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Preliminary communication

Carbon-13 spin–lattice relaxation in organometallic complexes

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Abstract

The results of inversion recovery spin–lattice relaxation time (T_1) measurements on 19 selected organometallic half-sandwich and sandwich complexes of Cr, Mn, Fe and Co are reported together with their ^{13}C NMR data. Large variations of the ^{13}C NMR T_1 values for C_5H_5 and CO moieties are observed, depending on field strength, temperature and solvent. The use of high field instruments usually leads to lower ^{13}C NMR T_1 values for these groups, but in certain cases the values for quaternary carbon atoms increase.

Introduction

Solution ^{13}C NMR spin–lattice relaxation (T_1) data for organometallic compounds have rarely been obtained in the past [1] owing to the assumed long relaxation times of functional groups such as cyclopentadienyl (C_5R_5, $R = H$ or CH_3) or CO bonded to metals and the consequently long instrument time needed to obtain the T_1 information. Recently however, T_1 measurements on inorganic [2] and organometallic complexes [3] have proved to be an important tool for obtaining structural information and details of metal–ligand interactions. As part of our program of investigations of the bonding properties of Main Group ligands coordinated to organometallic fragments, we report now the results of ^{13}C NMR T_1 measurements on selected compounds.

During the preparation of this manuscript, two detailed reports on ^{13}C NMR T_1 measurements on iron sandwich compounds, including and confirming some of the results reported here, appeared, together with a detailed account of the theoretical interpretation [4]. Thus, only a limited discussion without a theoretical treatment, is given below. Conclusions about the relaxation mechanism are omitted because the information obtained only further confirms the conclusions presented in reference 4.

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Table 1

^{13}C NMR chemical shifts and T_1 values at 75.5 MHz and 298 K for complexes 1–7 in $(CD_3)_2CO$

No.	E	$\delta(ECH_3)$ (T_1) (ppm) ((s))	$\delta(C_5H_5)$ (T_1) (ppm) ((s))	$\delta(CO)$ (T_1) (ppm) ((s))
$[C_5H_5Fe(CO)_2(E(CH_3)_3)]BF_4$ (E = group 15 elements)				
1	N	62.03 (1.1)	88.15 (2.4)	211.69 (3.1)
2	P	19.77 (2.6)	88.21 (5.2)	210.21 (7.2)
3	As	14.86 (4.7)	87.20 (7.6)	210.22 (11.6)
4	Sb	0.57 (6.6)	86.67 (7.4)	212.21 (12.3)
$[C_5H_5Fe(CO)_2(E(CH_3)_2)]BF_4$ (E = group 16 elements)				
5	S	27.64 (2.5)	88.28 (5.4)	210.02 (8.3)
6	Se	16.66 (4.4)	87.42 (7.2)	210.25 (11.5)
7	Te	−6.88 (5.5)	86.97 (5.8)	211.40 (16.3)

A report on the MAS ^{13}C NMR study (MAS ≡ magic angle spinning) of $[C_5H_5Fe(CO)_2(E(CH_3)_2)]BF_4$ (E = S, Se and Te) complexes, including solid state ^{13}C NMR T_1 data, has been submitted for publication [5].

Results and discussion

The ^{13}C NMR chemical shifts and their spin–lattice relaxation times (T_1) for 19 organometallic complexes are summarized in Tables 1–4.

Measurements on the cationic $[C_5H_5Fe(CO)_2]BF_4$ fragment (Table 1) indicate that T_1 values increase for the metal-bonded CO groups when the donor element E in ER_n is varied in the sequence E = N to Sb, $n = 3$; E = S to Te, $n = 2$. To a smaller extent, a similar effect is found for the C_5H_5 group. The observed T_1 values decrease in the order N < P < As < Sb for E = Group 15 donor elements and S < Se ≪ Te for E = Group 16 donor elements. This trend seems to indicate

Table 2

Solvent and/or temperature dependency of ^{13}C NMR T_1 values for complexes **2** and **5**

No.	E	Solvent [a]	T (K)	RF [b] (MHz)	ECH_3 T_1 (s)	C_5H_5 T_1 (s)	CO T_1 (s)
2	P	A	298	100.6	2.4	3.1	3.8
2	P	A	253	100.6	1.9	2.2	2.4
2	P	A	193	100.6	0.2	0.5	0.4
5	S	A	298	100.6	5.3	10.5	9.8
5	S	A	273	100.6	2.3	6.0	7.4
5	S	A	253	100.6	1.6	4.2	5.3
5	S	A	233	100.6	0.9	2.6	2.8
5	S	A	193	100.6	0.5	1.3	1.3
5	S	A	298	75.5	2.5	5.4	8.3
5	S	B	298	75.5	3.4	8.1	12.0
5	S	C	298	75.5	2.8	7.1	10.7

[a] A = $(CD_3)_2CO$; B = CD_3CN; C = CD_3NO_2. [b] RF = resonance frequency for ^{13}C nucleus.

Table 3

^{13}C NMR chemical shifts and T_1 values for neutral π-ligand metal carbonyl complexes **8–11** at 298 K

No.	Solvent [a]	Carbon	δ (ppm)	T_1 (25.2 MHz) (s)	T_1 (100.6 MHz) (s)
$C_5H_5Mn(CO)_3$					
8	A	C_5H_5	83.80	10.8	15.6
		CO	225.84	15.6	9.6
$CH_3C_5H_4Mn(CO)_3$					
9	A	CH_3	13.62	7.5	8.4
		C_5H_5(CH)	82.88	7.4	7.9
		C_5H_5(CH)	83.29	7.6	7.9
		C_5H_5(C)	103.62	41.0	35.1
		CO	225.97	12.3	8.3
1,3,5-$(CH_3)_3C_6H_3Cr(CO)_3$					
10	A	CH_3	20.61	7.5	7.3
		C_6H_3(CH)	93.32	4.7	4.6
		C_6H_3(C)	112.76	28.6	100
		CO	235.41	[b]	9.1
cis-1,3-$C_4H_6Fe(CO)_3$ (cis-1,3-C_4H_6 = 1,3-butadiene)					
11	D	$C_4H_6(CH_2)$	40.96	4.4	4.1
		C_4H_6(CH)	85.86	7.7	5.6
		CO	212.17	20.0	8.9

[a] A = $(CD_3)_2CO$, D = CD_2Cl_2. [b] Not observed.

the dominance of steric interactions (covalent radii for E decrease in the same order [6]) rather than bonding contributions between the iron center and the donor element E as discussed in detail elsewhere [7]. As observed in related investigations [8], and shown here for complexes **2** and **5**, the T_1 values are very sensitive to changes in the solvent, temperature, or magnetic field strength (Table 2) [9,10]: At lower temperatures, the T_1 values for all functional groups (ECH_3, C_5H_5 and CO) fall drastically, while the effects of solvent and magnetic field strength depend strongly on the nature of the compound under investigation (see also Tables 3 and 4).

Organic-group-bearing cyclopentadienyl or aryl moieties coordinated to metals (Tables 3 and 4) show a large splitting of their T_1 values upon substitution of H by CH_3. The now quaternary carbon atoms in these ligands show long relaxation times, while the remaining unsubstituted carbon atoms relax faster or with nearly identical T_1 values when compared with the unsubstituted ligand system. Measurements at higher magnetic field in general lead to lowering of all relaxation times, but in certain cases (e.g. complexes **10** and **18**), higher T_1 values were observed. The data and their general features are consistent with those observed at lower field strength by Roberts et al. [5] for ferrocenes and $[C_5H_5Fe(arene)]^+$ complexes.

The presented information on ^{13}C NMR T_1 values for various organometallic compounds should be useful in deciding the choice of instrument and experimental conditions for ^{13}C NMR measurements, including T_1 determinations for organometallic systems.

Table 4

^{13}C NMR chemical shifts and T_1 values for bis(π-ligand) metal complexes **12–19**

No.	Solvent [a]	Carbon	δ (ppm)	T_1 (25.18 MHz) (s)	T_1 (100.6 MHz) (s)
$(C_5H_5)_2Fe$					
12	A	C_5H_5	67.94	15.2	11.0
$(C_5(CH_3)_5)_2Fe$					
13	E	$C_5(CH_3)_5(CH_3)$	9.70	6.3	6.5
		$C_5(CH_3)_5(C)$	78.44	5.0	9.0
$C_5H_5Fe(C_6H_7)$					
14	D	C_5H_5	72.88	14.3	6.9
		$C_6H_7(CH_2)$	25.78	5.7	3.5
		$C_6H_7(CH)$	22.16	13.6	4.9
		$C_6H_7(CH)$	79.69	12.4	6.7
		$C_6H_7(CH)$	79.89	14.3	8.0
$[(C_5H_5)_2Co]PF_6$					
15	A	C_5H_5	85.67	11.1	8.3
$[C_5H_5Fe(C_6H_6)]PF_6$					
16	B	C_5H_5	77.13	11.9	3.8
		C_6H_6	88.80	10.6	3.8
$[C_5H_5Fe(C_6H_5CH_3)]PF_6$					
17	B	C_5H_5	77.47	11.1	[b]
		$C_7H_8(CH_3)$	20.69	8.5	[b]
		$C_7H_8(p\text{-}C)$	87.02	7.9	[b]
		$C_7H_8(m\text{-}C)$	88.21	7.7	[b]
		$C_7H_8(o\text{-}C)$	89.22	7.8	[b]
		$C_7H_8(C\text{-}1)$	104.51	35.4	[b]
$[C_5H_5Fe(p\text{-}(CH_3)_2C_6H_4)]PF_6$					
18	B	C_5H_5	77.79	4.8	7.8
		$C_8H_{10}(CH_3)$	20.17	2.7	6.2
		$C_8H_{10}(CH)$	88.55	2.5	4.4
		$C_8H_{10}(C)$	102.61	4.8	11.8
$[C_5H_5Fe(C_6(CH_3)_6)]PF_6$					
19	B	C_5H_5	78.95	0.8	[b]
		$C_{12}H_{18}(CH_3)$	17.79	0.7	[b]
		$C_{12}H_{18}(C)$	99.01	0.7	[b]

[a] A = $(CD_3)_2CO$; B = CD_3CN; E = C_6D_6. [b] Not measured.

Experimental

Compounds **1–4** [11], **5–7** [12], **14** [13] and **16–19** [14] were prepared by published methods. The remaining complexes were commercially available.

The ^{13}C NMR spectra were recorded at 25.18 MHz (Bruker AM 100), 75.5 MHz (Varian XL-300) and 100.6 MHz (Bruker AM 400) by the implemented inversion recovery method [10,15] in 5 mm NMR tubes at 298 K using $^1H/^{13}C$ probe heads. All samples were prepared immediately prior to the measurements under nitrogen as ca. 5% solution in the stated solvents and were degassed by repeated freeze/thaw cycles. Control measurements (ferrocene in benzene-d_6 and $[C_5H_5Fe(CO)_2$-

$(S(CH_3)_2)]BF_4$ in acetone-d_6) indicated a maximum error in T_1 values of ±5%. Measurements on undegassed samples gave much lower T_1 values.

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