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Mechanism of Isocyanide Insertion into the Methyl–Iron Bond of $[Fe(CO)_2L_2(CNR)CH_3]BPh_4$

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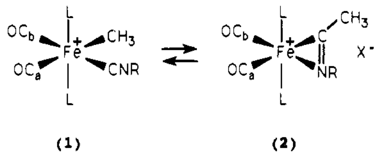
The equilibrium between alkyl $[Fe(CO)_2L_2(CNR)CH_3]BPh_4$ (**1**) and η^2-iminoacyl $[Fe(CO)_2L_2(\eta^2\text{-}C(CH_3){=}NR)]BPh_4$ (**2**) complexes ($L = P(CH_3)_3$, $R = C(CH_3)_3$), catalyzed by anions, was studied using selected monolabeled ^{13}CO derivatives. Scrambling of ^{13}CO between monolabeled alkyl and η^2-iminoacyl complexes demonstrates that the anion catalysis only affects the methyl migration, and the coordination of nitrogen to iron is not concerted with it.

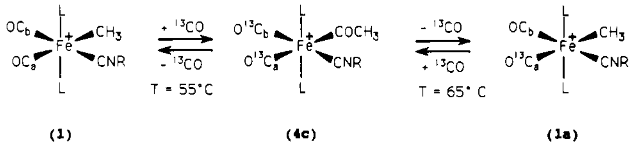
Introduction

A theoretical study[1] concluded that insertion of an isocyanide group into a metal–alkyl bond proceeds in the same manner as that for carbon monoxide, but with a higher activation energy (1.8 eV for isocyanide compared to 0.85 eV for carbon monoxide). In spite of this high activation energy, the isocyanide insertion is easy,[2] which was attributed to the catalysis of electrophiles or to the formation of η^2-iminoacyl structures.[1] A few examples of these structures are well characterized in the literature;[3] they show a greater stability than isoelectronic η^2-acyl structures.[4] In fact, while these latter structures usually exist in rapid equilibrium with alkyl ones,[5] a corresponding equilibrium for the η^2-iminoacyl structures is not observed. Recently[6] we described the equilibrium between $[Fe(CO)_2L_2(CNR)CH_3]BPh_4$ (**1**) and $[Fe(CO)_2L_2(\eta^2\text{-}C(CH_3){=}NR)]BPh_4$ (**2**) (Scheme I), catalyzed by the anions $X^- = I^-, Cl^-, Br^-, NO_3^-$, and ClO_4^-. A similar anion effect was observed by Halpern and co-workers[7] in the olefin insertion of platinum complexes. The anion catalytic effect of the reaction in Scheme I was also studied[8] kinetically, and it was attributed to both the formation of ion pairs and to a specific interaction of the ion with the complex. Such results, however, did not clarify whether the anion affects only the methyl migration or if its action is concerted with the coordination of the nitrogen to the iron resulting in the η^2-iminoacyl complex. The aim of this work was to discriminate between these two possibilities.

Scheme I



Scheme II



Experimental Section

$[Fe(CO)_2(PMe_3)_2CH_3I]$,[9] $[Ru(CO)_2(PMe_3)_2CH_3I]$,[10] $[Fe(CO)_2(PMe_3)_2(CNR)CH_3]BPh_4$[8] (**1**), and $[Fe(CO)_2(PMe_3)_2(\eta^2\text{-}C(CH_3){=}NR]BPh_4$[11] (**2**) were prepared as described in the literature. Solvents (CH_2Cl_2, CH_3OH, acetone, dichloroethane) were used without further purification. *tert*-Butyl isocyanide (CNR), $NaBPh_4$, NBu_4I, and NBu_4NO_3 are commercial products. ^{13}CO was supplied by Monsanto. IR spectra were recorded on a Model 983 Perkin-Elmer spectrophotometer, in CH_2Cl_2; ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrophotometer in CD_2Cl_2, using tetramethylsilane as internal reference for ^1H and ^{13}C spectra and 85% H_3PO_4 in D_2O as external reference for ^{31}P spectra. In this last case a positive sign indicates a shift to a lower field. Details of the IR and NMR spectra of the complexes described in this paper are given in Table I. The structures are given in Figure 1; the **a** and **b** indices correspond to carbon monoxide trans or cis to CH_3, $COCH_3$, or iminoacyl carbon.

$[Fe(^{13}CO_a)(^{13}CO_b)(PMe_3)_2(CNR)CH_3]BPh_4$ (1c). Complex $[Fe(^{13}CO)_2(PMe_3)_2CH_3I]$[12] (0.5 g) was dissolved in 17 mL of CH_3OH. A solution of equimolar CNR and $NaBPh_4$ (2 g) in CH_3OH was added at room temperature. Instantaneous precipitation of white needles of **1c** was observed (0.7 g, yield 85%).

$[Fe(^{13}CO_a)(^{13}CO_b)_2(PMe_3)_2CH_3]BPh_4$ (3c). Complex **3c** was obtained as described in ref 13.

Isomerization of 1c to 2c. **1c** (80 mg) was added to 16 mg of NBu_4I and dissolved in 0.5 mL of CD_2Cl_2 at 25 °C. After 2 h the equilibrium with the complex $[Fe(^{13}CO_a)(^{13}CO_b)(PMe_3)_2(\eta^2\text{-}C(CH_3){=}NR]BPh_4$ (**2c**) was obtained. The equilibrium constant ($K = 1.2 \pm 0.1$) was measured by the ratio of the intensity of the ^{13}C NMR isolated bands of **2c** and **1c**.

Reaction of 1 with CO. **1** (0.5 g) was dissolved in 50 mL of dichloroethane at 55 °C and reacted with CO (1 atm). Formation of $[Fe(CO)_2(PMe_3)_2(CNR)(COCH_3)]BPh_4$ (**4**) was observed. The reaction

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(1) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224–7236.
(2) (a) Singleton, E. *Adv. Organomet. Chem.* **1983**, *22*, 267–281. (b) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193–233.
(3) (a) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27–C29. (b) Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41–48. (c) Muller, A.; Seyer, V.; Eltzner, W. *Inorg. Chim. Acta* **1979**, *32*, L65–L66. (d) Van Bolhius, F.; De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299–308. (e) Zanella, P.; Paolucci, G.; Rossetto, G.; Benetollo, F.; Polo, A.; Fischer, D. L.; Bonbieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96–98. (f) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668–4669. (g) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390–392. (h) Zanella, P.; Brianese, N.; Casellato, U.; Ossala, F.; Porchin, M.; Rossetto, G.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1987**, 2039–2043.
(4) (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522–523. (b) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (c) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302. (d) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46–C48. (e) Franke, U.; Weiss, E. *J. Organomet. Chem.* **1979**, *165*, 329–340. (f) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. M.; Vollner, S. M.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5398. (g) Carmona, E.; Sanchez, L.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214–3222. (h) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640. (i) Hermes, A. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 394–401. (j) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550–1561. (k) Cardaci, G.; Bellachioma, G.; Zanazzi, P. F. *Organometallics* **1988**, *7*, 172–180.
(5) (a) Jablonski, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Am. Chem. Soc.* **1990**, *112*, 1632–1633. (b) Carmona, E.; Sanchez, L. *Polyhedron* **1988**, *7*, 163–165. (c) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1–C6.
(6) Cardaci, G.; Bellachioma, G.; Zanazzi, P. F. *Polyhedron* **1983**, 967–968.
(7) Clark, H. C.; Jablonski, C.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1541–1543.
(8) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *Gazz. Chim. Ital.* **1991**, *121*, 101–106.
(9) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227–234.
(10) Cardaci, G. *J. Organomet. Chem.* **1987**, *323*, C10–C12.
(11) Bellachioma, G.; Cardaci, G.; Zanazzi, P. F. *Inorg. Chem.* **1987**, *26*, 84–91.
(12) Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936–2940.
(13) Reichenbach, G.; Cardaci, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1982**, 847–850.

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Table I. Relevant NMR and IR Data

	NMR			IR		
complex	^{1}H δ, ppm (J, Hz)	^{31}P{^{1}H} δ, ppm (J, Hz)	^{13}C δ, ppm (J, Hz)	ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1} (Δ^a)	ν_{COCH_3}, cm^{-1}
1a	$\delta_{CH_3} = -0.13$ t ($^3J_{CH_3\text{-}P} = 8.0$)	$\delta_P = 20.4$ d ($^2J_{P\text{-}CO_a} = 15.3$)	$\delta_{CO_a} = 206.2$ t ($^2J_{C\text{-}P} = 15.2$)	2176 s	2018 s (7) 1949 s (36)	
1c	$\delta_{CH_3} = -0.13$ td ($^3J_{CH_3\text{-}P} = 8.0$; $^3J_{CH_3\text{-}CO_b} = 2.2$)	$\delta_P = 20.4$ dd ($^2J_{P\text{-}CO_b} = 25.1$; $^2J_{P\text{-}CO_a} = 15.3$)	$\delta_{CO_a} = 206.2$ td ($^2J_{C\text{-}P} = 15.2$; $^2J_{CO_a\text{-}CO_b} = 5.3$) $\delta_{CO_b} = 212.0$ tdq ($^2J_{C\text{-}P} = 25.2$; $^2J_{CO_a\text{-}CO_b} = 5.3$; $^3J_{CO_b\text{-}CH_3} = 2.2$)	2174 s	1983 s (42) 1941 s (43)	
2c	$\delta_{CH_3} = 2.87$ t ($^3J_{CH_3\text{-}P} = 2.4$)	$\delta_P = 20.9$ dd ($^2J_{P\text{-}CO_b} = 30.4$; $^2J_{P\text{-}CO_a} = 23.8$)	$\delta_{CO_a} = 211.6$ td ($^2J_{C\text{-}P} = 23.8$; $^2J_{CO_a\text{-}CO_b} = 1.3$) $\delta_{CO_b} = 216.3$ td ($^2J_{C\text{-}P} = 30.5$; $^2J_{CO_a\text{-}CO_b} = 1.3$)	1753 s	1968 s (47) 1907 s (45)	
3c	$\delta_{CH_3} = 0.05$ tt ($^3J_{CH_3\text{-}P} = 7.2$; $^3J_{CH_3\text{-}CO_b} = 2.2$)	$\delta_P = 17.1$ td ($^2J_{P\text{-}CO_b} = 24.5$; $^2J_{P\text{-}CO_a} = 14.7$)	$\delta_{CO_a} = 203.6$ tt ($^2J_{C\text{-}P} = 15.0$; $^2J_{CO_a\text{-}CO_b} = 5.6$) $\delta_{CO_b} = 208.5$ tdq ($^2J_{C\text{-}P} = 24.7$; $^2J_{CO_a\text{-}CO_b} = 5.6$; $^3J_{CO_b\text{-}CH_3} = 2.2$)		2034 w (51) 1973 s (50)	
4	$\delta_{COCH_3} = 2.49$ s	$\delta_P = 16.3$ s		2193 s	2036 s 1994 s	1634 s
4c	$\delta_{COCH_3} = 2.49$ s	$\delta_P = 16.2$ dd ($^2J_{P\text{-}CO_b} = 23.9$; $^2J_{P\text{-}CO_a} = 10.0$)	$\delta_{CO_a} = 203.6$ td ($^2J_{C\text{-}P} = 10.0$; $^2J_{CO_a\text{-}CO_b} = 6.5$) $\delta_{CO_b} = 208.8$ td ($^2J_{C\text{-}P} = 23.9$; $^2J_{CO_a\text{-}CO_b} = 6.5$)	2192 s	1990 s (46) 1951 s (43)	1635 s
5^b	$\delta_{CH_3} = -0.37$ t ($^3J_{CH_3\text{-}P} = 7.6$) $\delta_{P\text{-}CH_3} = 1.55$ t ($\lvert {}^2J_{H\text{-}P} + {}^4J_{H\text{-}P}\rvert = 7.6$) $\delta_{C(CH_3)_3} = 1.52$ d ($J = 2.3$)	$\delta_P = -7.22$ s	$\delta_{CO_a} = 190.2$ $\delta_{CO_b} = 197.5$ $\delta_{C(CH_3)_3} = 30.5$ s $\delta_{CH_3\text{-}P} = 17.8$ t ($\lvert {}^1J_{C\text{-}P} + {}^3J_{C\text{-}P}\rvert = 33.6$) $\delta_{CH_3} = -16.0$ s	2193 s	2051 s 2005 s	
5a	$\delta_{CH_3} = -0.37$ td ($^3J_{CH_3\text{-}P} = 7.6$; $^3J_{CH_3\text{-}CO_b} = 0.7$)	$\delta_P = 7.22$ d ($^2J_{P\text{-}CO_a} = 8.0$)	$\delta_{CO_a} = 190.2$ t ($^2J_{CO_a\text{-}P} = 8.1$)	2193 s	2041 s (10) 1936 s (36)	

[a] Δ is the difference (cm^{-1}) with respect to unlabeled complex. [b] ^{13}C spectrum is ^{1}H decoupled.

reached equilibrium after 5 h. By decarbonylation of **4** at 65 °C with nitrogen flow, complex **1** was obtained.

[Fe(^{13}CO$_a$)(CO$_b$)(PMe$_3$)$_2$(CNR)CH$_3$]BPh$_4$ (1a). Complex **1** (100 mg) was dissolved in 1,2-dichloroethane and reacted under stirring with 20 mL of ^{13}CO for 5 h at 55 °C. After decarbonylation at 65 °C under nitrogen flow, formation of complex **1a** was observed (60%). After two further carbonylations with ^{13}CO, 90% of **1** is labeled, giving the complex [Fe(^{13}CO$_a$)(^{13}CO$_b$)(PMe$_3$)$_2$(CNR)(COCH$_3$)]BPh$_4$ (**4c**). Complex **4c** decarbonylates under nitrogen flow at 65 °C giving complex **1a**.

Isomerization of 1a. Complex **1a** (100 mg) was dissolved in 1 mL of CD$_2$Cl$_2$, and 20 mg of NBu$_4$I was added. After 2 h the equilibrium was reached. ^{13}C NMR spectrum shows the formation of all monolabeled methyl (**1a**, **1b**) and η^2-iminoacyl (**2a**, **2b**) complexes: the ratios of intensity are **1a**:(**1b** + **2a**):**2b** = 1:1.9:0.9. These ratios indicate equal concentrations of **1a** and **1b** and of **2a** and **2b**. The concentration ratio between η^2-iminoacyl and methyl is 1.2 ± 0.1.

[Ru(CO)$_2$(PMe$_3$)$_2$(CNR)CH$_3$]BPh$_4$ (5). [Ru(CO)$_2$(PMe$_3$)$_2$CH$_3$I] (200 mg) and CNR (36 mg) (molar ratio 1/1) were dissolved in 15 mL of CH$_3$OH containing 1 g of NaBPh$_4$. After 15 min, precipitation of white needles of complex **5** was observed. Anal. Calcd for $C_{38}H_{50}O_2BNP_2Ru$: C, 62.81; H, 6.94; N, 1.93. Found: C, 63.1; H, 7.06; N, 1.93. Complex **5** (100 mg), dissolved in 5 mL of CH$_2$Cl$_2$, reacted with 20 mg of NBu$_4$I at room temperature, giving the complex [Ru(CO)(PMe$_3$)$_2$(CNR)(COCH$_3$)I]: IR (cm^{-1}) ν_{CO}, 1972; ν_{COCH_3}, 1602; ν_{CN}, 2175. The same reaction is observed in acetone. Complex **5** with NBu$_4$NO$_3$ does not react in CH$_2$Cl$_2$ up to 35–40 °C.

[Ru(^{13}CO$_a$)(CO$_b$)(PMe$_3$)$_2$(CNR)CH$_3$]BPh$_4$ (5a). Complex **5a** was obtained as described for complex **5**, starting with [Ru(^{13}CO$_a$)(CO$_b$)(PMe$_3$)$_2$CH$_3$I], prepared as described in ref 14. Complex **5a** (20 mg) and NBu$_4$NO$_3$ (5 mg) in CD$_2$Cl$_2$ do not scramble labeled CO after a week.

Measurement of T_1. The longitudinal relaxation time constants (T_1) were measured using the nonselective inversion recovery method, (180–τ–90–waiting time)$_n$.[15] The measurements were performed at 25 °C in CD$_2$Cl$_2$. The samples were degassed and measured under N$_2$. Typically 10τ values were employed with a waiting time of 5T_1. Fitting of the experimental data to the exponential equation of the longitudinal relaxation allowed the following values of T_1 to be obtained (they were estimated to be accurate to ±5%): complex **3c**, T_1(CO$_a$) = 26 s, T_1(CO$_b$)

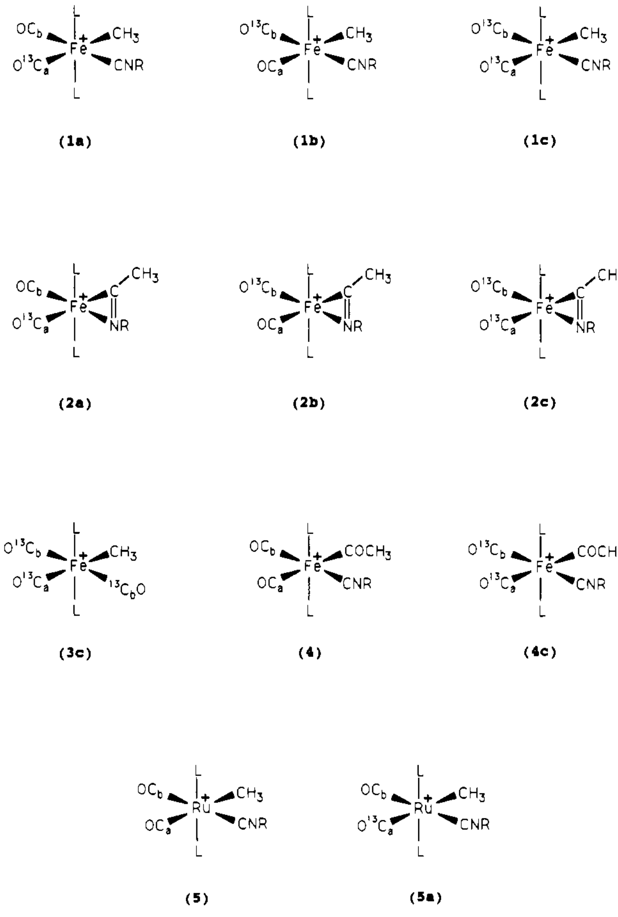

Figure 1. Structures of the complexes.

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(14) Cardaci, G.; Reichenbach, G.; Bellachioma, G.; Wassink, B.; Baird, M. C. *Organometallics* **1988**, *7*, 2475–2479.

(15) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987; pp 61–65.

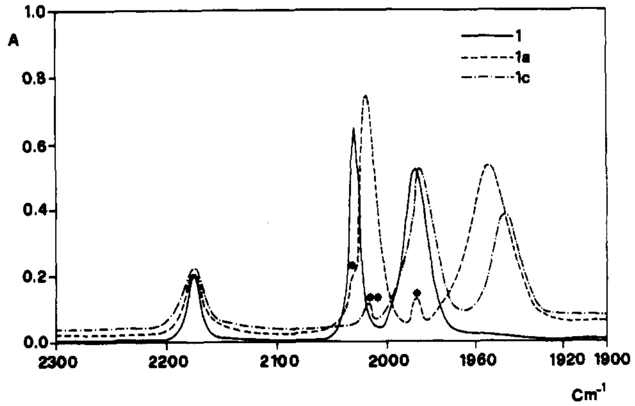


Figure 2. IR spectra of complexes **1**, **1a**, and **1c**. An asterisk denotes an impurity of the unlabeled complex **1**. Two asterisks denote an impurity of the monolabeled complex **1a**.

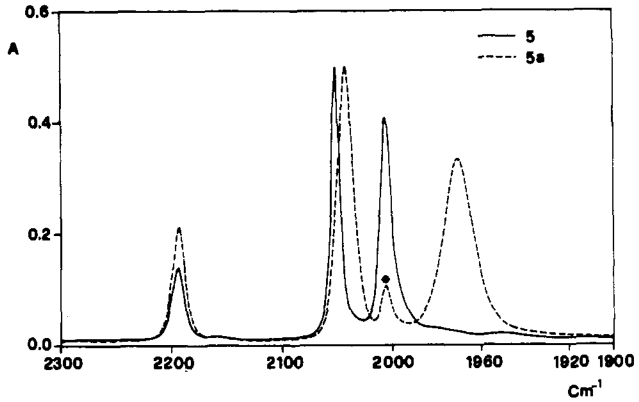


Figure 3. IR spectra of complexes **5** and **5a**. An asterisk denotes an impurity of the unlabeled complex **5**.

= 24 s; complex **1c**, $T_1(CO_a)$ = 17 s, $T_1(CO_b)$ = 12 s; complex **2c**, $T_1(CO_a)$ = 17 s, $T_1(CO_b)$ = 18 s.

Results

Complex **1a** was synthesized, as shown in Scheme II, by reaction of complex **1** with ^{13}CO. An equilibrium with the labeled acetyl complex **4c** was obtained. By decarbonylation of **4c**, complex **1a** was obtained. It was not possible to synthesize complex **1a** by reaction of $[Fe(^{13}CO_a)(CO_b)(PMe_3)_2(CH_3)I]$ and CNR in CH_3OH and $NaBPh_4$, because a mixture of the monolabeled **1a** and **1b** was obtained. By contrast, the corresponding ruthenium complex **5a** was prepared via reaction of $[Ru(^{13}CO_a)(CO_b)(PMe_3)_2(CH_3)I]$[14] with CNR in CH_3OH in the presence of $NaBPh_4$; complex **5** is also prepared in this manner.

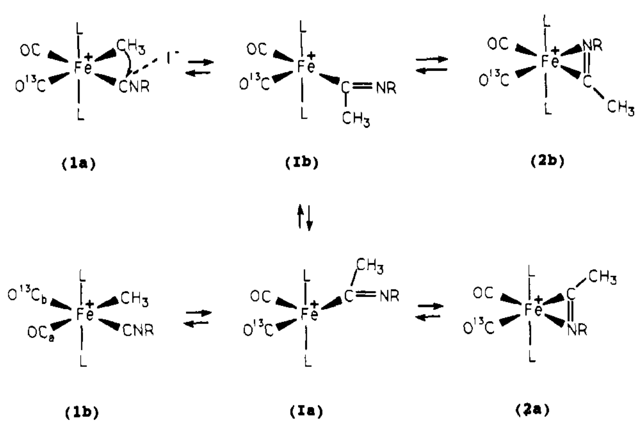
The labeled ^{13}CO complexes were characterized by IR and NMR spectroscopy (Table I). IR spectra of complexes **1**, **1a**, and **1c**, and **5** and **5a** are reported in Figures 2 and 3 to show the isotopic shift of the CO bands.

In order to obtain information on the band intensities, the ^{13}C NMR spectra were performed without proton decoupling and with a delay time of 50 s. On the basis of the longitudinal relaxation time (T_1) and the pulse width (2.5 times lower than $\pi/2$) this delay was sufficient to obtain a less than 3% concentration error.[16]

Discussion

(a) IR and NMR Spectra. The monolabeled complexes show a total isotopic shift of $\approx$45 cm^{-1} (see the Δ values in Table I) in the CO stretching frequencies distributed between all the CO stretchings, thus indicating a strong coupling among all CO ligands.[17] This is in agreement with the general behavior of the carbonyl complexes.[18]

Scheme III



In order to obtain information on the stereochemistry and the relative concentration of the labeled isotopomers, NMR spectra were used. Stereochemical information was obtained on the basis of the ^{13}C chemical shifts of the CO ligands and the C–C, C–P, and H_3C–^{13}CO coupling constants. The study of a few series of organometallic complexes[12,14,19] shows the chemical shifts of the CO_a substituent, trans to methyl, acetyl, or carbon-iminoacyl, are lower than that of CO_b (see Table I). The coupling constant for cis P–CO_a is lower than that for cis P–CO_b.[14,19,20] This behavior can be explained on the basis of the influence of the ligand trans to the CO substituent: the higher the trans effect for the ligand, the lower the P–CO coupling constant.[12,14,21] This difference is greater for Fe and decreases with the increasing atomic number of the metals of the same group (Ru).[14]

The CO–CO coupling constants show a behavior similar to those between phosphorus atoms.[12] The CO–CO cis coupling constants are lower than the CO–CO trans constants; for iron complexes the cis coupling constants are in the 4–8 Hz range while trans coupling constants are in the 10–20 Hz range.

A new tool for assigning the stereochemistry of these complexes is the coupling constant between the CH_3 proton and the ^{13}CO substituents. For the iron complexes, this coupling constant is around 2 Hz when the ^{13}CO group is cis to CH_3 (CO_b), while it is not measurable if the ^{13}CO substituent is trans to CH_3 (CO_a). This significant result was demonstrated by studying complex **3c**. The assignment of the CO band to the CO_a and CO_b substituents was based on the intensity ratio of the two CO bands (1/2). The CO_b band is a triplet ($^2J_{CO_b-P}$ = 24.7 Hz) of doublets ($^2J_{CO_a-CO_b}$ = 5.6 Hz) of quartets ($^3J_{CO_b-CH_3}$ = 2.2 Hz). The CO_a band is a triplet ($^2J_{CO_a-P}$ = 15.0 Hz) of triplets ($^2J_{CO_a-CO_b}$ = 5.6 Hz). This coupling constant was also observed for complexes **1c** ($^3J_{CO_b-CH_3}$ = 2.2 Hz) and $[Fe(^{13}CO_a)(^{13}CO_b)(PMe_3)_2(CH_3)I]$ ($^3J_{CO_b-CH_3}$ = 1.7 Hz). An explanation of this behavior can be based on the trans effect of the ligand trans to CO_a and CO_b. A ligand with a strong trans effect lowers the coupling constant. A similar behavior has been also observed for the $^3J_{P-CH_3}$ couplign constants.[14,22]

(b) Mechanism. In a recent study[8] on the mechanism of the X^- anionic catalysis shown in Scheme I, it was concluded that the catalytic action is due to the formation of ion pairs and to a specific interaction with the isocyanide group.[23] However, it was

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(16) Cookson, D.; Smith, B. E. *Anal. Chem.* **1982**, *54*, 2591–2593.

(17) (a) Burdett, J. K.; Poliakoff, M.; Timmey, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 948. (b) Darensbourg, D. J.; Nelson, H. H.; Hide, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

(18) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975; pp 33–36.

(19) Wright, S. C.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 6899–6902.

(20) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(21) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294–4307.

(22) Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2593–2597.

(23) (a) Morris, D. E.; Basolo, F. *J. Am. Chem. Soc.* **1968**, *90*, 2531–2535. (b) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160–3166. (c) Brown, T. L.; Bellus, P. A. *Inorg. Chem.* **1978**, *17*, 3726–3727. (d) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213–1214. (e) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *Inorg. Chem.* **1981**, *20*, 1918–1921.

not clear whether the catalytic action of the anion was concerted with the coordination of the nitrogen atom to the metal or if this coordination occurred after the methyl migration. In order to discriminate between these two possibilities we studied the distribution of the monolabeled products derived from the selected monolabeled complex **1a**.

In the presence of NBu_4I, complex **1a** isomerized and the equilibrium ^{13}C NMR spectrum showed the formation of complexes **1a**, **1b**, **2a**, and **2b**. Owing to the partial superimposition of the **1b** and **2a** bands, the ratio intensities **1a**:(**1b** + **2a**):**2b** = 0.9:1.9:1 were measured. On the basis of the equilibrium constant at 25 °C ($K = 1.2 \pm 0.1$), the ratios **1a**:**1b** and **2a**:**2b** are 1. The statistical formation of all possible monolabeled alkyl and dihaptoiminoacyl complexes indicates that the intermediate I can rotate before the coordination of the nitrogen atom (Scheme III). Therefore the catalytic action of the anion affects the methyl migration step: anions compel the methyl to migrate into the isocyanide carbon by either forming an ion pair[24] or by behaving as nucleophiles (as was observed recently for phosphine oxide[25]).

The thermodynamic stabilization of the η^2-iminoacyl structure is the drawing power of the reaction. The CO insertion does not occur because the η^2-acyl bond is less stable than the η^2-iminoacyl one.[4] This result agrees with Hoffmann's calculation,[1] which suggests that the isocyanide insertion can occur by stabilization due to the η^2-iminoacyl structure.

The isoelectronic ruthenium complex **5** reacts with halides, giving neutral complexes[26] $[Ru(CO)(PMe_3)_2(COCH_3)(CNR)X]$, and no insertion of isocyanide is observed. This is due to the more covalent character of the Ru–X bond with respect to iron.[27] Even when the anion has a low tendency to coordinate, such as NO_3^-, no isocyanide insertion is observed. This could be due to the stabilization of the alkyl with respect to the η^2-iminoacyl complex owing to less steric hindrance in the ruthenium complex.[28] Furthermore, no dynamic process is observed as is demonstrated by the absence of scrambling in the monolabeled **5a** complex in the presence of NBu_4NO_3.

In conclusion, the results of this work can be summarized as follows:

(a) The unsaturated intermediate (I) is dynamic and rearranges itself before the coordination of nitrogen.

(b) The anion catalysis operates only in the methyl migratory step.

(c) The CO insertion is easier than the CNR one;[8] in fact, in the presence of CO, the CO insertion is observed with the formation of complex **4**.

(d) The observation of isocyanide insertion in the absence of nucleophiles is due to the greater thermodynamic stability of the η^2-iminoacyl structure compared to the η^2-acyl one.

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(24) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1958.

(25) (a) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345–347. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 366.

(26) (a) Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331–1338. (b) Sanders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1153–1156.

(27) (a) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *125*, 231–252. (b) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 953–961.

(28) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980; pp 822–980. (b) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271–281.

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Ketyl Complexes of $(silox)_3Ti$ (silox = $^tBu_3SiO^-$)

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Treatment of $TiCl_4(THF)_2$ or ZrX_4 (X = Cl, I) with 3.0 equiv of Na(silox) in THF afforded $(silox)_3TiCl$ (**1**, 85%) or $(silox)_3ZrX$ (X = Cl, **2**, 68%; I, **3**, 65%). According to electrochemical experiments, the reduction of **1**–**3** was feasible; orange, crystalline $(silox)_3Ti$ (**4**) was produced in 76% yield upon exposure of **1** to Na/Hg in DME, but a Zr(III) analogue could not be isolated. XPS data are used to rationalize the stability of low-valent siloxide complexes. UV–vis and EPR spectra of **4** were consistent with a D_{3h} geometry and $^2A_1{}' (d_{z^2})^1$ ground state ($g_{iso} = 1.9554$, $g_{\parallel} = 1.9997$, $g_{\perp} = 1.9323$; $a_{iso} = 155$ MHz (~56.7 G)). Addition of L to **4** provided various thermally unstable adducts, $(silox)_3TiL$ (**4**–L; L = DME, CNMe, CN^tBu, NC^tBu, PMe_3, NH_3), whereas ketones and aldehydes reacted to give ketyls or compounds indicative of ketyl reactivity. Acetone and **4** produced a 1:1 mixture of $(silox)_3Ti(OCMe_2H)$ (**5a**) and $(silox)_3Ti(OMeC{=}CH_2)$ (**6a**), while acetaldehyde and **4** afforded a 1:1 mixture of $(silox)_3TiOEt$ (**5b**) and $(silox)_3TiOCH{=}CH_2$ (**6b**). Sterically hindered substrates (L = $^tBu_2CO$, ^tBuCHO, 3,3,5,5-tetramethylcyclohexanone, PhMeCO, 4,4′-dimethylbenzophenone) generated transient ketyls whose EPR spectra are indicative of carbon-centered radicals (**4**–OC^tBu_2, $g = 1.9985$; **4**–OCH^tBu, $g = 2.0001$; **4**–$OC_6H_6Me_4$, $g = 1.9920$; **4**–OCMePh, $g = 2.002$; **4**–OC(*p*-tolyl)$_2$, $g = 2.0005$). Benzophenone and **4** provided an equilibrium mixture of the ketyl $(silox)_3Ti(OCPh_2{}^\bullet)$ (**4**–$OCPh_2$, $g = 2.0004$) and $[(silox)_3Ti(OCPh_2)]_2$ (**7**), which arises from a C_α–$C_{p\text{-}Ph}$ coupling reminiscent of trityl radical (K_{eq}(25 °C) = $[\mathbf{4}\text{–}OCPh_2]^2/[\mathbf{7}] = 7.5 \times 10^{-7}$, $\Delta H_{diss} = 18$ (1) kcal/mol, $\Delta S = 33$ (3) eu). Addition of Ph_3SnH to **7** yielded $(silox)_3TiOCPh_2H$ (**8**) and $Ph_3SnSnPh_3$. Ketyl formation was also reversible, since addition of 4,4′-dimethylbenzophenone to **7** produced some of the mixed diarylketone dimer $(silox)_3Ti\text{–}O(tolyl)_2\overline{C(H)C(CH)_2C(CH{=}C}H){=}C(Ph)OTi(silox)_3$ (**9**). EPR studies of **4**–OCRR′ were clearly supportive of the ketyl formulation; tentative evidence for a chair → chair interconversion in **4**–$OC_6H_6Me_4$ and equilibration of the Ph rings in **4**–$OCPh_2$ is also presented. The EPR and UV–vis spectra of **4** are rationalized in terms of a relatively strong ligand field. The *g* values and hyperfine couplings of the ketyls are used to assess the binding of the $R'RC{=}O$ substrates, and sterics play the major role.

Introduction

Applications of inorganic and organometallic reagents to organic synthesis comprise an active and productive area of chemical research.[1-3] The stabilization and isolation of inherently reactive organic fragments through binding to transition-metal centers is

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Negishi, E. I. *Organometallics in Organic Synthesis*; Wiley-Interscience: New York, 1980.