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On the reaction of $Fe(CO)_5$ with $Ti(NMe_2)_4$: synthesis of $(CO)_4FeC(NMe_2)OTi(NMe_2)\{OC(NMe_2)\}_2Fe(CO)_3$

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Abstract

$Ti(NMe_2)_4$ reacts with $Fe(CO)_5$ in pentane or toluene by insertion of coordinated CO groups into Ti–N bonds. Whereas with a 1:1 mole ratio of the reactants **1** is formed quantitatively, use of longer reaction times and an excess of $Fe(CO)_5$ gives the metallocyclic carbene complex **2**. The compounds have been characterized by ^1H, ^{13}C NMR, IR, and Mössbauer spectroscopy.

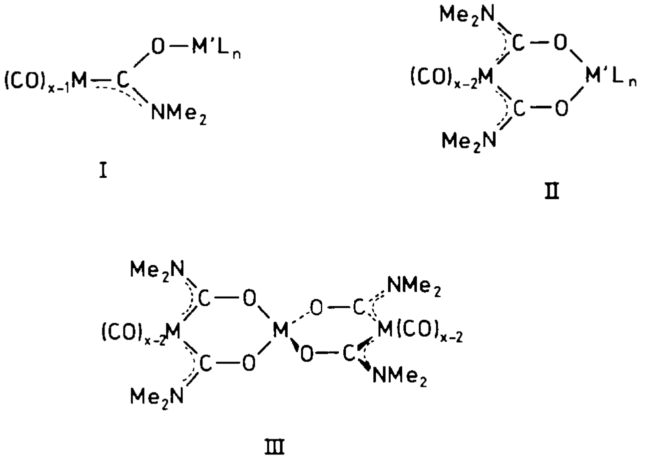
1. Introduction

Fischer carbene complexes contain one or two "heteroatoms" at the carbene carbon atom and are most commonly generated by successive addition of a hard nucleophile and a hard electrophile to a carbonyl group of suitable transition metal compounds [1]. In earlier reports, we showed that similar Fischer carbenes could be obtained in a single step by insertion of carbon monoxide ligands from $M(CO)_x$ compounds into M′–N bonds of dialkylamides, L_nM' NR_2, of some Group 4, 13, and 14 elements [2–4]. Thus, depending on the nature of the amide introduced, compounds with the structural features **I** to **III**, (Scheme 1) could be obtained; formation of a type **I** complex from $Mn_2(CO)_{10}$ was reported previously [5].

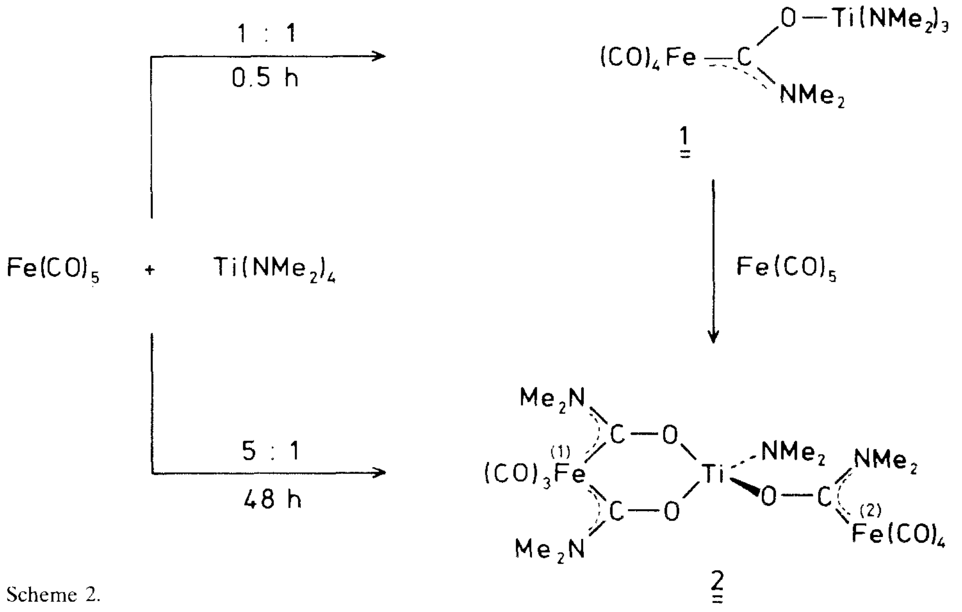
Whereas $[Al(NMe_2)_3]_2$ or $Ti(NMe_2)_4$ give only carbene compounds of type **I**, tin amides containing more than one Sn–N function, such as $Sn(NMe_2)_4$, $R_2Sn(NMe_2)_2$ ($R = CH_3$, C_2H_5), or $[Sn(NMe_2)_2]_2$, react almost immediately with $Fe(CO)_5$ to give metallocyclic carbenes of type **II** or **III** [4,6]. Although the formation of one carbene ligand on a transition metal should decrease the electrophilic properties of the remaining carbonyl carbon atoms, no type **I** compound could be isolated in this case. The tin-substituted ammonia, $N(SnMe_3)_3$, however, reacts quite differently, and produces $(CO)_4Fe(SnMe_3)_2$ quantitatively [7]. We describe below another type of compound that is obtained when $Ti(NMe_2)_4$ is allowed to react with $Fe(CO)_5$ under more vigorous conditions.

2. Results and discussion

We found that the results of the reactions of $Ti(NMe_2)_4$ with $Fe(CO)_5$ strongly depend on the reaction conditions. Whereas use of a 1:1 ratio of the components results in almost immediate precipitation of the bright yellow addition product **1** from benzene solution, prolongation of the reaction to about 48 h



Scheme 1.



Scheme 2.

and use of a five-fold excess of $Fe(CO)_5$ lead to the formation of the deep red complex **2**, as depicted in Scheme 2.

Activation of the last Ti–N bond was not observed and further prolongation of the reaction time or use of higher reaction temperatures led to decomposition of **2**. A 1 : 2 addition product, formulated as $Ti(NMe_2)_4 \cdot 2\ Fe(CO)_5$, was mentioned earlier, but no properties were reported [8]. Our structural suggestion for **2**, containing the structural features of **I** and **II** in the same molecule, is based on Mössbauer, NMR, and IR spectroscopic data.

The Mössbauer spectrum exhibits four lines of equal intensity at −0.880, −0.590, 0.892, and 1.150 mm/s, which can be assigned to two iron atoms in different chemical environments. The individual lines of the spectrum allow three possible combinations for the isomer shift values and the quadrupole doublets of the two types of iron atoms. However, one combination with small QS values for both iron sites (0.290 and 0.268 mm/s) can be ruled out (not shown in Table 1). Earlier studies have shown that compounds of the type $Fe(CO)_4L$ with formal zero valent five-fold coordinated iron atoms with L occupying an axial or an equatorial position always exhibit QS values well above 1.5 mm/s [9,10]. The choice between attributing the remaining parameter combinations A and B and the assignments to the $Fe(CO)_3$ or $Fe(CO)_4$ groups is less obvious. But from the parameters for **1**, which contains the same structural unit as one iron atom in **2**, the assignment A appears more realistic than B. This assignment is confirmed by the fact that metallocyclic carbenes obtained from $Fe(CO)_5$ and bifunctional tin amides exhibit smaller QS values but with slightly increased isomer shifts [11]. Similarly, in phosphane compounds, the quadrupole splitting also decreases on going from a $(CO)_4FeL$ complex to a *cis*-$(CO)_3FeL_2$ complex by about the same amount of *ca.* 0.50 mm/s, if L are comparable ligands ($\Delta E^Q = 2.58$ mm/s for $L = P(C_6H_5)_3$ [12] and 2.12 mm/s for $L_2 = (C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ [13]).

The ^1H and ^{13}C NMR spectra of **2** show the presence of five chemically different methyl groups as indicated by five singlets in a 1 : 1 : 2 : 2 : 2 intensity ratio. The signals can be assigned to three types of NMe_2 groups, and are consistent with the formation of a metallocyclic dicarbene ligand at one iron atom, a carbene ligand at the other one, and a remaining Ti–NMe_2 bond. In both carbene systems, the signals of the NMe_2 group are split into *cis* and *trans* methyl protons consistent with a rotation barrier around the $C_{carbene}$–N axes arising from a partial CN double bond, which is typical for aminocarbene ligands. The spectra also imply the presence of a mirror plane formed by the atoms Fe-1, Ti, N (at Ti), and O (at the monocar-

TABLE 1. Mössbauer parameters for **1** and **2** [a]

	δ $Fe(CO)_3$	ΔE^Q	δ $Fe(CO)_4$	ΔE^Q	Ref.
1	–	–	0.121	1.880	[7]
2 A	0.151	1.482	0.135	2.030	This
B	0.006	1.772	0.280	1.740	work

[a] In mm/s, at 77 K relative to $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

bene) and free rotation around the Ti–O and C–O bonds at the monocarbene part of the molecule. The ^{13}C NMR parameters for the $Fe(CO)_4$ fragment of **2** are close to those for **1**, with deviations of < 1 ppm. The signal from the remaining $TiNMe_2$ grouping in **2** has shifted by about 3.5 ppm to lower field relative to that for the three equivalent NMe_2 groups in **1**.

In the carbene/CO region, the ^{13}C NMR spectrum of **2** exhibits only three signals whereas four were expected, two for each type of carbene carbon atoms and two for the CO groups on the two chemically non-equivalent iron atoms. The absence of one signal may be attributed to accidental coincidence of the carbonyl resonances of $Fe(CO)_3$ and $Fe(CO)_4$ groups at 217 ppm; an identical shift for the CO groups is found in **1**. In general NMR spectroscopy at room temperature cannot distinguish between equatorial and axial CO groups in a trigonal bipyramidal environment of the iron atom because of rapid intramolecular CO exchange even at low temperature [14–16]. The signals at 233.3 and 225.6 ppm are assigned to the mono- and dicarbene carbon atoms, respectively [17–19].

Only bands of terminal CO groups appear in the $\nu(CO)$ region of the IR spectrum of **2**; the four bands observed arise from superimposition of the patterns for $Fe(CO)_3$ and $Fe(CO)_4$ groups. The presence of medium-intense bands at about 1500 cm^{-1} is consistent with the presence of partial $C_{carbene}$–N double bonds.

An X-ray diffraction study to confirm our proposed structure for **2** was not possible because suitable crystals could not be obtained. Further studies in this field are in progress.

3. Experimental details

All manipulations were carried out under a N_2 atmosphere. Solvents were thoroughly dried and stored over molecular sieves. NMR spectra were recorded on Varian T 60 (^1H) and CFT 20 (^{13}C) instruments. IR spectra were obtained on a Perkin-Elmer 457 spectrometer. The Mössbauer data were collected at 77 K *versus* $^{57}Co(Pd)$ source. Microanalyses were performed by the analytical service of the Fachbereich Chemie of the University of Marburg (Germany).

Because of the low volatility of the complexes, satisfactory mass spectra could not be obtained. Only peaks with $m/z < 200$ were observed.

3.1. Preparation of $(CO)_4FeC(NMe_2)OTi(NMe_2)_3$ (1)

Complex **1** was prepared by modification of a procedure described earlier [3]. Thus, 2.09 g (10.7 mmol) of $Fe(CO)_5$ was added to a solution of 2.24 g of $Ti(NMe_2)_4$ in 50 ml of pentane at −30°C and the mixture stirred for 0.5 h. The solution was concentrated and cooled to about −40°C. The resulting bright yellow precipitate was filtered off and dried *in vacuo*.

3.2. Preparation of $(CO)_3Fe(C(NMe_2)O)_2Ti(NMe_2)OC(NMe_2)Fe(CO)_4$ (2)

3.2.1. Method A

A mixture of 1.8 g (8.0 mmol) of $Ti(NMe_2)_4$ and 7.9 g (40 mmol) of $Fe(CO)_5$ in 50–70 ml of toluene was stirred in the dark for 50 h at room temperature. The resulting dark red solution was filtered and concentrated *in vacuo* until crystallization began. Addition of pentane and storage of the mixture at 0°C for several hours gave dark red crystals, which were washed with pentane and dried *in vacuo* (3.5 g, 71% yield). Anal. Found: C, 34.52; H, 3.85; N, 8.80. $C_{18}H_{24}Fe_2N_4O_{10}Ti$ calcd.: C, 35.09; H, 3.93; N, 9.10%.

3.2.2. Method B

An equimolar mixture of **1** and $Fe(CO)_5$ in toluene was stirred at room temperature for 18 to 20 h during which the colour of the solution turned from yellow to

TABLE 2. ^1H, ^{13}C NMR and IR data for 1 and 2

	^1H NMR (ppm)		^{13}C NMR (ppm)			IR (cm^{-1})		
	C-NMe_2	Ti-NMe_2	C-N*Me*$_2$	Ti-NMe_2	*C*-NMe_2	CO	(CO)	(C-N)
1	2.38(1)	3.10(6)	36.35	43.96	232.30	217.56	2040	1500
	3.22(1)		44.49				1955	
							1920	
2	2.92(1) ^{a}	3.07(2)	37.19 ^{a}	47.55	233.28 ^{a}	217.40	2038	1520
	3.39(1) ^{a}		44.56 ^{a}				2025	1500
							1990	
	3.02(2) ^{b}		35.28 ^{b}		225.60 ^{b}	217.40	1951	
	3.49(2) ^{b}		40.35 ^{b}					

^{a} At $Fe(CO)_4$. ^{b} At $Fe(CO)_3$.

deep red. Addition of pentane and cooling to −20°C gave dark red crystals of **2** in 80% yield.

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