbene dissociation mechanisms. By contrast, in the complex $[Fe(\eta-C_3H_3)(PH_3)(CO)(COMe)]$ the energies for the two different dissociations vary significantly. The activation energy barrier to decarbonylation *via* tertiary phosphine dissociation, at 84 kJ mol⁻¹, is much higher than that to decarbonylation *via* CO dissociation, 170 kJ mol⁻¹. This suggests that while decarbonylation *via* phosphine dissociation will be favoured in $[Fe(\eta-C_3H_3)(PH_3)(CO)(COMe)]$ —indeed this has been shown experimentally for $[Fe(\eta-C_5H_5)(PPh_3)(CO)(COMe)]$,¹⁸ in $[Fe(\eta-C_5H_5)(IH)(CO)(COMe)]$ decarbonylation *via* N-heterocyclic carbene dissociation will not be favoured with respect to the CO dissociation mechanism.

Conclusion

The compounds $[Fe(\eta-C_5H_3)(IMes)(CO)(Me)]$, and $[Fe(\eta-C_5H_3)(L)(CO)(COMe)]$ have been synthesised. DFT studies on the reactivity of $[Fe(\eta-C_5H_3)(CO)_2(Me)]$ with PH₃ and IH have shown that CO exchange is energetically favoured for IH, and energetically disfavoured for PH₃. The products of CO-induced migratory insertion, $[Fe(\eta-C_5H_3)(L)(CO)(COMe)]$ are more stable with respect to the parent alkyl $[Fe(\eta-C_5H_5)(L)(CO)(Me)]$ compounds. This stabilisation is larger when L = IH than when L = PH₃. The activation energy to carbonylation of $[Fe(\eta-C_5H_3)(L)(CO)(Me)]$ interactions was seen in both instances, but this was significantly more pronounced for L = IH.

Experimental

All manipulations of air- and/or moisture-sensitive compounds were carried out under an inert atmosphere of dinitrogen, in either an inert-atmosphere box or using standard Schlenk line techniques. Dinitrogen was purified by passage through columns containing 4A molecular sieves and either manganese(II) oxide suspended on vermiculite (vacuum line), or BASF catalyst (dry box). Solvents and solutions were transferred by passage through stainless steel cannulae, using a positive pressure of dinitrogen. Filtrations of air- and/or moisture-sensitive compounds were achieved by using modified stainless steel cannulae, fitted with glass fibre filter discs at one end. All glassware and stainless steel cannulae were dried overnight at 150 °C. Solvents used in the preparation of air- and/or moisture-sensitive compounds were dried by passage through an alumina column under a positive pressure of dinitrogen. Dinitrogen was passed through the dried solvents for twenty minutes before use. Deuterated solvents were degassed using three freeze-pump-thaw cycles and were vacuum distilled from potassium or sodium.

Solution NMR spectra were recorded with either a Varian UNITY *plus* (¹H: 500.0 MHz, ¹³C: 125.7 MHz) or a Varian Mercury 300 (¹H: 300.2 MHz, ¹³C: 75.5 MHz). The spectra were internally referenced relative to the residual protio-solvent (¹H) and solvent (¹³C) resonances relative to trimethylsilane (¹H, ¹³C, $\delta = 0$ ppm). Chemical shifts are reported in parts per million (δ). IR spectra were recorded on either a Perkin-Elmer 1710 FTIR spec-

trometer or a Perkin-Elmer 1600 FTIR instrument in the range 4000–400 cm⁻¹. Samples were prepared as Nujol mulls between KBr plates. Data are quoted in wavenumbers (cm⁻¹). Samples for mass spectrometry were recorded on a Micromass GCT GC/GC-MS. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, University of Oxford.

Materials

The compounds $[Fe(\eta\text{-}C_5H_5)(CO)_2(Me)]^{22}$ and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene were prepared as reported previously.^{23}

[Fe(η-C₅H₅)(IMes)(CO)(Me)]. A solution of 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene (500 mg, 1.64 mmol) in toluene (10 ml) was added to a solution of $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ (627 mg, 3.26 mmol) in toluene (10 ml). The resulting solution was then stirred for 72 h to give an orange-brown suspension. Filtration, followed by removal of solvents under reduced pressure, afforded an oily orange solid. This was washed with pentane $(3 \times 10 \text{ ml})$ to leave 1 as an orange powder. Crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of pentane into a saturated diethyl ether solution of [Fe(η - C_5H_5)(IMes)(CO)(COMe)]. Yield of 1 = 81.0 mg (10.1%). ¹H NMR (C_6D_6): δ 0.12 [s, 3H, FeCH₃], 1.98 [s, 6H, *o*-CH₃C₆H₂], 2.04 [s, 6H, o-CH₃C₆H₂], 2.05 [s, 6H, p-CH₃C₆H₂], 3.92 [s, 5H, η-C₅H₅], 6.20 [s, 2H, NCHCHN], 6.79 [s, 2H, ArH], 6.85 [s, 2H, ArH]; ${}^{13}C{}^{1}H$ NMR: δ 0.140 [s, FeCH₃] 18.40 [s, $o-CH_3C_6H_2$], 18.80 [s, o-CH₃C₆H₂], 21.08 [s, p-CH₃C₆H₂], 82.58 [s, η-C₅H₅], 123.94 [s, NCHCHN], 129.40 [s, Mes C_{3 or 5}], 129.30 [s, Mes C_{3 or 5}], 136.52 [s, Mes C_{2.6}], 137.51 [s, Mes C₄], 138.87 [s, Mes C₁], 206.75 [s, NCN], 223.28 [s, FeCO]. IR (Nujol, KBr): 1886s. m/z (FI+) 468 (80%) [M]⁺, 440 (25%) [M - CO]⁺, 305 [IMesH]⁺. Anal. (%). Found (calc.): C 71.5 (71.8) H 6.9 (6.9) N 6.0 (6.0).

[$Fe(\eta-C_5H_5)$ (IMes)(CO)(COMe)]. A solution of 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene (500 mg, 1.644 mmol) in toluene (10 ml) was added to a solution of $[Fe(\eta-$ C₅H₅)(IMes)(CO)₂(Me)] (627 mg, 3.26 mmol) in toluene (10 ml). The resulting solution was stirred at 60 °C for 72 h to give an orange-brown suspension. Filtration, followed by removal of solvents under reduced pressure, afforded an oily orange solid. This was washed with pentane $(3 \times 10 \text{ ml})$ to leave 2 as an orange powder. Yield of 2 = 302 mg (37.0%). ¹H NMR (C₆D₆): δ 2.03 [s, 6H, o-CH₃C₆H₂], 2.13 [s, 6H, o-CH₃C₆H₂], 2.31 [s, 6H, p- $CH_3C_6H_2$], 2.48 [s, COCH₃], 4.14 [s, 5H, η -C₅H₅], 6.12 [s, 2H, NCHCHN], 6.82 [s, 1H, ArH], 6.85 [s, 1H, ArH]; $^{13}C\{^{1}H\}$ NMR: δ 18.30 [s, o-CH₃C₆H₂], 18.80 [s, o-CH₃C₆H₂], 20.90 [s, p-CH₃C₆H₂], 50.50 [s, COCH₃], 83.50 [s, η-C₅H₅], 127.60 [s, HCN], 128.20 [s, Mes C_{3 or 5}], 129.20 [s, Mes C_{3 or 5}], 136.50 [s, Mes C_{2.6}], 137.50 [s, Mes C₄], 138.80 [s, Mes C₁], 199.50 [s, NCN], 221.86 [s, FeCO], 270.52 [s, COCH₃]. IR (Nujol, KBr): 1632s, 1924s. m/z (FI+) 496 (100%) [M]⁺, 468 (20%) [M - CO]⁺, 440 (10%) [M - 2CO]⁺. Anal. (%). Found (calc.): C 69.0 (70.2) H 6.7 (6.5) N 5.8 (5.6).

Decarbonylation of [Fe(\eta-C₅H₅)(IMes)(CO)(COMe)]. A solution of [Fe(η -C₅H₅)(**IMes)(CO)(COMe)**] (30 mg, 0.060 mmol) in d₆-benzene (0.4 ml) was introduced into a Young's Tap NMR tube. The subsequent decarbonylation reaction was monitored by ¹H NMR spectroscopy. After 44 h in solution, 26% of the

sample had decarbonylated to give $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$. After 1 month ¹H NMR data indicated that the solution had equilibrated to a 1 : 1 mixture of $[Fe(\eta-C_5H_5)(IMes)(CO)(COMe)]$: $Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$.

Carbonylation of $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$. A solution of $[Fe(\eta-C_5H_5)(IMes)(CO)(Me)]$ (30 mg, 0.064 mmol) in either nitromethane or dichloromethane (see Table 3) was introduced into a Fisher–Porter bottle. This was purged five times with CO. The solution was then stirred under an atmosphere of CO (either 1.5 or 5 atm). After removal of solvents under reduced pressure, the residues were then examined by ¹H NMR spectroscopy to determine the amount of $[Fe(\eta-C_5H_5)(IMes)(CO)(COMe)]$ formed. The reaction conditions used for these carbonylations and the percentage conversion are summarised in Table 3. Conversion yields were estimated by integration of the cyclopentadienyl/alkyl environments in the ¹H NMR spectra.

Calculations

Optimised geometries of $[Fe(\eta-C_5H_5)(IH)(CO)(Me)]$ I, $[Fe(\eta-C_5H_5)(IH)(CO)(COMe)]$ II, $[Fe(\eta-C_5H_5)(PH_3)(CO)(COMe)]$ II, $[Fe(\eta-C_5H_5)(PH_3)(CO)(COMe)]$ IV and $[Fe(\eta-C_5H_5)(CO)_2(Me)]$ were calculated using Vosko, Wilke and Nusairs²⁴ local functional with the Becke88²⁵ and the Perdew86²⁶ exchange and correlation gradient corrections, on ADF version 2000.02.^{27–33} The basis sets used were uncontracted triple-zeta Slater-type orbitals (STOs). The cores of atoms were frozen, C and O up to the 1s level, P and Fe up to the 2p level. Transition states and reactive intermediates were confirmed by performing frequency calculations.

Crystallography

A crystal was selected under an inert atmosphere, encased in perfluoro-polyether oil, and mounted on the end of a glass fibre. Data collections were performed using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo-K α radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package.³⁴ Formula: C₂₈H₃₂FeN₂O, M = 468.42, orthorhombic, space group $P2_{12}_{12}_{1}$, T = 150 K, a = 17.0569(2), b = 17.5875(2), c = 32.3450(4) Å, V = 9703.1(2) Å³, Z = 16, 69648 reflections measured, 20964 unique, $\mu = 0.644$, $R_{int} = 0.050$, wR = 0.0402.

The crystal structure was solved using direct-methods program SIR92,³⁵ which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS³⁶ program suite. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Crystal structure diagrams were produced using the CRYSTALS³⁶ program suite.

CCDC reference number 290045.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516328e

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