2936 *Inorg. Chem.* **1984**, *23*, 2936–2940

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Mechanism of Carbon Monoxide Insertion in the $[Fe(CO)_2(PMe_3)_2(Me)X]$ Complexes

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Received August 3, 1983

The insertion-reaction mechanism of the title complex is studied with X = CN, NCS, or I, by measuring the isotopic exchange with ^{13}CO. The structure of the isotopomers formed has been determined on the basis of ^{13}C NMR spectra. The results are explained in terms of a mechanism involving a trigonal-bipyramidal intermediate, which undergoes a reversible attack by the entering group from three different directions. The rate of attack depends on both the direction and the nature of X. While the CN derivative exchanges only the two terminal CO groups, the other derivatives also exchange the acetyl CO group. This latter exchange takes place through an ionic dissociation of the acetyl complex.

Introduction

The carbon monoxide insertion[1-3] is assumed to proceed via migration of the alkyl group to the carbon monoxide ligand cis to it.[4] This mechanism is supported by theoretical calculations.[5] However, it is not possible to exclude a mechanism proceeding through a migration of the CO group into the metal–alkyl bond.[6] This mechanism has been hypothesized for the complexes $[Fe(CO)_2(PMe_3)_2(Me)I]$ and $[Fe(CO)_2(PMe_3)_2(Me)_2]$ on the basis of preliminary experiments.[7] It is also suggested by the preparation and the structural characterization of acetyl complexes that have an η^2 structure in complexes with electron-deficient d orbitals,[8,9] in complexes of rare and transuranic metals,[10] and in d^6 ruthenium complexes.[11]

In this paper we have studied the reaction of $[Fe(CO)_2L_2(Me)X]$ ($L = PMe_3$) with ^{13}CO in order to obtain more information about the mechanism of the insertion reaction and in particular about the formation of an η^2 intermediate.[12]

Results

(a) X = CN. The complex $[Fe(CO)_2L_2(Me)CN]$ reacts in CH_2Cl_2 with CO (p = 1 atm) at room temperature to give the cis acetyl complex $[Fe(CO)_2L_2(COMe)CN]$.[13] The reaction performed with ^{13}CO follows Scheme I. At room temperature the exchange of only one carbonyl group is observed, and thus the formation of the monolabeled complex **2A**. The assignment of this structure is based on ^{13}C NMR spectra (vide infra). The formation of only one isotopomer is demonstrated by the fact that the decarbonylation of the solid monolabeled product, performed under vacuum at 60 °C, gave the unlabeled methyl complex **1**. The ^{13}CO exchange proceeds very slowly at 40 °C in CH_2Cl_2 to give the bilabeled product **3** (reaction time ca. 20 days). The formation of the complex labeled at the acetyl carbonyl was never observed. On decarbonylating complex **3** we obtained the monolabeled methyl complex **4**, which reacted with CO to give the monolabeled acetyl complex **2B**. The CO stretching frequencies of the different complexes are reported in Table I.

Scheme I

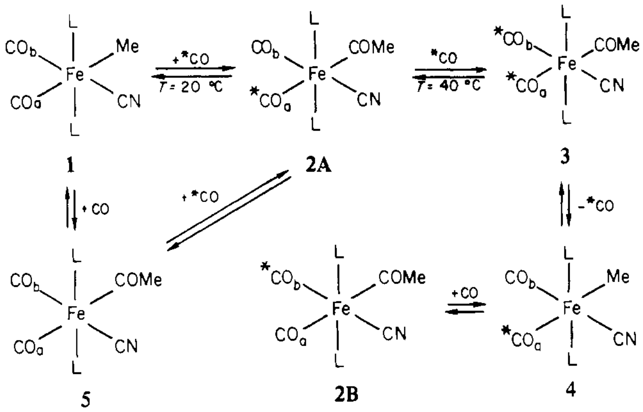

Table I. CO Stretching Frequencies (CH_2Cl_2) of the Complexes

complexes ($L = PMe_3$)	ν_{CO}, cm^{-1}	ν_{COMe}, cm^{-1}
$[Fe(CO)_2L_2(Me)CN]$ (**1**)	2001.9, 1946.3	
$[Fe(^*CO_a)(CO)L_2(Me)CN]$ (**4**)	1989, 1917.3	
$[Fe(^*CO_b)(CO)L_2(Me)CN]$ (**6**)	1994.5, 1919	
$[Fe(^*CO)_2L_2(Me)CN]$ (**1′**)	1956.5, 1902.2	
$[Fe(CO)_2L_2(COMe)CN]$ (**5**)	2020, 1968.5	1590.4
$[Fe(CO)_2L_2(^*COMe)CN]$ (**3′**)	2020.5, 1969.2	1557
$[Fe(^*CO_a)(CO)L_2(COMe)CN]$ (**2A**)	2006.1, 1938.0	1591.2
$[Fe(CO)(^*CO_b)L_2(COMe)CN]$ (**2B**)	2006.8, 1940	1592
$[Fe(^*CO_a)(CO)L_2(^*COMe)CN]$ (**2A′**)	2005.5, 1938.3	1562
$[Fe(CO)(^*CO_b)L_2(^*COMe)CN]$ (**2B′**)	2006.0, 1939	1559.2
$[Fe(^*CO)_2L_2(COMe)CN]$ (**3**)	1975.2, 1927.2	1592.5
$[Fe(^*CO)_2L_2(^*COMe)CN]$ (**5′**)	1973.6, 1924.3	1557.5
$[Fe(CO)_2L_2(Me)I]$	1997.5, 1936.7	
$[Fe(^*CO_a)(CO)L_2(Me)I]$	1979.6, 1906.3	
$[Fe(^*CO)_2L_2(Me)I]$	1952.9, 1894.1	
$[Fe(CO)_2L_2(COMe)I]$	2014.0, 1959.3	1586
$[Fe(^*CO)(CO)L_2(COMe)I]$	1992.4, 1935.3	1585.7
$[Fe(CO)_2L_2(Me)NCS]$	2001.0, 1943.9	
$[Fe(^*CO_a)(CO)L_2Me(NCS)]$	1982.1, 1917.9	
$[Fe(^*CO)_2L_2Me(NCS)]$	1956.2, 1900	
$[Fe(CO)_2L_2(COMe)(NCS)]$	2024.4, 1965	1595
$[Fe(^*CO)(CO)L_2(COMe)(NCS)]$	1998.8, 1942.5	1594.9
$[Fe(^*CO)_2L_2(^*COMe)(NCS)]$	1974.6, 1921	1561
trans-$[Fe(^*CO)_2L_2(^*COMe)I]$ (**8**)	1997.2, 1917.4	1556.5
trans-$[Fe(^*CO)_2L_2(^*COMe)Cl]$ (**9t**)	1992.0, 1915.0	?
cis-$[Fe(^*CO)_2L_2(^*COMe)Cl]$ (**9c**)	1969.0, 1909.2	1559

The complexes labeled at the acetyl group were obtained following Scheme II. The complex $[Fe(^{13}CO)_2L_2(^{13}COMe)CN]$ (**5′**) was prepared by reaction of KCN with $[Fe(^{13}CO)_3L_2Me][BPh_4]$ (**7**), whose preparation has already been described.[14] The totally labeled methyl complex **1′** was

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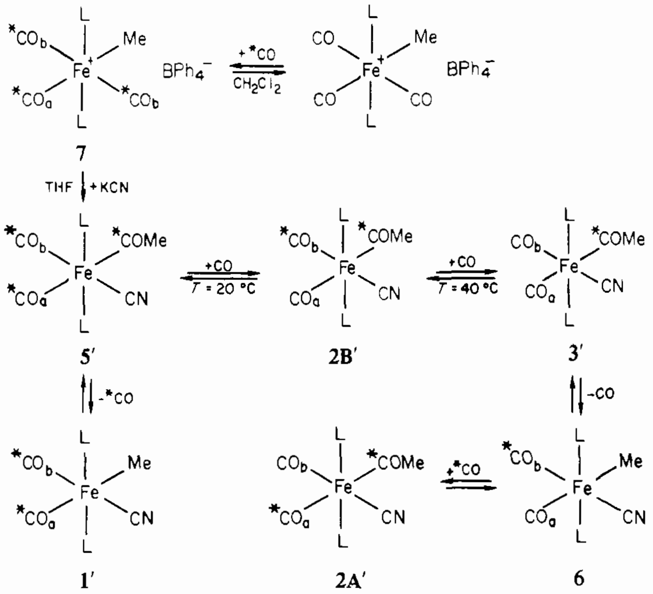
Scheme II



obtained by decarbonylating **5'** with a nitrogen stream. The isotopic exchange between CO and **5'** gave **2B'**, at room temperature, while a further exchange at 40 °C gave **3'**. Decarbonylation of **3'** gave the methyl complex **6**. The complex **6** reacted with ^{13}CO to give the complex **2A'**, in which the ^{13}CO label is trans to the acetyl group. The CO stretching frequencies of the complexes in Scheme II are reported in Table I.

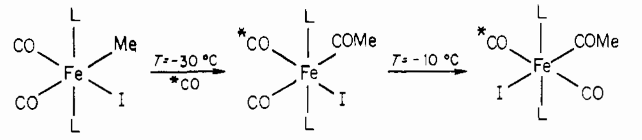
Since the reaction rates of the monolabeling and bilabeling of the acetyl complex are very different, both processes can be measured by following the exchange rate of [Fe(CO)$_2$L$_2$(COMe)CN] (**5**) with ^{13}CO. At 40 °C and p_{CO} = 1 atm, the pseudo-first-order rate constant for the monolabeling (k_I) is 3.3×10^{-4} s^{-1} and that for the bilabeling (k_{II}) is 1.0×10^{-6} s^{-1}.

(b) X = NCS. Also in this case the reaction with CO at atmospheric pressure goes to completion, but it is faster that the reaction when X = CN. The decarbonylation reaction is complete in 30 min at room temperature under a nitrogen stream. The reaction at room temperature with ^{13}CO readily produces the monolabeled compound and then the bilabeled and totally labeled complexes. Since the rates are not very different, it was difficult to identify the isotopomers formed in the first step. The problem was solved by carrying out the reaction at −15 °C and stopping it when the monolabeled complex was formed. This complex was quickly decarbonylated and the ratio between the unlabeled and the monolabeled complex determined by IR spectroscopy, assuming that the band intensity is not influenced by the labeling. From this measurement it is possible to determine the ratio between the two isotopomers, which is 10:1. This ratio was confirmed by studying the isotopic exchange between [Fe(CO)$_2$L$_2$(COMe)NCS] and ^{13}CO and by measuring its mono- and bilabeling reaction rates. The two pseudo-first-order rate constants at 20 °C are 2.2×10^{-3} and 1.8×10^{-4} s^{-1}, respectively. The ratio is 12:1, which is in accord with the figure found by our other method.

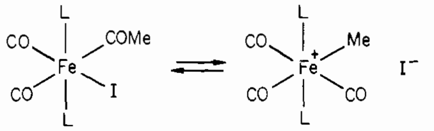
The different isotopomers could not be isolated in this case, but their stretching CO bands were measured in solution and are reported in Table I.

(c) X = I. Unlike the other two complexes, the cis acetyl complex isomerizes to the trans derivative.[13,15,16] To avoid the isomerization, the carbonylation was performed at low temperatures (<−15 °C). Preliminary results obtained by Pankowski and Bigorgne[7] had shown that the methyl complex reacts *stereospecifically* with ^{13}CO to give the cis acetyl complex (through CO migration), which, at −10 °C, transforms into the trans acetyl complex following Scheme III.

Scheme III



Scheme IV

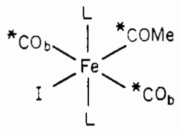


Our results produce quite different conclusions. The carbonylation was performed in *n*-hexane at −39 °C and p_{CO} = 1 atm. Decarbonylation of the complex in solution at −39 °C gave both the unlabeled methyl complex and small quantities of [Fe(*CO$_a$)(CO)L$_2$(Me)I].

The relative quantity of the latter increased upon lengthening the reaction time, in accordance with the fact that the reaction is an equilibrium reaction and that the two monolabeled isotopomers A and B are formed in the first step of the reaction with different rates. Unlike the case of X = CN or NCS, in this compound the ratio of the two isotopomers is useless in determining the rate ratio. When the reaction time was increased further, we observed the formation of the bilabeled complex and of the complex labeled in the acetyl group. The same results were obtained by leaving the solution of the acetyl complex in the presence of ^{13}CO at room temperature. In CH$_2$Cl$_2$ similar results were obtained, with an increase of all the reaction rates.

To understand the mechanism of the labeling of the acetyl group, we performed some experiments on the stability and the reactivity of the cis and trans acetyls. The infrared spectrum in KBr of the trans acetyl complex showed the same CO stretching bands shown in solution, while that of the cis acetyl showed the presence of the characteristic bands of the [Fe(CO)$_3$L$_2$(Me)]I complex. Such bands disappeared if the pellet was dissolved in CH$_2$Cl$_2$ at −50 °C. It proves the presence of the equilibrium in the solid state as shown in Scheme IV. The presence of a limited ionization also in solution is shown by the fact that in CH$_2$Cl$_2$ the cis acetyl reacts entirely with NaBPh$_4$ to give the precipitate [Fe(CO)$_3$L$_2$(Me)][BPh$_4$], while the trans acetyl does not react. It is further confirmed by the presence in a concentrated solution ($C = 1.28 \times 10^{-1}$ M), of infrared bands, characteristic of the ionic species, from which a dissociation constant of about 3.0×10^{-5} M at room temperature was measured.

(d) ^{13}C NMR Spectra. The ^{13}C NMR spectra are reported in Table II. The assignments of the ^{13}C resonances in the complexes **7**, **8**, and **9t** are undoubted. In particular the complex **7** shows two signals, which are assigned to CO$_a$ and CO$_b$ on the basis of the intensity ratio. The coupling constant between them is 4.8 Hz. The complexes **8** and **9t** in which the CO and the COMe groups are cis to each other show a coupling constant of 5–6 Hz.



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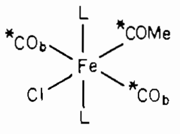
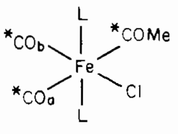


9t



9c

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Table II. ^{13}C NMR Spectra (CD_2Cl_2) of the Complexes

complex	δ_{CO_a}	δ_{CO_b}	δ_{COMe}
5′	209.0 (m) J_{CO_a-P} = 11 Hz $^2J_{CO_a-CO_b}$ = 6 Hz	211.4 (t of dd) J_{CO_b-P} = 20 Hz $^2J_{CO_b-COMe}$ = 6 Hz	272.9 (t of dd) J_{COMe-P} = 22 Hz $^2J_{CO_a-COMe}$ = 11 Hz
2A	208.8 (t) J_{CO_a-P} = 11 Hz		
2B′		211.8 (t of d) J_{CO_b-P} = 20 Hz $^2J_{CO_b-COMe}$ = 6 Hz	272.9 (t of d) J_{COMe-P} = 22 Hz
9c	208.2 (complex m) J_{CO_a-P} = 13 Hz $^2J_{CO_a-CO_b}$ = 7 Hz	213.3 (t of dd) J_{CO_b-P} = 26.7 Hz $^2J_{CO_b-COMe}$ = 8.9 Hz	272.7 (t of dd) J_{COMe-P} = 23.5 Hz $^2J_{CO_a-COMe}$ = 15.5 Hz
9t		217.5 (t of d) J_{CO_b-P} = 24.9 Hz $^2J_{CO_b-COMe}$ = 5 Hz	268.1 (t of t) J_{COMe-P} = 18.7 Hz
8[a]		214.2 (t of d) J_{CO_b-P} = 26.8 Hz $^2J_{CO_b-COMe}$ = 6 Hz	270.1 (t of t) J_{COMe-P} = 20.2 Hz
7	204.7 (t of t) J_{CO_a-P} = 15.7 Hz $^2J_{CO_a-CO_b}$ = 4.8 Hz	209.6 (t of d) J_{CO_b-P} = 25.4 Hz	

[a] C_6D_6 solvent.

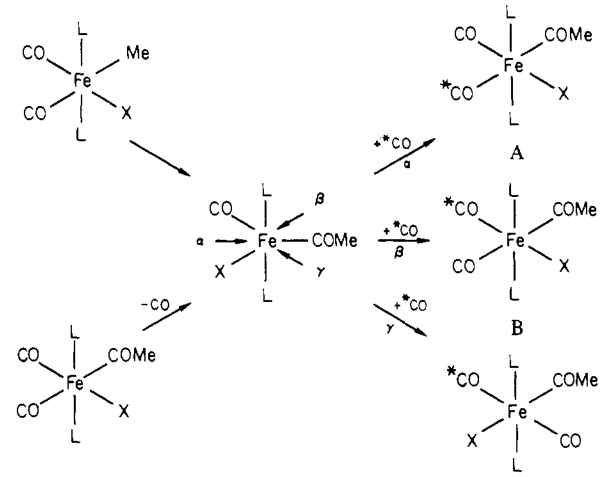
The assignment of the resonances of the other complexes is more difficult. By comparing the δ values of the complexes **5′** and **9c** both one CO resonance and the COMe resonance are little affected, whereas the other CO resonance is much more affected (Table II); therefore, we assign this last resonance to the CO group trans to the X group, i.e. to the CO_b group. The complex **2A**, prepared by reaction of ^{13}CO with the complex **1** or with the complex **5** shows only the resonance at 208.8 ppm, which, therefore, corresponds to the group CO_a trans to COMe. This assignment is confirmed by the spectrum of the complex **2B′**, prepared by reaction of **5′** with CO. In this case it is the upfield resonance that is absent, indicating that the unlabeled entering CO occupies the position trans to COMe. The previous evidence allows us to assign the structure of the discussed complexes.

A further support of this assignment derives from the analysis of the measured coupling constants ($^2J_{CO-COMe}$(cis), $^2J_{CO-COMe}$(trans), $^2J_{CO-CO}$(*cis*)). In fact, from the complexes **7**, **8**, and **9t** we obtain the cis coupling constants, which are in the range 4.8–6 Hz. The complexes **5′** and **9c** show six coupling constants: we assign the lower four (5–9 Hz) to the cis coupling and the higher ones (11–15.5 Hz) to the groups that are trans to one another, as recently found in various carbonyl and acetyl complexes.[17] Because the complex **2B′** has a low coupling constant ($^2J_{CO-COMe}$ = 6 Hz), we think that the labeled CO group is cis to the COMe group.

Discussion

All the labeled complexes were isolated only for the derivatives with X = CN. In the complex labeled on one terminal CO the total isotopic schift of ca. 45 cm^{-1} is distributed between the two CO frequencies, indicating a strong coupling between them.[18] In accordance with the Teller–Redlich rule,[19] the product of the ratios of the stretching frequencies of the labeled and the unlabeled complex is a constant. A comparison of the frequencies of the isotopomers A and B, and A′ and B′, obtained by following Schemes I and II, shows that the position of the ^{13}CO does not appreciably influence the frequency of the stretching band. Therefore, the IR technique is not able to distinguish between the two isotopomers. This is confirmed by the comparison of stretching frequencies of the methyl complexes **4** and **6**, where the labeled CO is trans or cis, respectively, to the methyl group (see Table I). The Teller–Redlich rule is also followed by the bilabeled complexes. The frequency shift for acetyl group is ca. 30 cm^{-1} and is close to that obtained for aldehydes and ketones.[20]

Scheme V



On observing the course of the carbonylation and decarbonylation process, we can affirm that during the carbonylation with ^{13}CO both isotopomers A and B are formed: their ratio varies on varying X. This ratio has been measured when X = CN by measuring the rate of mono- and bilabeling of the acetyl complex, and it was 300:1.

To understand the reaction mechanism it is very important to identify the structure of the monolabeled isotopomers A and B. Unfortunately, the stretching frequencies are useless. The problem was solved by using the ^{13}CO NMR spectra of the labeled complexes. The values of the chemical shift (δ) and

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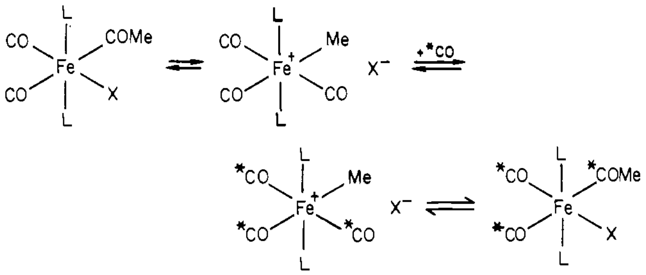
Scheme VI



those of the coupling constants clearly show that the structures of **2B′** and **2A** are those shown in Schemes I and II. This assignment is in agreement with the strong trans effect of the COMe group in d^6 complexes, recently discussed in similar iron complexes.[21]

The formation of the isotopomers **2A** in the carbonylation of the complex **1** with ^{13}CO rules out the formation of a square-pyramidal intermediate, which would mainly form the isotopomer **2B**. All this evidence supports a trigonal-bipyramidal intermediate, following Scheme V. When X = CN or NCS only the directions α and β are active and only the cis isomers are obtained; when X = I the γ direction is also active, even though it reacts much more slowly. A similar mechanism has been hypothesized by Mawby and co-workers for isostructural ruthenium complexes.[22]

The formation of a trigonal-bipyramidal intermediate does not allow information to be obtained about the intimate mechanism, i.e. if it proceeds through a methyl or a CO migration. The formation of an η^2 acyl intermedate cannot be excluded in light of a recent characterization of an η^2 iminoacyl derivative with similar complexes,[23] but if a η^2 acyl intermediate is formed, it is not kinetically relevant, since it should activate the position cis to the acetyl group[24] and give only the monolabeled isotopomer with B structure.

The formation of complexes labeled at the acetyl group cannot be explained either by the activation of the α and β directions or by the activation of the γ direction, which produces the trans acetyl complex. The reactivity data for the iodine complex suggest a further reaction path proceeding through the ionization of the acetyl complex, following Scheme VI. The isotopic exchange that has been already studied for the $[Fe(CO)_3L_2(Me)][BPh_4]$ complex is very fast[14] and through a dissociative path gives a complete scrambling of CO. The reaction of Scheme VI works only when X = I or NCS, although at a lower rate than the insertion reaction. Such behavior is in accordance with the reactivity of the alkyl complexes with Lewis bases, recently studied by our group.[14]

Experimental Section

The complexes $[Fe(CO)_2L_2(Me)CN]$ (**1**), $[Fe(CO)_2L_2(Me)NCS]$, $[Fe(CO)_2L_2(COMe)CN]$ (**5**), and $[Fe(CO)_2L_2(COMe)NCS]$ were prepared as previously described.[13] The complexes $[Fe(CO)_2L_2(Me)I]$ and *trans*-$[Fe(CO)_2L_2(COMe)I]$ were prepared following the method reported in ref 15. ^{13}CO (90%) was purchased from Sorin. All solvents were purified following the methods in the literature.[25] Infrared spectra were recorded on Perkin-Elmer 521 or 983 spectrophotometers; ^1H NMR spectra, on a Jeol CHL-60 spectrometer. ^{13}C NMR spectra were performed with a Varian XL-200 NMR spectrometer, using CD_2Cl_2 and C_6D_6 as solvents and internal references. The δ values are referred to Me_4Si. $[Cr(acac)_3]$ was used to reduce the longitudinal relaxation time (T_1).[26]

Reaction of $[Fe(CO)_2L_2(Me)CN]$ with ^{13}CO. A 100-mg sample of **1** and 90% ^{13}CO were introduced in a reactor thermostated at 20 °C. CH_2Cl_2 (5 mL) was added with a syringe, and the resultant mixture was stirred. The reaction was complete after 1 h. The reaction product **2A** was obtained in crystalline form by adding *n*-hexane; yield 70%. This product was heated at 60 °C under high vacuum (ca. 10^{-4} torr) for 12 h: the decarbonylation was complete, and the complex **1** was again obtained.

In a different experiment, the complex **2A** and 90% ^{13}CO were introduced in a reactor thermostated at 40 °C. CH_2Cl_2 (5 mL) was added, and the resultant mixture was stirred. A slow labeling of the second CO group was observed. The reaction was complete in about 20 days. Decarbonylation of this solution at 40 °C under a nitrogen stream gave the methyl complex **4** in which the ^{13}CO label is trans to the methyl group. Carbonylation of this complex, performed as for **1** but with CO, gave the complex **2B**, which must have the ^{13}CO label in a different position from **2A** irrespective of the absolute position, due to the preparation methods, which are symmetrically opposed to each other.

Preparation of $[Fe(^{13}CO)_2L_2(^{13}COMe)CN]$ (5) and Its Unlabeled Derivatives. The complex $[Fe(^{13}CO)_3L_2(Me)][BPh_4]$ (90 mg) obtained as in ref 13 reacted in tetrahydrofuran (THF) at 20 °C with a 2:1 excess of KCN, under vigorous stirring. The reaction was complete in 24 h. The solution was filtered and evaporated to dryness. The solid was extracted with benzene. The solution was filtered and evaporated to dryness again. The product was a mixture of **5′** and **1′**, which was transformed into **5′** by carbonylating it with ^{13}CO. All the other labeled compounds were obtained following Scheme II.

Reaction of $[Fe(CO)_2L_2(Me)NCS]$ with ^{13}CO. $[Fe(CO)_2L_2(Me)NCS]$ (50 mg) and 90% ^{13}CO were introduced in a reactor thermostated at 20 °C. CH_2Cl_2 (5 mL) was added with a syringe, and the resultant mixture was stirred for 24 h. The final complex $[Fe(^{13}CO)_2L_2(^{13}COMe)NCS]$ was crystallized by adding *n*-hexane. When the reaction was carried out at −20 °C, the rapid formation of the monolabeled complex, $[Fe(^{13}CO)(CO)L_2(COMe)NCS]$, was observed. In 2 h its decarbonylation, at −20 °C under a nitrogen stream, gave a mixture of $[Fe(CO)_2L_2(Me)NCS]$ and $[Fe(^{13}CO)(CO)L_2(Me)NCS]$ in a ratio of 10:1, as measured on the basis of the CO stretching bands.

Reaction of $[Fe(CO)_2L_2(Me)I]$ with ^{13}CO and CO. From a procedure identical with that described above and a reaction time of ca. 15 h, *trans*-$[Fe(^{13}CO)_2L_2(^{13}COMe)I]$ was obtained. The partially labeled derivatives of *cis*-$[Fe(CO)_2L_2(COMe)I]$ and *trans*-$[Fe(CO)_2L_2(COMe)I]$ could not be isolated and were spectroscopically characterized in CH_2Cl_2 and *n*-hexane.

To control the reactivity of the cis acetyl complex, it was prepared in CH_2Cl_2 at −30 °C. The solution was evaporated to dryness at −30 °C under a stream of CO, and IR spectra of the residue were done in Nujol mull and in KBr. The spectrum in Nujol mull showed bands at 2084 and 2018 cm^{-1} of the $[Fe(CO)_3L_2(Me)]I$ salt and bands at 1995.5, 1949, and 1579.5 cm^{-1} of the cis acetyl complex. Small quantities of the methyl complex were also observed (ν_{CO} = 1994.5, 1942 cm^{-1}). In KBr the spectrum showed the bands of the salt (ν_{CO} = 2084, 2021, 2017.5 cm^{-1}) and those of the cis acetyl complex (ν_{CO} = 1986, 1948.5, 1580 cm^{-1}). Small quantities of the methyl complex were observed (ν_{CO} = 1982.5, 1923.5 cm^{-1}). No cis–trans isomerization was observed, as shown by the absence of the band at 1590.5 cm^{-1}, characteristic of the trans acetyl complex.

Reaction of $[Fe(CO)_2L_2MeCl]$ with ^{13}CO. An equilibrium mixture of (**9t**) and (**9c**) (ratio 1:3) was prepared from the methyl complex (100 mg) and ^{13}CO in CH_2Cl_2 at room temperature. The labeling was complete in 6 h.

Kinetic Measurements. The exchange rates for $[Fe(CO)_2L_2(COMe)CN]$ were determined at 40 °C and p_{CO} = 1 atm. The pseudo-first-order rate constants for the monolabeling (k_I) were measured by monitoring both the disappearance of the stretching bands of the unlabeled complex (ν_{CO} = 2020, 1968.5 cm^{-1}) and the appearance of the stretching band of the monolabeled complex. The pseudo-first-order rate constant for the bilabeling (k_{II}) was measured by monitoring the disappearance of the stretching band of the

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monolabeled complex, after that the monolabeling was complete. The exchange rates for $[Fe(CO)_2L_2(COMe)NCS]$ were determined at 20 °C and $p_{CO} = 1$ atm. k_I was measured following the disappearance of the band of higher frequency of the unlabeled acetyl complex ($\nu_{CO} = 2024.4$ cm^{-1}); k_{II} was measured by following both the disappearance of the band at higher frequency of the monolabeled complex ($\nu_{CO} = 1982.1$ cm^{-1}) and the appearance of the band at lower frequency of the bilabeled complex ($\nu_{CO} = 1921$ cm^{-1}), after that the monolabeling was completed.

Acknowledgment. This work was supported financially by the Italian National Research Council (CNR, Programma Finalizzato Chimica Fine e Secondaria). We thank Drs. N. Nicolai and S. Aime for providing the ^{13}C NMR spectra.

Registry No. **1**, 78240-85-4; **1′**, 89153-48-0; **2A**, 89153-50-4; **2A′**, 89153-51-5; **2B**, 89195-38-0; **2B′**, 89195-98-2; **3**, 89144-33-2; **3′**, 89153-49-1; **4**, 89153-47-9; **5**, 78250-85-8; **5′**, 89144-34-3; **6**, 89195-37-9; **8**, 91083-45-3; **9t**, 91083-46-4; **9c**, 91176-78-2; $[Fe(CO)_2(PMe_3)_2(Me)I]$, 33542-07-3; $[Fe(^*CO_a)(CO)(PMe_3)_2(Me)I]$, 91176-79-3; $[Fe(^*CO)_2(PMe_3)_2(Me)I]$, 88003-85-4; $[Fe(CO)_2(PMe_3)_2(COMe)I]$, 78306-61-3; $[Fe(^*CO)(CO)(PMe_3)_2(COMe)I]$, 89195-36-8; $[Fe(CO)_2(PMe_3)_2(Me)NCS]$, 78240-86-5; $[Fe(^*CO_a)(CO)(PMe_3)_2Me(NCS)]$, 91176-80-6; $[Fe(^*CO)_2(PMe_3)_2Me(NCS)]$, 89144-37-6; $[Fe(CO)_2(PMe_3)_2(COMe)(NCS)]$, 78688-00-3; $[Fe(^*CO)(CO)(PMe_3)_2(COMe)(NCS)]$, 89144-38-7; $[Fe(^*CO)_2(PMe_3)_2(^*COMe)(NCS)]$, 89144-39-8; CO, 630-08-0.

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Synthetically Versatile (Trifluoromethanesulfonato)metal Amine Complexes

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Received August 11, 1983

Facile synthetic routes to complexes of the labile unidentate coordinated trifluoromethanesulfonate ($^-OSO_2CF_3$) ion are reported for $M(NH_3)_5(OSO_2CF_3)^{n+}$ (M = Rh(III), Ir(III), Cr(III), Ru(III) where $n = 2$; M = Pt(IV) where $n = 3$), $M(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ (M = Co(III), Rh(III), Cr(III)), *cis*-$M(en)_2(OSO_2CF_3)_2^+$ (M = Rh(III), Ir(III), Cr(III)), and *trans*-$M(en)_2Cl(OSO_2CF_3)^+$ (M = Rh(III), Ir(III)). The utility of these synthetically versatile intermediates in the preparation of a variety of complexes containing neutral ligands is illustrated. Rate constants for the aquation of the triflato complexes in 0.1 M CF_3SO_3H at 25 °C span 3 orders of magnitude and for the pentaammine complexes show a reactivity order of Ru(III) > Co(III) ~ Cr(III) ~ Rh(III) ≫ Ir(III) ≫ Pt(IV). For the pentakis(methylamine) complexes, the aquation rate is greater for Co(III), slightly greater for Rh(III), and smaller for Cr(III) in comparison to the corresponding pentaammine complexes. The aquations of $M(en)_2X(OSO_2CF_3)^+$ proceed largely without isomerization (<5%), and the triflato complexes are prepared stereospecifically by this route. For the *cis*-$M(en)_2(OSO_2CF_3)_2^+$ ions, consecutive first-order aquation processes are observed with rate constants $k_1 \sim 2k_2$.

Introduction

As a consequence of the large inductive effects of the CF_3– and $-SO_2$– groups, the (trifluoromethyl)sulfonyl group (CF_3SO_2) is one of the strongest electron-withdrawing groups known.[1-3] The trifluoromethanesulfonate anion ($CF_3SO_3^-$, triflate) has been shown to be a useful leaving group in organic chemistry.[3,4] The lability of coordinated triflate was established following the synthesis of $Cr(OH_2)_5(OSO_2CF_3)^{2+}$ by Scott and Taube.[5] Few other triflato complexes were reported until the recent synthesis of the complexes $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, and *fac*-$[Co(dien)(OSO_2CF_3)_3]$ (en = 1,2-ethanediamine; dien = 3-azapentane-1,5-diamine).[6,7] These complexes proved to be useful synthetic intermediates for reactions under mild conditions.[7-9] The triflate anion is only slightly less labile than perchlorate when coordinated in pentaamminecobalt(III) complexes (aquation rate constants are 0.1 and 0.027 s^{-1}, respectively, at 25 °C, $\mu = 1.0$ M),[7,10] and its complexes are not potentially explosive as are the perchlorates. Triflate salts also have useful solubilities in a variety of nonaqueous solvents, which can be a synthetic advantage.

The present article reports syntheses of triflato complexes involving Co(III), Rh(III), Ir(III), Ru(III), Pt(IV), and Cr(III),[11] their reactivity, and use for further syntheses under mild conditions.

Experimental Section

Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, all molar absorptivities being reported in M^{-1} cm^{-1}. ^1H NMR spectra were measured with JEOL PMX60 or JEOL Minimar (100-MHz) spectrometers, at ~30 °C with neat CF_3SO_3H (for all triflato complexes) or D_2O as solvents and sodium (trimethylsilyl)propionate as internal reference. ^{13}C NMR spectra were recorded with a JEOL FX-60 spectrometer, using dioxane as reference. All chemical shifts (ppm) are reported as downfield shifts from these references. Infrared spectra were recorded (KBr disk) with a Perkin-Elmer Model 457 instrument. For the more labile triflato complexes, substitution of Br^- for $CF_3SO_3^-$ occurred in KBr disks. In these instances, chloroform mulls were prepared, and spectra were recorded after the chloroform had evaporated from the surface of the KBr disks.

Anhydrous trifluromethanesulfonic acid (CF_3SO_3H, 3M Co.) was vacuum distilled (bp 50 °C (10 mmHg)). The precursors $[Rh(NH_3)_5Cl]Cl_2$,[12] $[Cr(NH_3)_5Cl]Cl_2$,[13] $[Ir(NH_3)_5Cl]Cl_2$,[14] $[Ru(NH_3)_5$-

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