Journal of Organometallic Chemistry, 118 (1976) 199—204
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SOLUTION PROPERTIES OF THE $HFe_3(CO)_{11}^-$ ION

JOHN R. WILKINSON and LEE J. TODD *
*Department of Chemistry *, Indiana University, Bloomington, Indiana 47401 (U.S.A.)*

(Received March 23rd, 1976)

Summary

A variable temperature ^{13}C NMR study of $HFe_3(CO)_{11}^-$ has revealed that at least two dynamic processes are occurring over the range —107 to +30° C. Infrared and ^{13}C NMR studies of the $HFe_3(CO)_{11}^-$ ion in various solution environments show that the bridging carbonyl unit is very basic and forms acid—base complexes with BF_3 as well as $HN(C_2H_5)_3^+$. These acid—base interactions apparently cause the fluxional processes of the $HFe_3(CO)_{11}^-$ ion to stop at a higher temperature.

Introduction

The anion $[HFe_3(CO)_{11}]^-$ has a solid state structure which is closely related to that of $Fe_3(CO)_{12}$ [1]. Recently a variable temperature (+40 to —30° C) ^{13}C NMR study of this anion was reported [2]. At +40° C one carbonyl resonance at 221 ppm was observed. However at —30° C two signals in a 1 to 10 intensity ratio at 259.8 and 214.8 ppm respectively were observed. These lower temperature NMR data were consistent with the known solid state structure and it was therefore assumed that the slow exchange limit had been reached [2]. In the course of another investigation concerning the ^{13}C NMR properties of bridging carbonyl groups in acid media, we have uncovered new findings concerning the solution properties of the $[HFe_3(CO)_{11}]^-$ ion. The first results of both of these studies are presented in this report.

Experimental

Instrumentation and ^{13}C NMR procedures

IR spectra were obtained on a Perkin—Elmer 137G instrument in a conventional IR solution cell, with a thickness of 0.1 mm, employing a solvent blank. The ^{13}C spectra were obtained on a Varian XL-100-15 spectrometer operating at 25.2

---

* Contribution No. 2836.

MHz under conditions of proton decoupling. Trisacetylacetonatochromium(III), about 0.05 *M*, was added as a relaxation agent [8]. Chemical shifts were measured relative to internal solvent and converted to internal TMS using the conversion factor $\delta(\mathrm{TMS}) = \delta(\mathrm{CH_2Cl_2}) + 53.89$ ppm.

Materials

The compounds $(C_2H_5)_3NH[HFe_3(CO)_{11}]$ [3] and $(C_2H_5)_4N[HFe_3(CO)_{11}]$ [4] were prepared by literature methods. The salt $(Ph_3P)_2N[HFe_3(CO)_{11}]$ was prepared by a modification of the procedure of Graham [4]. All ^{13}C NMR samples were enriched in ^{13}CO by stirring the sample in CH_2Cl_2 solution under an atmosphere of 90% ^{13}CO at ambient temperature. The complex $(C_2H_5)_3NH[HFe_3(CO)_{11} \cdot BF_3]$ was prepared by the addition of $BF_3 \cdot O(C_2H_5)_2$ to the NMR sample of $(C_2H_5)_3NH[HFe_3(CO)_{11}]$ at —78°C. The complex $[(C_5H_5)Fe(CO)_2 \cdot BCl_3]_2$ was prepared by bubbling BCl_3 thru a CH_2Cl_2 solution of $[(C_5H_5)Fe(CO)_2]_2$ [5].

Results and discussion

Properties of $HFe_3(CO)_{11}^-$ in various environments

In Table 1 are presented the infrared stretching frequencies in the carbonyl region of triethyl- and tetraethyl-ammonium salts of $HFe_3(CO)_{11}^-$ in various solvents. The terminal carbonyl stretching region, 2100 to 1970 cm^{-1}, is too complex to conveniently analyze. However, examination of the changes in the stretching frequency of the bridge carbonyl ligand with solvent and with cation variation demonstrates an interesting trend.

The $\nu(CO)$ (bridge) of $(C_2H_5)_4N[HFe_3(CO)_{11}]$ changes from 1709 to 1735 cm^{-1} with increasing polarity of the solvent. In contrast $\nu(CO)$ (bridge) of $(C_2H_5)_3NH[HFe_3(CO)_{11}]$ is observed at 1639 and 1650 cm^{-1} in benzene and CH_2Cl_2 solution respectively but is found at 1736 and 1742 cm^{-1} in the more polar solvents nitromethane and acetonitrile. Carbon monoxide basicity is characteristic of the bridging ligand in polynuclear metal carbonyl derivatives [5]. This property may be enhanced in a polynuclear anion such as $HFe_3(CO)_{11}^-$ as has been demonstrated by its successful bridge alkylation [9]. We suggest that the decrease in $\nu(CO)$ (bridge) for the triethylammonium salt in nonpolar solvents is due to the formation of the tight ion pair complex I. When the more polar nitromethane and acetonitrile are used as solvents the ion pair bond is disrupted and the $\nu(CO)$ (bridge) of the free $HFe_3(CO)_{11}^-$ is observed. In the case of $(C_2H_5)_4N[HFe_3(CO)_{11}]$ this type of ion pairing is not possible and $\nu(CO)$ (bridge) of the free $HFe_3(CO)_{11}^-$ ion is observed with small changes due to solvent variations.

Dynamics of the $HFe_3(CO)_{11}^-$ ion

The ^{13}C NMR spectrum of $(C_2H_5)_3NH[HFe_3(CO)_{11}]$ at various temperatures is presented in Fig. 1. It is observed that at temperatures lower than —30°C changes occur in the spectrum indicating that a limiting spectrum had not been obtained as previously reported [2]. At —107°C seven peaks in a 1 : 1 : 1 : 2 : 2 : 2 : 2 ratio, reading upfield, are observed in the carbonyl region of the spectrum. This is exactly the ratio and number of peaks expected based on the X-ray structure of the $HFe_3(CO)_{11}^-$ ion [1]. It therefore appears that at this lower temperature

(continued on p. 203)

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF $HFe_3(CO)_{11}^-$ SALTS [a]

Solvent	Cation	ν(CO) terminal				ν(CO) bridge
C_6H_6	$(C_2H_5)_3NH^+$	2070w,	2008vs	1980s,	1956m,	1639m
	$(C_2H_5)_4N^+$	2073w,	(2008vs, 2000vs)	—	—	1709m
CH_2Cl_2	$(C_2H_5)_3NH^+$	2975w.	(2012vs, 2004vs)	1980s,	1949m,	1650m
	$(C_2H_5)_4N^+$	2070w,	2000vs	1972s,	1946m,	1718m
CH_3NO_2	$(C_2H_5)_3NH^+$	2066w,	2000vs	1976s,	1946m,	1730m
	$(C_2H_5)_4N^+$	2075w,	2000vs	1976s,	1949m,	1733m
CH_3CN	$(C_2H_5)_3NH^+$	2073w,	2004vs	1980s,	1946m,	1742m
	$(C_2H_5)_4N^+$	2073w,	2004vs	1988s,	1947m,	1735m

[a] Spectra calibrated with polystyrene film.

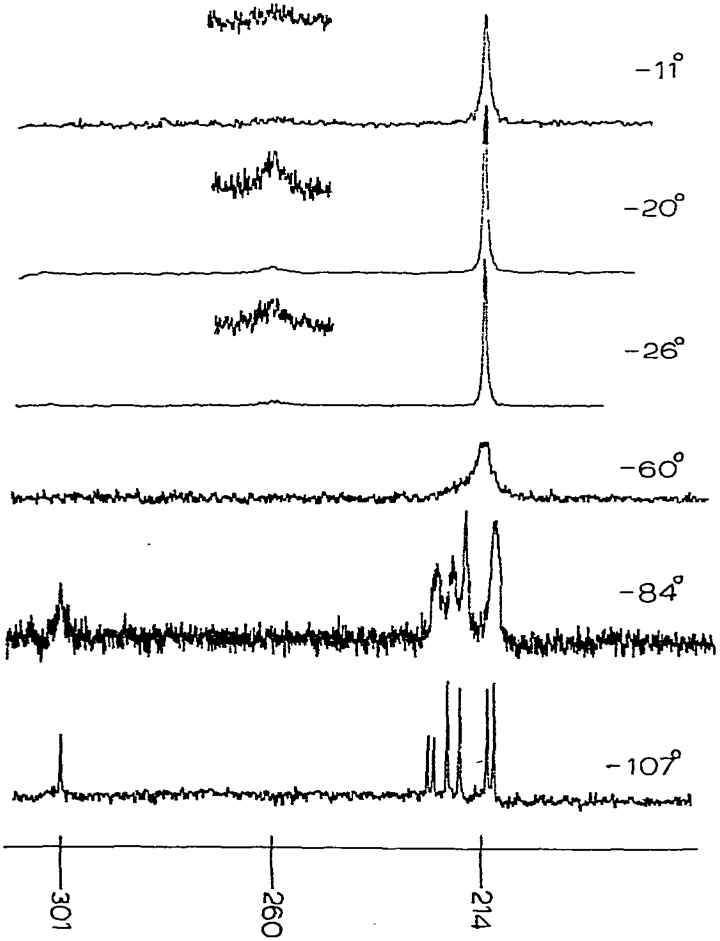


Fig. 1. The variable temperature ^{13}C NMR spectra of $(C_2H_5)_3NH[HFe_3(CO)_{11}]$ from —11 to —107°C. At room temperature one peak at 221 ppm is observed in accordance with ref. [2].

SCHEME 1

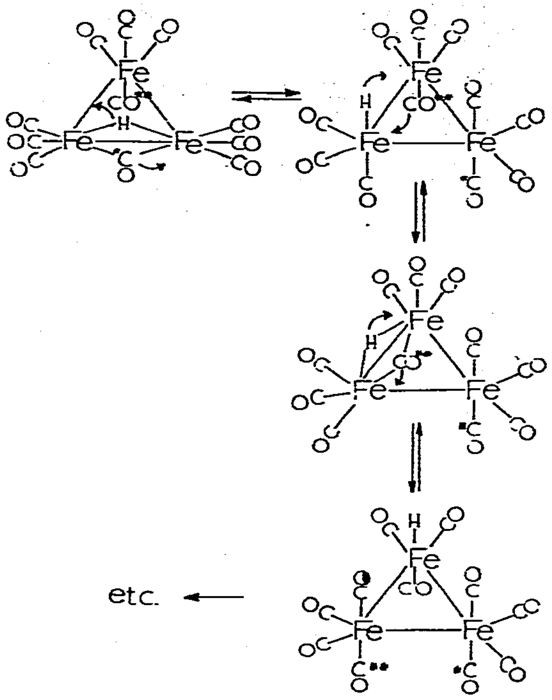
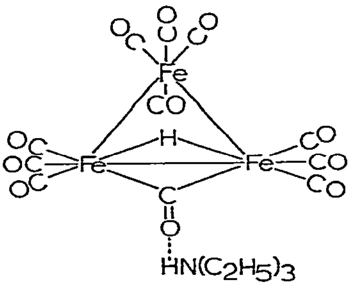


TABLE 2

LOW TEMPERATURE ^{13}C NMR DATA OF THE $HFe_3(CO)_{11}$ ION IN VARIOUS ENVIRONMENTS

Compound	Solvent	T (°C)	Carbonyl Carbons δC (ppm) (rel. intensity)	Carbonyl Carbons $J(^{13}C-^{1}H)$ (Hz)
$(C_2H_5)_3NH[HFe_3(CO)_{11}]$	$CHCl_2F/CH_2Cl_2$ 3 : 1	—107	301.3(1)	12.9
			222.4(1)	—
			221.4(1)	broad peak
			218.3(2)	9.7
			215.7(2)	2.7
			209.9(2)	—
			208.5(2)	broad peak
$(Ph_3P)_2N[HFe_3(CO)_{11}]$	$CHCl_2F/CH_2Cl_2$ 3 : 1	—120	285.7(1)	
			223.8(1)	
			221.3(1)	
			219.3(2)	
			215.8(2)	
			210.4(2)	
			208.9(2)	
$(C_2H_5)_3NH[HFe_3(CO)_{11}]$	$CHCl_2F/CH_2Cl_2$, $BF_3 \cdot O(C_2H_5)_2$	—87	355.1(1)	
			218.9(1)	
			215.5(3)	
			212.0(2)	
			209.1(2)	
			206.1(2)	

the slow exchange limit has probably been reached. Only at the low temperature limit were we able to observe proton coupling. The rather large proton coupling to the bridge carbonyl is of interest. Upon warming to −20° C the low field signal at 301.3 ppm and a peak from the 222.4—208.5 ppm group coalesce at approximately 260 ppm. Only carbonyl scrambling of the bridge carbonyl (301.3 ppm resonance) and one of the unique terminal carbonyl groups (222.4 or 221.4 resonances) can yield a coalescence peak as low as 260 ppm. We propose the mechanism shown in Scheme 1 to account for this scrambling process. By this permutation process only CO * and CO ** scramble by pair-wise opening and closing of the hydride and carbonyl bridge units. The complete carbonyl scrambling which occurs at room temperature involves an additional exchange process.



(I)

In Table 2 are presented the low temperature ^{13}C NMR data of the $HFe_3(CO)_{11}$ ion in various solution elements.

It is observed that the bridge carbonyl resonance (most deshielded signal) differs by 69.4 ppm in the various solvent and cation environments. In the case of $(Ph_3P)_2N[HFe_3(CO)_{11}]$ the bridge carbonyl resonance at 285.7 ppm probably represents a weakly complexed or free bridging group. While for $(C_2H_5)_3NH$-$[HFe_3(CO)_{11}]$ a hydrogen-bonded ion pair is important (as described above). In the presence of $BF_3 \cdot O(C_2H_5)_2$, we propose that a relatively strong acid-base complex $HFe_3(CO)_{11} \cdot BF_3^-$ is formed with bonding through the bridging carbonyl oxygen atom. In this case the bridging carbonyl resonance is observed at much lower field (355.1 ppm). Unfortunately when this interesting complex was allowed to warm to room temperature, it decomposed which precluded its isolation.

A downfield shift of organic carbonyl carbon signals upon complexation with acids has been observed previously for aliphatic and aromatic ketones [6,7]. We have measured the ^{13}C NMR shielding value of the bridging carbonyl signal (309.0 ppm) of $[(C_5H_5)Fe(CO)_2]_2$ (CH_2Cl_2 solvent) at −85° C in the presence of excess BCl_3. A previous ^{13}C NMR study of the free dimer at −85° C (a temperature at which the structure appears to be static) gave a bridging carbonyl shielding value of 274.4 ppm [8]. Thus a downfield shift of a bridging carbonyl signal upon complexation with an acid is consistent with results observed with a known acid—base complex [5]. It is interesting to note that the fluxional process of the $HFe_3(CO)_{11}^-$ ion was slowed down at a higher temperature in the presence of

$BF_3 \cdot O(C_2H_5)_2$ as has been suggested previously for $[(C_5H_5)Fe(CO)_2]_2$ in the presence of trialkylaluminum compounds [10]. The effect of Lewis acids on other polynuclear metal carbonyl fluxional processes is under study.

Acknowledgement

This work was supported by a grant from the Indiana University Office for Research and Development.

References

1 L.F. Dahl and J.F. Blount, Inorg. Chem., 4 (1965) 1373.
2 A. Forster, B.F.G. Johnson, J. Lewis, T.W. Matheson, B.H. Robinson and W.G. Jackson, J. Chem. Soc. Chem. Commun., (1974) 1043.
3 W. McFarlane and G. Wilkinson, Inorg. Syn., 8 (1966) 178.
4 E.E. Isaacs and W.A.G. Graham, J. Organometal. Chem., 85 (1975) 237.
5 J.S. Kristoff and D.F. Shriver, Inorg. Chem., 13 (1974) 499.
6 D.R. Crist, Z. Hsieh, G.J. Jordan, F.P. Schinco and C.A. Maciorowski, J. Amer. Chem. Soc., 96 (1974) 4932.
7 G.A. Olah and A.M. White, J. Amer. Chem. Soc., 91 (1969) 5801.
8 O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.
9 D.F. Shriver, D. Lehman and D. Strope, J. Amer. Chem. Soc., 97 (1975) 1594.
10 A. Alich, N.J. Nelson, D. Strope and D.F. Shriver, Inorg. Chem., 11 (1972) 2976.