Journal of Organometallic Chemistry, 303 (1986) 397–409
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

XVI *. STRUCTURE OF TRIORGANOSTANNYL DERIVATIVES OF DIMETHYLAMINOMETHYLFERROCENE AND *N*,*N*-DIMETHYLBENZYLAMINE

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(Received September 24th, 1985)

Summary

A series of new stannylated derivatives of dimethylaminomethylferrocene (DMAMF) and *N*,*N*-dimethylbenzylamine have been synthesised and their structures investigated by ^{1}H, ^{13}C and ^{119}Sn NMR together with ^{57}Fe and ^{119}Sn Mössbauer spectroscopy. Polystannylated derivatives were synthesised from DMAMF and BuLi in the presence of TMED. The methylene protons of the CH_2NMe_2 group were diastereotopic for all the DMAMF derivatives synthesised. The chemical shift differences of these protons is discussed in terms of conformational changes. ^{13}C and ^{119}Sn shifts were used to establish the substitution patterns in the polystannylated derivatives. ^{13}C shifts for the 2-substituted derivatives of both DMBA and DMAMF were reasonably additive, for both the free amines and the quaternary ammonium salts. The Mössbauer data show no evidence of pentacoordination in any of the derivatives.

Introduction

The use of the dimethylaminomethyl group to stabilise organometallic systems has been known for some time. Thus *N*,*N*-dimethylbenzylamine (DMBA) is lithiated selectively in the 2-position [2] owing to coordination by the NMe_2 group. This

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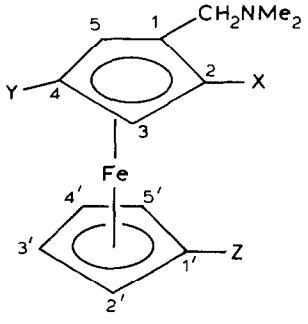
0022-328X/86/$03.50

finding was extended to dimethylaminomethylferrocene [3] (DMAMF) and led to the synthesis of a number of new 2-substituted ferrocenes [4]; these now include mercury [5,6], manganese [7], platinum [8,9] and palladium [9] derivatives. In addition new chiral triorganotin halides have been prepared from 2-lithio *N,N*-dimethylbenzylamine [10]. These have distorted trigonal-bipyramidal geometries [11] as a result of intramolecular coordination by the NMe_2 group.

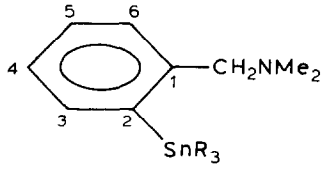
We have very recently studied the structures and reactivities of some stannylated ferrocenes using both ^{57}Fe and ^{119}Sn Mössbauer spectroscopy in conjunction with ^{119}Sn NMR. We present here an extension of this work to both DMAMF and DMBA systems to provide information about the effect of the internal ligand CH_2NMe_2 on the structure.

Results and discussion

We have synthesised a number of new derivatives of DMAMF and DMBA with the following substitution patterns.



DMAMF



DMBA

(X = R_3Sn, Y = Z = H;
X = Y = R_3Sn, Z = H;
X = Z = R_3Sn, Y = H;
X = Y = Z = R_3Sn;
R = Me, Bu, Ph)

The polysubstituted DMAMF derivatives were prepared by lithiating the parent compound in the presence of excess TMED followed by addition of excess R_3SnCl, and were separated by repeated column chromatography on alumina. The monosubstituted compounds were prepared by a similar method but omitting the TMED. The DMBA series was obtained by treating the monolithiated parent with an excess of R_3SnCl. The use of TMED as a promoter of lithiation of aromatics is well established [12].

^1H NMR spectra

The ^1H NMR data for the dimethylaminomethyl group for both series of compounds are listed in Table 1. Of particular interest are the methylene resonances.

TABLE 1

H NMR DATA FOR METHYLENE AND METHYL PROTONS OF STANNYLATED DIMETHYLAMINOMETHYLFERROCENES AND *N,N*-DIMETHYLBENZYLAMINE (δ ($CDCl_3$) ppm from external TMS) AND RELATED DERIVATIVES

Substituents			CH_2	J (Hz)	$\Delta\delta$ [a]	CH_3
2	4	1′				
Dimethylaminomethylferrocenes						
–	–	–	3.15	0.0	0.0	2.03
– [b,c]	–	–	4.45	0.0	0.0	2.70
Me_3Sn	–	–	2.67, 3.60	13	0.93	2.03
Me_3Sn	–	Me_3Sn	2.80, 3.62	13	0.82	2.07
n-Bu_3Sn	–	–	2.97, 3.40	12	0.43	2.10
n-Bu_3Sn [b]	–	–	3.90, 5.58	13	1.68	3.42
n-Bu_3Sn	n-Bu_3Sn	–	2.95, 3.28	12.5	0.33	2.01
n-Bu_3Sn	n-Bu_3Sn	n-Bu_3Sn	2.81, 3.20	12.4	0.39	2.05
Ph_3Sn [d]	–	–	2.68, 3.40	12.5	0.72	1.73
Ph_3Sn [b]	–	–	3.62, 5.08	12	1.46	2.80
Ph_3Sn	–	Ph_3Sn	2.70, 3.27	13	0.57	1.72
Ph_3Sn [b]	–	Ph_3Sn	3.65, – [e]	13	–	2.82
HgCl	–	HgCl	3.23, 3.83	14	0.60	2.40
N,N-dimethylbenzylamines						
H			3.33	0	0	2.15
H [b]			5.00	0	0	3.25
n-Bu_3Sn			3.18	0	0	1.97
n-Bu_3Sn [b]			4.68	0	0	3.38
Ph_3Sn			3.20	0	0	1.42
Ph_3Sn [b]			4.60	0	0	2.97

[a] $\Delta\delta$ = difference in chemical shift between the diastereotopic methylene protons. [b] Methiodide derivative. [c] In acetone-d_6. [d] Internal TMS. [e] Masked by Cp resonances.

In the DMBA series both CH_2 protons are magnetically equivalent, implying free rotation about the C(1)–CH_2 bond. In the parent unsubstituted molecule, as expected, quaternisation causes a downfield shift of 1.67 ppm, which is larger than the shift for the ferrocene series (1.30 ppm).

Because of the above free rotation, each methylene proton in the 2-substituted derivatives experiences a time-averaged effect of both the neighbouring substituent and H(6). n-Bu_3Sn and Ph_3Sn produce almost identical upfield shifts (Δ) of about 0.15 ppm. The value of Δ increases to 0.3–0.4 ppm on quaternisation. Since the geometry at C(1) in both the ferrocene and benzylamine systems is very similar, the above shifts are useful in identifying the CH_2 protons in the former series. The magnetic non-equivalence of these protons has been well documented [13], it is due to the inherent asymmetry of 1,2(X,Y) disubstituted, ferrocenes, and is not dependent on restricted rotation. Thus the CH_2 groups appears as two doublets (AB) with a coupling constant of 10–14 Hz for a wide range of substituents. The difference in chemical shift between H_A and H_B (δ_{AB}) will depend largely on two factors, the anisotropy of the group X, and the conformational equilibria shown in (Fig. 1). Whitesides and Roberts [14] have discussed this problem in detail, taking chiral ethers as an example of the effect of molecular asymmetry. They concluded that the phenomenon is best explained in terms of preferred conformers.

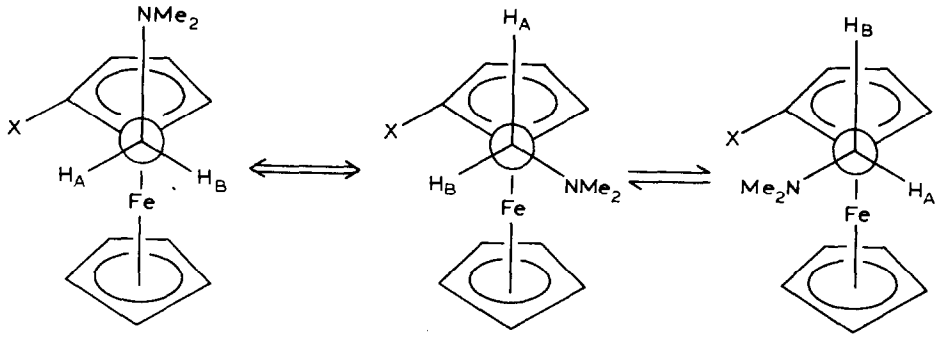


Fig. 1. Conformational equilibria for 2-X DMAMF derivatives.

It is of interest in this context, that 2-methyl and 2-ethyl DMAMF show values of δ_{AB} of 0.09 and 0.19 ppm, respectively [15], whereas 2-hydroxy DMAMF has δ_{AB} of 0.62 ppm [16]. In the former cases restricted rotation about C(1)–CH_2 is unlikely, and since the OH group is less bulky than either of the alkyl groups the large δ_{AB} values must be due either to the magnetic anisotropy of the lone pairs on oxygen or the presence of hydrogen-bonded structures of the type shown in Fig. 2.

The former is less likely in view of the insensitivity of such shifts to changes in solvent acidity [14]. The consequences of such a structure would be to place one of the CH_2 protons H_B in a deshielded space, whereas the other (H_A) remains shielded by the anisotropy of the ferrocene group [17,18]. Another way of producing such rigid conformations is to increase the bulk of the 2-substituent. In 2-triorganotin DMAMF series, molecular models indicate severe restriction to rotation about the C(1)–CH_2 bond owing to interactions with the lower Cp ring. A reasonably stable conformation may be envisaged as in Fig. 3 (conformation **a**).

The shielding effect of a neighbouring R_3Sn has already been noted, and probably results from the anisotropy of the Sn–C bonds which should be more polarisable than C–C bonds. H_A in conformation (**a**) is about 2.9 Å from the centre of the nearest Sn–Me bonds. The shielding of the *axial* protons in cyclohexane is about 0.9 ppm, and the distance between the centre of the C(2)–C(3) bond responsible for this effect and the proton is about 2.5 Å. The angle subtended at this hydrogen by the C–C bond is 65°, which is almost identical with that for the

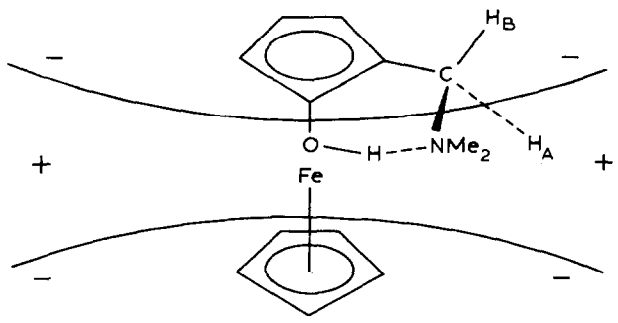


Fig. 2. Anisotropic shielding (+) and deshielding (−) in DMAMF derivatives.

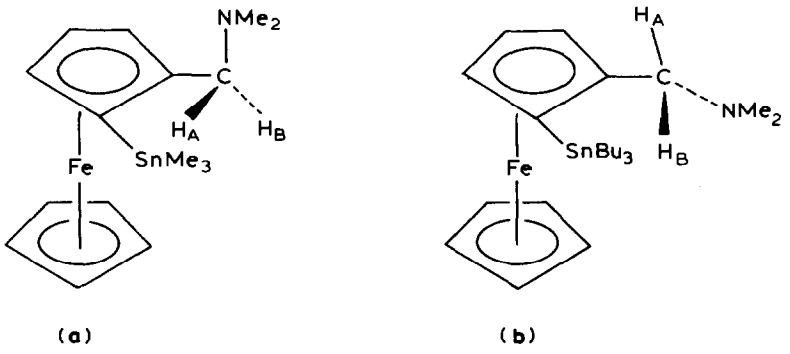


Fig. 3.

$Sn-CH_3/H_A$ case as measured from models. For bulkier groups on tin, conformation (**a**) becomes more crowded. The steric compression can be alleviated by rotation to conformer (**b**). Here the H_A originally shielded by Me_3Sn has moved into a deshielding zone resulting from the ferrocene anisotropy, and differences between H_A and H_B are therefore smaller. This is evident in Table 1, particularly for the n-Bu_3Sn derivatives. The quaternised derivatives show even greater separation of H_A and H_B, presumably due to further conformational changes enforced by the bulkier N^+Me_3 group. However, in all cases the methyl protons remained magnetically equivalent.

^{13}C NMR

The ^{13}C data and assignments for the DMBA series are listed in Table 2. Assignments are based on additivity factors obtained from Ref. 19. Surprisingly, no additivity factors are available for the very common n-Bu_3Sn substituent. It is likely however that the parameters will be very similar to those for Me_3Sn, whose values were therefore used in the correlations. The agreement between experimental and calculated values is good except for C(2) for the 2-Ph_3Sn DMBA and its methiodide. This is probably due to changes in the anisotropy of the neighbouring phenyl groups

(Continued on p. 404)

TABLE 2

ADDITIVITY OF ^{13}C CHEMICAL SHIFTS (δ (ppm)) FOR *N,N*-DIMETHYLBENZYLAMINES (obsd. (calcd.))

2-substituent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other resonances
n-Bu_3Sn	145.8	142.3	137.1	126.3	128.1	128.9	CH_2, 66.7; NCH_3; 45.3
	(147.0)	(142.7)	(135.7)	(126.8)	(128.0)	(129.1)	Bu, 10.4, 13.6, 27.5, 29.2
n-Bu_3Sn [a]	137.9	147.4	137.9	129.7	128.8	133.6	CH_2, 72.1; NCH_3, 52.7
	(136.3)	(147.1)	(137.3)	(131.1)	(129.6)	(133.5)	Bu, 11.6, 13.2, 26.9, 28.6
Ph_3Sn	146.2	146.2	137.6	127.0	128.9	129.4	CH_2, 65.3; NCH_3, 44.9
	(148.4)	(149.1)	(137.1)	(127.7)	(128.5)	(130.0)	Ph_3Sn, 128.1, 136.8, 142.0
Ph_3Sn [a]	137.6	143.5	139.5	134.8	130.6	134.8	CH_2, 70.4; NCH_3, 52.3
	(137.7)	(153.5)	(138.7)	(132.0)	(130.1)	(134.4)	Ph_3Sn, 129.3, 129.9, 136.8, 137.1

[a] Methiodide.

TABLE 3.

ADDITIVITY OF ^{13}C SHIFTS FOR DIMETHYLAMINOMETHYLFERROCENE DERIVATIVES (obsd. (calcd.)) (δ in ppm from TMS)

Substituents	C(1)	C(2)	C(3)	C(4)	C(5)	Cp	CH_2	NCH_3	Others
H [a]	83.9	70.0	67.8	67.8	70.0	68.6	58.3	44.8	–
H [a,b]	77.9	72.4	70.6	70.6	72.4	69.6	67.3	52.8	–
2-$SnMe_3$	90.3	70.9	74.1	69.7	72.0	68.3	59.9	44.6	Me_3Sn −8.27
	(90.2)	(70.8)	(74.3)	(70.6)	(72.6)				
2,-1-($SnMe_3$)	90.5	71.1	72.3	68.8	75.3	–	60.3	44.9	Me_3Sn (C(2)) −8.61
	[68.6] [c]	[74.2] [c]	[72.3] [c]	[71.3] [c]	[73.7] [c]				Me_3Sn (C(1)) −11.7
2-$SnBu_3$	90.6	71.3	74.9	69.8	72.2	68.6	60.5	45.0	Bu 10.6, 13.7,
	(90.2)	(70.8)	(74.3)	(70.6)	(72.6)				27.5, 29.4

[a] Data from ref. 20. [b] Data for methiodide. [c] These values are assigned to the monosubstituted Cp ring.

TABLE 4

^{57}Fe AND ^{119}Sn MÖSSBAUER PARAMETERS (isomer shift (*IS*), quadrupole splitting (*QS*) and linewidths (LW) all in mm s^{-1}) AND ^{119}Sn NMR CHEMICAL SHIFTS ($\delta(^{119}Sn)$ [a] (ppm) from Me_4Sn) FOR STANNYLATED DIMETHYLAMINOMETHYLFERROCENES AND *N,N*-DIMETHYLBENZYLAMINES

Substituents			^{57}Fe			^{119}Sn			$\delta(^{119}Sn)$
2	4	1′	*IS*	*QS*	LW [b]	*IS*	*QS*	LW [b]	
Dimethylaminomethylferrocenes									
Me_3Sn	–	–	–	–	–	1.08(1)	0.00	0.92(6)	−15.0
n-Bu_3Sn	–	–	0.54(2)	2.36(3)	0.33(6)	1.15(1)	0.00	1.04(4)	−26.3
n-Bu_3Sn [c]	–	–	0.52(1)	2.34(1)	0.28(1)	1.19(1)	0.00	1.04(2)	−26.7
Me_3Sn	–	Me_3Sn	–	–	–	–	–	–	−6.6, −15.4
n-Bu_3Sn	n-Bu_3Sn	–	0.54(1)	2.33(1)	0.34(2)	1.18(1)	0.00	1.18(4)	−23.7
n-Bu_3Sn [c]	n-BuSn	–	0.52(1)	2.32(1)	0.26(1)	1.14(1)	0.00	1.49(7)	−26.7
Ph_3Sn	–	Ph_3Sn	0.52(1)	2.32(1)	0.35(1)	1.10(1)	0.00	1.08(2)	−107.9, −116.1
Ph_3Sn [c]	–	Ph_3Sn	–	–	–	1.16(1)	0.00	0.96(2)	−73.9, −114.0
n-Bu_3Sn	n-Bu_3Sn	n-Bu_3Sn	0.54(1)	2.33(1)	0.32(2)	1.22(1)	0.00	1.26(4)	−11.4, −18.7, −23.8
n-Bu_3Sn [c]	n-Bu_3Sn	n-Bu_3Sn	0.53(1)	2.28(1)	0.26(1)	1.07(1)	0.00	1.01(5)	
N,N-dimethylbenzylamines									
n-Bu_3Sn	–	–	–	–	–	1.19(1)	0.00	1.44(4)	−49.5
n-Bu_3Sn [c]	–	–	–	–	–	1.21(1)	0.61(1)	0.89(2)	−41.2
Ph_3Sn	–	–	–	–	–	1.11(1)	0.00	1.40(4)	−164.4
Ph_3Sn [c]	–	–	–	–	–	1.16(1)	0.00	1.12(4)	−134.9

[a] Positive value downfield from Me_4Sn. [b] Full width at half height. [c] Values for the corresponding methiodide.

as a result of enforced conformational changes of the two bulky 1,2-substituents. The corresponding data for the DMAMF series appear in Table 3. One of the problems in ^{13}C NMR of substituted ferrocenes is the unambiguous identification of the C(2, 5) and C(3, 4) resonances, but this has now been achieved by the use of specific deuterium-labelled (H(2), H(5)) derivatives [20]. This has enabled correlations be made which show that substituent effects at the 3,4-position in ferrocenes are qualitatively similar to those at the *para*-position in benzene. Similar correlations between the 2,5-position in ferrocenes and the *ortho*-position in benzene (bz) are also found. These can be summarised as follows, using ferrocene and benzene as references for each system.

$$\Delta Fc(3, 4) = 0.775\,\Delta bz\,(\textit{para}) + 0.69 \quad (1)$$
(number of points $N = 8$, $r = 0.985$)

$$\Delta Fc(2, 5) = 0.888\,\Delta bz\,(\textit{ortho}) + 0.07 \quad (2)$$
($N = 8$, $r = 0.989$)

Values of Δbz for the Me_3Sn substituent have been obtained by Adcock et al. [21] which has enabled $\Delta Fc(3, 4)$ and $\Delta Fc(2, 5)$ to be evaluated (0.5 and +6.6 ppm respectively), i.e. The C(2), C(5) are less shielded than C(3), C(4) which is also true for the Me_3Si substituent [22].

Using the above additivity factors the spectra of the mono-stannylated DMAMF derivatives can be readily assigned (Table 3). For the di- and tri-stannylated compounds, unambiguous assignments were not possible owing to the narrow range of most of the Cp shifts. The C(1) quaternary carbons, however, can be readily identified from their intensities, and appear at 90.5 and 90.2 ppm, respectively.

It is noteworthy that where the second Cp ring is also substituted the C(3) and C(4) and the C(2) and C(5) resonances are not identical (see ^{119}Sn NMR). In the case of the bis-Bu_3Sn compound, the appearance of an intense signal at 68.5 ppm indicated a free Cp ring.

The calculated values of C(1) shifts for the [1,2,5]-, [1,2,4]- and [1,2,3]-substituted derivatives are 96.3, 92.6 and 92.6 ppm, respectively, which again seems to rule out the symmetrical species. (The [1,2,3] compound is also unlikely for steric reasons.) There is also a multiplicity in the Bu resonances which would not be observed for a symmetrical species.

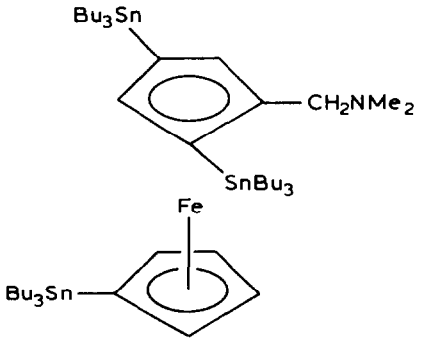
The above was confirmed by the appearance of highly characteristic IR bands at 820, 1000 and 1100 cm^{-1} for unsubstituted Cp rings and also a sharp resonance at 4.00 ppm in the ^1H NMR spectrum. In addition the CH_2 protons are still magnetically non-equivalent, which would not be the case for the symmetrical 2,5-$(Bu_3Sn)_2$DMAMF. It is thus likely that the tris(Bu_3Sn) derivative is, in fact, 2,4,1′-$(Bu_3Sn)_3$DMAMF. In contrast the bis(Ph_3Sn) derivative is 2,1-$(Ph_3Sn)_2$DMAMF, since both ^1H NMR and ^{13}C NMR spectra show no free Cp ring resonances. This compound can be very readily mercurated with $HgCl_2$ to give 2,1′ bis chloromercuri-DMAMF, redolent of the reaction with bis(Ph_3Sn)-ferrocene [1].

One further point of interest is the rate of quaternisation of the NMe_2 group. For 2-stannylated DMAMF derivatives, reaction with MeI occurred fairly readily although noticably slower than for DMAMF. Distannylated DMAMF reacted even

more slowly, and 2,4,1′-tris Bu_3Sn DMAMF only with difficulty. These results are readily understandable in terms of increasing steric hindrance to approach to the NMe_2 group.

^{119}Sn NMR

Values of ^{119}Sn shifts ($\delta(^{119}Sn)$) are listed in Table 4. There are significant differences between the signals from the tin substituents on the two Cp rings. Thus for the Me_3Sn substituents the mono-derivative shows a resonance at −15.0 ppm while the bis derivative shows two signals at −15.4 and −6.6 ppm. The latter is thus assigned to the lower monosubstituted ring. This difference in $\delta(^{119}Sn)$ has proved useful in assigning the resonances of the other bis and tris derivatives. For 2,1′-bis-triphenylstannyl DMAMF, the two observed resonances differ by 8.2 ppm, a value almost identical with that of the bis-Me_3Sn compound. The low field signal (−107.9) is therefore assigned again to the lower ring. This is supported by the $\delta(^{119}Sn)$ of bis-triphenylstannylferrocene of −105.2 ppm [1]. 2,4-bis-Bu_3Sn DMAMF shows only one signal (although the signal is rather broad), whereas 2,4,1′-tris-Bu_3Sn DMAMF displays three peaks of equal area. It is probable that there is restriction of Cp ring rotation, and that the molecule exists in a fixed conformation.



The signal at −23.8 ppm is quite close to that for 2-Bu_3Sn DMAMF (−26.3) and may be assigned as such. Since 1,1′-bis-tributylstannylferrocene absorbs at 0.0 ppm [1], it is likely that the downfield signal is due to the 1-Bu_3Sn substituent. This leaves the tin resonance of the 4-substituent at −18.7 ppm.

Quaternisation has little effect on the value of $\delta(^{119}Sn)$ for the Bu_3Sn derivatives of both the DMAMF and the DMBA systems, but marked changes occur when Ph_3Sn substituents are present. A downfield shift of almost 30 ppm occurs on quaternising 2-Ph_3Sn DMBA, and there is an even greater downfield shift (42 ppm) for the DMAMF analogue. (This deshielding is probably due to a thorough space interaction of the positive charge. CH_2NMe_2 substituents themselves cause variable upfield shifts. For the Bu_3Sn series, this shift is about 26 ppm in the ferrocenes and about 5 ppm for the benzylamines. For the Ph_3Sn series the reverse is true, upfield shifts for the ferrocenes (~ 10 ppm) being smaller than those for the benzylamines (~ 25 ppm).

^{57}Fe, ^{119}Sn Mössbauer spectra

The data are listed in Table 4. In the ^{57}Fe Mössbauer spectra there are no significant variation in the isomer shift (*IS*). Quaternisation had no measurable

effect on quadrupole splittings (*QS*) except for the tristannylated derivative, for which there is a significantly smaller *QS*. However *QS* values for the stannylated ferrocenes were all below that of ferrocene itself, indicating electron-withdrawal by the organotin moiety. Such a reduction is the result of electron-withdrawal via ligand based orbitals (e_1) on the ferrocene, and is well documented [24].

With the exception of those for 2-Bu_3Sn DMBA the ^{119}Sn spectra show zero *QS* values, and indicating no pentacoordination involving the NMe_2 group. The linewidths for the three singlet spectra are all broad. The detected *QS* for the quaternised Bu_3DMBA is thus likely to have its origin in steric effects, since only tetraorganotin derivatives containing bulky substituents or substituents having differing group electronegativities have hitherto shown measurable quadrupole splittings, (see Ref. 25 for a discussion of steric effects on linewidth tetraorganotins).

Through-bond inductive effects would be small since the effect would have to be transmitted through four bonds. It is possible that the positive charge on the nitrogen is affecting the electric field gradient at the tin. However, this charge is at least 5 Å from the tin atom, and is therefore unlikely to have a significant effect. In addition the parent derivative also has a broad signal.

The isomer shifts for the triphenyltin derivatives are less than those for Ph_4Sn. The disubstituted phenyl ring does not appear to donate as much electron density to the tin atom as the other phenyl groups. The low *IS* values in conjunction with the observed broad lines support a steric origin of the phenomenon. It is appropriate to recall that the $\delta(^{119}Sn)$ from NMR spectra for the Ph_3Sn DMBA species show marked upfield shifts which are probably related to these steric compressions.

The above effects are also apparent for the tributylstannyl derivatives (c.f. *IS* for Bu_4Sn 1.35 mm s^{-1}, ref. 26).

For the DMAMF series, the ^{119}Sn *IS* values for all the non-quaternised derivatives are all smaller than the corresponding symmetrical tetraorganotin compounds, R_4Sn, indicating that the ferrocenyl substituent is a poorer electron donor than the corresponding substituents in R_4Sn. *IS* values increase with the number of R_3Sn substituents (1.15, 1.18 and 1.22 mm s^{-1} for mono, bis and tris-tributylstannyl DMAMF derivatives respectively). Such a trend is due to increased S electron density at the tin sites as a result of electron-withdrawal from the Cp rings by the R_3Sn substituents (c.f. the reduced *QS* values in the ^{57}Fe Mössbauer spectra).

Experimental

Synthesis of monostannylated derivatives

The DMAMF and DMBA compounds were prepared by first lithiating DMAMF or DMBA with n-BuLi in dry hexane, then adding R_3SnCl. A typical procedure is described below.

Preparation of 2-tributylstannyldimethylaminomethylferrocene

Dimethylaminomethylferrocene (DMAMF) (12.2 g, 0.05 mol) in dry ether (50 ml) was treated with n-BuLi (80 ml, 1.5 *M* in hexane, 0.125 mol) under N_2. The mixture was stirred for 1 h then refluxed for 15 min to complete the lithiation. Bu_3SnCl (38.4 g, 32 ml, 0.118 mol) in dry ether (50 ml) was added dropwise. After the addition, the mixture was allowed to stand 24 h then decomposed with water. The organic layer was separated and washed with saturated KF solution to remove any unreacted Bu_3SnCl. The organic phase was dried and evaporated to give an oil which was

chromatographed on neutral alumina, eluting first with petroleum ether (40–60°C) then with CH_2Cl_2/EtOAc (10/1). The main orange-brown fraction was collected and evaporated to give 8 g (30%) 2-Bu_3Sn DMAMF as a brown oil.

Analysis: Found: C, 57.1; H, 8.3; N, 2.6. $C_{25}H_{43}FeNSn$ calcd.: C, 56.4; H, 8.1; N, 2.6%. ^1H NMR ($CDCl_3$) 0.5–2.3 m (27H), 2.13 s (6H), 3.2 q (2H), 4.05 s (6H), 4.28 ppm tr. (2H).

2-Bu_3Sn DMAMF (0.6 g, 1.1 mmol) was dissolved in dry benzene (5 ml) and MeI (2 ml) added. The mixture was left at room temperature for 2 h. The golden plate like crystals of the methiodide were filtered off and dried. Yield 0.6 g (79%). M.p. 185°C (dec.).

Analysis: Found: C, 46.1; H, 7.0; N, 2.0. $C_{26}H_{46}FeINSn$ calcd.: C, 46.3; H, 6.9; N, 2.1%. ^1H NMR ($CDCl_3$) 0.5–2.0 m (27H), 3.42 s (9H), 3.92 d (1H), 4.20 tr (1H), 4.30 s (5H), 4.70 tr (1H), 5.05 br.s (1H), 5.58 d (1H).

The following derivatives were prepared in the same way: 2-Ph_3Sn DMAMF (17%) oil. Analysis: Found: C, 62.5; H, 5.1; N, 2.2. $C_{31}H_{31}FeNSn$ calcd.: C, 62.9; H, 5.3; N, 2.4%. ^1H NMR ($CDCl_3$ int. TMS) 1.77 s (6H), 3.1 q (2H), 4.05 s (5H), 4.1–4.35 m, (3H), 7.1–7.9 m (15H). The methiodide was prepared as above.

Preparation of 2,1′-bistriphenylstannyldimethylaminoethylferrocene

n-BuLi (80 ml, 1.5 in hexane, 0.125 mol) was treated with TMED (14.5 g, 18.8 ml, 0.125 mol). A solution of DMAMF (12.2 g, 0.05 ml) in dry hexane (50 ml) was added dropwise and the mixture stirred at room temperature for 1 h. Ph_3SnCl was added portionwise as a solid over a period of 15 min. After stirring for 10 h at room temperature the solution was deep red. Water (5 ml) was added and the whole filtered to give an orange solution. This was evaporated and chromatographed on neutral alumina eluting with CH_2Cl_2/EtOAc (10/1) to give 33 g (70%) of an orange solid, m.p. 125°C.

Analysis: Found: C, 62.1; H, 4.8; N, 1.1. $C_{49}H_{45}FeNSn_2$ calcd.: C, 62.5; H, 4.8; N, 1.5%. ^1H NMR ($CDCl_3$) 1.73 s (6H), 3.0 q (2H), 4.0–4.4 m (7H), 7.2–7.8 m (30H). The product was converted to the methiodide in 65% yield.

Also prepared by the same method: 2,1′-$(Me_3Sn)_2$DMAMF (20%). Analysis: Found: C, 40.7; H, 6.1; N, 2.5. $C_{19}H_{33}FeNSn_2$ calcd.: C, 40.1; H, 5.8; N, 2.5%. ^1H NMR ($CDCl_3$) 0.28 s (9H), 0.32 (9H), 2.07 (6H), 3.2 q (2H), 3.8–4.3 m (8H).

In addition, a small quantity of 2-Me_3Sn DMAMF (< 5%) was isolated from later fractions in the chromatographic separation. This was characterised by its ^1H NMR spectrum.

^1H NMR ($CDCl_3$) 0.25 s (9H), 2.03 s (6H), 3.15 q (2H), 3.97 s (6H), 4.2 brs (3H).

2,4,1′-$(Bu_3Sn)_3$ DMAMF (9%). This was obtained by rechromatography of the main fraction from the first column treatment. The compound was isolated as a brown oil from the first band eluting with petroleum ether.

Analysis: Found: C, 52.3; H, 9.3; N, 1.2. $C_{49}H_{95}NFeSn_3$ calcd.: C, 53.0; H, 8.6; N, 1.3%. ^1H NMR ($CDCl_3$) 0.2–2.3 m (81H), 2.05 s (6H), 3.15 q (2H), 3.7–4.3 m (6H).

The other major band from the rechromatography was the fifth in sequence of elution, and from this was isolated 2,4-$(Bu_3Sn)_2$ DMAMF in 5% yield as a brown oil.

Analysis: Found: C, 53.5; H, 8.5; N, 1.3. $C_{37}H_{69}NFeSn_2$ calcd.: C, 54.1; H, 8.5; N, 1.7%. ^1H NMR ($CDCl_3$) 0.6–2.4 m (54H), 2.01 s (6H), 3.2 q (2H), 4.0 s (5H), 3.8–4.3 m (2H).

Both products were converted to the methiodides as above but required several days and yields were low.

Reaction of 2,1'-$(Ph_3Sn)_2$DMAMF (I) with $HgCl_2$

0.5 g I (0.5 mmol) in acetone (5 ml) was treated dropwise with $HgCl_2$ (0.14 g, 0.5 mmol) in acetone (2 ml). An immediate yellow precipitate occurred. This was filtered off to give 0.25 g (69%) 2,1-$(HgCl)_2$DMAMF.

Analysis: Found: C, 20.7; H, 2.3; N, 1.9. $C_{13}H_{15}Cl_2FeHg_2N$ calcd.: C, 19.1; H, 2.2; N, 2.0%.

Preparation of stannylated N,N-dimethylbenzylamines

The general preparative method for these derivatives is given. 2-Lithio-*N*,*N*-dimethylbenzylamine was prepared from DMBA (13.6 g, 15 ml, 0.1 mol) and n-BuLi (65 ml, 1.5 *M* in hexane 0.1 mol) using the method of Hauser et al. [2]. R_3SnCl (0.1 mol) in Et_2O (50 ml) was added and the whole left for 2 h. The mixture was quenched with KF (aq) to remove any unreacted R_3SnCl. After conventional work-up the compounds were isolated in excellent yields. (2-Bu_3Sn DMBA (75%) colourless oil, 2-Ph_3SnDMBA (85%) white solid m.p. 75°C). ^{1}H NMR data are listed in Table 1.

Analysis of 2-Ph_3SnDMBA: Found: C, 66.7; H, 6.0; N, 2.5. $C_{27}H_{27}NSn$ calcd.: C, 67.0; H, 5.6; N, 2.9%.

Quaternisation of 2-Bu_3SnDMBA (II)

II (5 g, 11.8 mmol) was dissolved in AR benzene (20 ml) and MeI (5 ml) added. The solution became turbid almost immediately. After standing overnight the solvent was removed and the resultant oil triturated with hexane at 0°C to give a white solid (5 g, 75%), m.p. 91°C. The solid was very soluble in $CHCl_3$ and benzene.

Analysis: Found: C, 46.6; H, 7.6; N, 2.4. $C_{22}H_{42}INSn$ calcd.: C, 46.7; H, 7.5; N, 2.5%.

Adopting a similar method 2-Ph_3SnDMBA was quaternised in 70% yield and obtained as white plates, m.p. 199°C.

Analysis: Found: C, 53.8; H, 4.9; N, 2.0. $C_{28}H_{30}INSn$ calcd.: C, 53.7; H, 4.8; N, 2.2%.

Spectroscopic instrumentation

^{1}H NMR spectra were recorded with a Varian EM 360 instrument housed in a constant temperture room. ^{13}C and ^{119}Sn were recorded with a Bruker WP80 FT spectrometer.

Mössbauer data were obtained as described previously [24].

Acknowledgements

One of the authors (J.A.) wishes to thank the University of Shahid Chamran for financial support during this work. The authors are indebted to Joanne Warmsley for running the ^{13}C and ^{119}Sn NMR spectra and to Mr. Chris Frampton for running and fitting the Mössbauer spectra.

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