Steric Effects in [(η^5-C_5H_4Me)Fe(CO)(L)($SnMe_3$)] Complexes: a ^{119}Sn NMR Study

LAURENCE CARLTON, GARY PATTRICK and NEIL J. COVILLE

Department of Chemistry, University of the Witwatersrand, Johannesburg, P.O. Wits 2050 (South Africa)

(Received October 3, 1988)

Abstract

A correlation between $\delta(^{119}Sn)$ and the Tolman cone angle, θ, for a series of complexes [(η^5-C_5H_4Me)Fe(CO)(L)($SnMe_3$)] (L = CO, $P(OMe)_3$, $PMePh_2$, PPh_3, $P(CH_2C_6H_5)_3$) has been observed.

In recent publications we have reported on the use of ^{1}H and ^{13}C NMR spectroscopy in the detection of ligand orientational effects in complexes of the type [(η^5-C_5H_4R)M(CO)(L)I] (R = Me, tBu, etc.; M = Fe, Ru; L = group 15 donor ligand, RNC) [1]. From these studies it has become apparent that the steric size of both L and R can be detected by NMR parameters associated with the cyclopentadienyl protons [2].

In extending this work to an investigation of other ligands containing atoms that are NMR active (e.g. Si, Sn etc.) we had occasion to synthesize a series of complexes [(η^5-C_5H_4Me)Fe(CO)(L)$SnMe_3$]. The complexes were synthesized by standard procedures starting from [(η^5-C_5H_4Me)Fe$(CO)_2SnMe_3$] which was prepared from Na[(η^5-C_5H_4Me)Fe$(CO)_2$] [3]* and $SnMe_3Cl$. Irradiation of [(η^5-C_5H_4Me)Fe$(CO)_2SnMe_3$] with L (L = $P(OMe)_3$, $PMePh_2$, PPh_3, $P(CH_2C_6H_5)_3$) in benzene gave the required products, typically as air and moisture sensitive oils or solids. The complexes were characterized by IR and NMR (^{1}H, ^{31}P, ^{119}Sn) spectroscopy and pertinent data are reported in Table 1.

As anticipated the influence of the group 15 donor ligand on the ring proton NMR parameters could be detected and a typical spectrum for L = PPh_3 is shown in Fig. 1 (ring methyl decoupled). An orientational preference of the PPh_3 ligand is readily observed with coupling of the PPh_3 with H4, (J(P–H) = 5.17 Hz; Fig. 2). The small separation of Δ(H2–H5) = 0.05 Hz as well as the larger separation Δ(H3–H4) = 0.14 Hz suggests that the bulky $SnMe_3$ group is also displaced away from the ring methyl group.

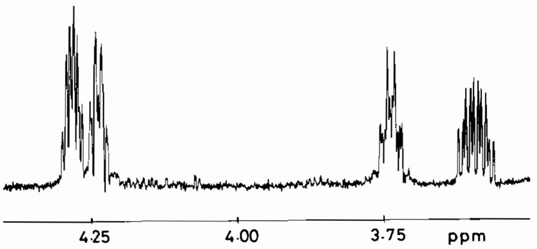

Fig. 1. ^{1}H NMR spectrum of [(η^5-C_5H_4Me)Fe(CO)(PPh_3)-$SnMe_3$] showing the ring resonances H1–H4 (see Fig. 2 for numbering system). Coupling constants were determined from decoupling experiments: J(P–H5) = 1.8 Hz, J(P–H4) = 5.2 Hz, J(P–H3) = 7.8 Hz and J(P–H2) Hz.

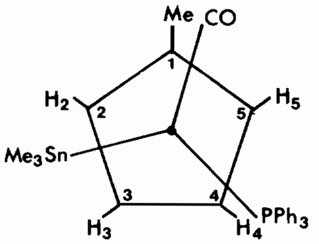

Fig. 2. Possible conformation of the solution structure of [(η^5-C_5H_4Me)Fe(CO)(PPh_3)$SnMe_3$].

More significant is the discovery of a good correlation between $\delta(^{119}Sn)$ and the Tolman cone angle, θ [4] (Fig. 3). This is a remarkable correlation as a steric parameter is seemingly being plotted against an electronic parameter. Attempts to correlate $\delta(^{119}Sn)$ (or other NMR parameters; Table 1) with electronic parameters associated with the ligand L were made. Although it is apparent that the Sn resonance moves upfield as L is varied, no linear correlation between the other parameters such as $\delta(^1H)$ and the ring protons is observed.

A consideration of the paramagnetic shielding term, σ^P, suggests an explanation for our observed result. The paramagnetic shielding term is given by the expression $\sigma^P = -1/\Delta E\ (Q_p + Q_d)$ where ΔE is the average electronic excitation energy and Q_p and Q_d depend on the size of and electron imbalance in the valence p and d orbitals [5]. Tin chemical shifts are usually interpreted with ΔE being a

---

*It is to be noted that [(η^5-C_5H_4Me)Fe$(CO)_2SnMe_3$] has been previously reported but no details of the synthesis or spectroscopic properties of the complex were given [3].

0020-1693/89/$3.50

TABLE 1. IR and NMR data for [(η^5-C_5H_4Me)Fe(CO)(L)$SnMe_3$] complexes[a]

L	δ(CO) (cm^{-1})^b	$\delta(^1H)$ (ppm)^{c,d}		$\delta(^{119}Sn)$ (ppm)^e	$\delta(^{31}P)^f$	$^2J(^{119}Sn{-}H)$	$^2J(^{119}Sn{-}^{31}P)$	θ^g
		C_5H_4*Me*	Sn*Me*$_3$					
CO	1985, 1940	1.46	0.47	141.7		47.0		90
P(OMe)$_3$	1915	1.69	0.55	119.5		42.0	479.2	107
PMePh$_2$	1905	1.64	0.17	100.6	60.5	38.9	376.0	136
PPh$_3$	1895^h	1.81	0.33	88.9	81.1	39.6	357.3	145
P(CH$_2$Ph)$_3$	1910	1.61	0.68	80.5	63.5	37.5	363.8	165

[a]NMR data recorded on a Bruker AC 200 spectrometer. [b]Recorded in hexane. [c]Recorded in C_6D_6 relative to TMS. [d]Cyclopentadienyl proton resonances were recorded between 4.5 and 3.5 ppm. [e]Recorded in C_6D_6 relative to $SnMe_4$ (ext). [f]Recorded in C_6D_6 relative to H_3PO_4 (ext). [g]Tolman cone angle, ref. 4. [h]Recorded in benzene.

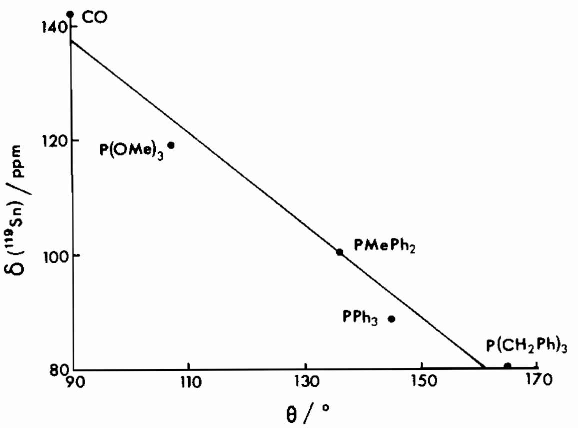

Fig. 3. Plot of Tolman cone angle θ against $\delta(^{119}Sn)$ for the [(η^5-C_5H_4Me)Fe(CO)(L)$SnMe_3$] complexes.

constant and variations in $\delta(^{119}Sn)$ being associated with changes in Q_p and Q_d. However Harris *et al.* [6] have proposed that ΔE may not be constant when Sn is bonded to a transition metal due to the presence of (d–d)π bonding. It is thus proposed that as the cone angle of L is increased in [(η^5-C_5H_4Me)Fe(CO)(L)($SnMe_3$)] the distortion of the ligands from the axis of a regular octahedron becomes larger resulting in reduced (d–d)π bonding between Fe and Sn. This would increase ΔE, reduce σ^p and cause $\delta(^{119}Sn)$ to move upfield as the size of L increases. Further experiments to verify this proposal are presently underway.

Acknowledgements

We wish to thank the University and the FRD for financial support.

References

1 J. du Toit, D. C. Levendis, J. C. A. Boeyens, M. S. Loonat, W. Pickl, L. Carlton and N. J. Coville, *J. Organomet. Chem.*, in press.
2 K. du Plooy, C. F. Marais, L. Carlton, R. Hunter, J. C. A. Boeyens and N. J. Coville, *Inorg. Chem.*, submitted for publication.
3 R. B. King, *Organometallics Syntheses*, Vol. 1, Academic Press, New York, 1965; D. Condon, M. E. Deane, F. J. Lalor, N. G. Connelly and A. C. Lewis, *J. Chem. Soc., Dalton Trans.*, (1977) 925.
4 C. A. Tolman, *Chem. Rev.*, *77* (1977) 313.
5 P. J. Smith and A. P. Tupianiskas, *Annu. Rev. NMR Spectrosc.*, *8* (1978) 292.
6 D. H. Harris, M. F. Lappert, J. S. Poland and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, (1975) 311.