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Preliminary communication

Alkyl isocyanate insertion into an iron–hydrogen bond

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Carboxamido complexes of transition metals have been prepared by the reaction of cationic metal carbonyl complexes with primary and secondary amines[1,2]. For example[1]:

$$C_5H_5Fe(CO)_3^+ + 2\ RNH_2 \rightarrow C_5H_5Fe(CO)_2(CONHR) + RNH_3^+ \qquad (1)$$

It was of interest to determine whether these derivatives could also be prepared by the insertion of an alkyl isocyanate into a metal–hydrogen bond. To this end, we carried out the following reaction:

$$C_5H_5Fe(CO)_2H + RNCO \rightarrow C_5H_5Fe(CO)_2CONHR$$

where R = t-Bu

The hydride, $C_5H_5Fe(CO)_2H$, was generated *in situ* by the reaction of 22.6 mmol of $Na[C_5H_5Fe(CO)_2]$ with 29.4 mmoles of t-butyl chloride in 150 ml of tetrahydrofuran (THF) at –78° according to the method of Green[3]. After adding 40.3 mmoles of t-BuNCO, the mixture was slowly warmed to room temperature and stirred for 12 hours. Following evaporation to dryness, the residue was extracted with four 150 ml aliquots of warm pentane. These were cooled at –20° to give a violet-brown powder of $(C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$ (Found: C, 52.79; H, 4.92; N, 3.40; m.p. 164–165°. $C_{18}H_{19}Fe_2NO_3$ calcd.: C, 52.85; H, 4.68; N, 3.42 %. Parent ion in the 70 eV mass spectrum at *m/e* 409.) The vast majority of the unextracted residue was also $(C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$.

The pentane extractions were then evaporated to dryness. Sublimation of the residue under high vacuum at 70° gave a mixture of yellow and pale yellow crystals on the water-cooled probe. The sublimate was resublimed at 30° over a period of about 3 days to yield 35 mg of yellow $C_5H_5Fe(CO)_2[CONHC(CH_3)_3]$ (Found: C, 52.46; H, 5.48; N, 5.37, m.p. 95–97°. $C_{12}H_{15}FeNO_3$ calcd.: C, 52.01; H, 5.46; N, 5.06%. Parent ion in the 70 eV mass spectrum at *m/e* 277.)

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On raising the temperature to 55° 165 mg of the pale yellow $C_5H_5Fe(CO)[CNC(CH_3)_3][CONHC(CH_3)_3]$ sublimed (Found: C, 57.72; H, 7.14; N, 8.45. $C_{16}H_{24}FeN_2O_2$ calcd.: C, 57.85; H, 7.28; N, 8.43%.) Although no $(C_5H_5)_2Fe_2(CO)_4$ was found in the reaction mixture, $C_5H_5Fe(CO)_2H$ is known[3] to decay to $(C_5H_5)_2Fe_2(CO)_4$ under mild conditions. Hence it seemed possible that $(C_5H_5)_2Fe_2(CO)_4$ could have been formed as an intermediate which reacted with t-BuNCO to give one or more of the observed products. This possibility was eliminated by the lack of any reaction between $(C_5H_5)_2Fe_2(CO)_4$ and t-BuNCO in THF at room temperature over a period of several days.

Of the three products obtained, the minor one was the desired t-BuNCO insertion product, $C_5H_5Fe(CO)_2[CONHC(CH_3)_3]$, whose IR and NMR spectra (Table 1) are consistent with this formulation[1]. The next most abundant product, $C_5H_5Fe(CO)[CNC(CH_3)_3][CONHC(CH_3)_3]$, is related to that compound by the replacement of one CO group by a t-BuNC group. The three absorptions in the infrared spectrum at 2109, 1939 and 1609 cm^{-1} may be assigned to ν(C—N) of the t-BuNC group, ν(C—O) of the CO, and ν(C—O) of the carboxamido group. The NMR spectrum exhibits three singlets which may be assigned to C_5H_5 (τ 5.38), $CONHC(CH_3)_3$ (τ 8.73) by analogy with $C_5H_5Fe(CO)_2[CONHC(CH_3)_3]$, and $CNC(CH_3)_3$ (τ8.50). The NH proton was not located probably because of broadening by the nitrogen. The source of the t-BuNC ligand in this complex must be the t-BuNCO. Although this reaction is not understood, there are other examples in the literature[4] of the conversion of alkyl isocyanates to isocyanide ligands.

The major product of the reaction is the dimer, $(C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$, which must be very similar structurally to $(C_5H_5)_2Fe_2(CO)_4$. By comparison with the spectrum of $C_5H_5Fe(CO)[CNC(CH_3)_3][CONHC(CH_3)_3]$, the high frequency absorption at ~ 2110 cm^{-1}* (Table 1) can be assigned only to ν(C—N) of a terminal

TABLE 1

INFRARED AND ^{1}H NMR DATA

Compound	Solvent	ν(CO) (cm^{-1})	^{1}H NMR (ppm)[a]	
			C_5H_5	$C(CH_3)_3$
$C_5H_5Fe(CO)_2[CONHC(CH_3)_3]$	hexane	2022s, 1959vs, 1633m	5.04	8.74
$C_5H_5Fe(CO)[CNC(CH_3)_3]$-$[CONHC(CH_3)_3]$	hexane	2109m (2071 w(sh)), 1939s, 1609m	5.38	8.50, 8.73
$(C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$	hexane	2108m (2067 w(sh)), 1953s, 1771vs	5.40	8.84
	CCl_4	2115m (2059 w(sh)), 1952s, 1756vs		
	CH_2Cl_2	2119m (2065 w(sh)), 1949s, 1750vs		
	KBr	2110s (2054 w(sh)), 1941vs, 1744s		

[a] In acetone-d_6 solvent at room temperature. All resonances are singlets.

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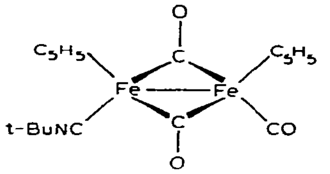
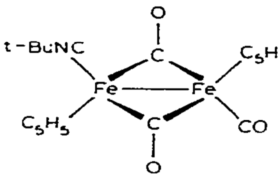
*Like the ν(C—N) absorption of the t-BuNC ligand in $C_5H_5Fe(CO)[CNC(CH_3)_3][CONHC(CH_3)_3]$, this band exhibits an unexpected weak shoulder at slightly lower frequency. The origin of this shoulder in either compound is not obvious.

t-BuNC ligand. The low frequency absorption at ~ 1750 cm^{-1} must be a bridging carbonyl mode, while the intermediate band at ~ 1950 cm^{-1} is in the expected position for a terminal CO group. These assignments support the *cis* and/or *trans* isomers of the carbonyl bridged dimer as being the most likely structures for the molecule.



cis



trans

For comparison, the carbonyl absorptions of the isomers of $(C_5H_5)_2Fe_2(CO)_4$ in CCl_4 solvent are reported at 2005, 1958, and 1781 cm^{-1} for the *cis* isomer and at 1958 and 1781 for the *trans* [5]. Although the relative amounts of the $(C_5H_5)_2Fe_2(CO)_4$ isomers were solvent dependent, the IR spectrum of $(C_5H_5)_2Fe(CO)_3[CNC(CH_3)_3]$ changes very little with the solvent as shown in Table 1. Even in a KBr pellet, the compound also shows only three absorptions, but the relative intensities are more nearly equal.

The NMR spectrum of $(C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$ shows only one resonance for the C_5H_5 groups suggesting that the $CNC(CH_3)_3$ ligand is exchanging rapidly between the two Fe atoms. The NMR spectrum of $(C_5H_5)_2Fe_2(CO)_4$ also exhibits only one resonance at room temperature presumably because of the rapid interconversion of the *cis* and *trans* isomers [6].

The analogous methyl isocyanide complex, $(C_5H_5)_2Fe_2(CO)_3(CNCH_3)$, has been prepared[7] by a different route; it too has the isocyanide ligand in a terminal position. In contrast, an X-ray study[8] of the phenyl isocyanide derivative, $(C_5H_5)_2Fe_2(CO)_3(CNC_6H_5)$ shows the isocyanide ligand in a bridging position.

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