

Synthesis and multinuclear NMR data of the ferrocenes (Me₃Ecp)₂Fe (E = C, Si, Ge, Sn, Pb)

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Abstract

The substituted cyclopentadienyl anions Me₃Ecp[−] with E = C, Si, Ge, Sn, Pb have been prepared from either the mono- or disubstituted cyclopentadienes, including the hitherto unknown (Me₃Pb)₂C₅H₄. Representative examples have been characterized by ¹³C NMR spectroscopy. Treatment with iron(II) chloride yielded the ferrocenes (Me₃Ecp)₂Fe, which have been investigated by ¹H, ¹³C, ²⁹Si, ¹¹⁹Sn, and ²⁰⁷Pb NMR spectroscopy. ¹³C–¹³C coupling and selective proton decoupling were used for the assignment of the ¹³C and ¹H signals. The shifts δ(¹³C) reflect the electron-releasing or -withdrawing power of the substituents Me₃E, but the isotope shifts ¹Δ¹³C(*i*)(¹³C(*j*)) do not show a similar trend. There is evidence that δ(¹¹⁹Sn) and δ(²⁰⁷Pb) are influenced by the coordination. The analysis of the coupling constants reveals that ¹J(¹³C(1)–¹³C(2/5)) varies with the electronegativity of E. Because of the small range (4.5–5.0 Hz) of ¹J(⁵⁷Fe–¹³C) the effect of E is apparent only when E = C is replaced by E = Si. As for the coupling between E and ¹³C or ¹H, the square root of the reduced coupling constant *K* is related linearly to the atomic number of E; exceptions are ¹K(²⁰⁷Pb–¹³C).

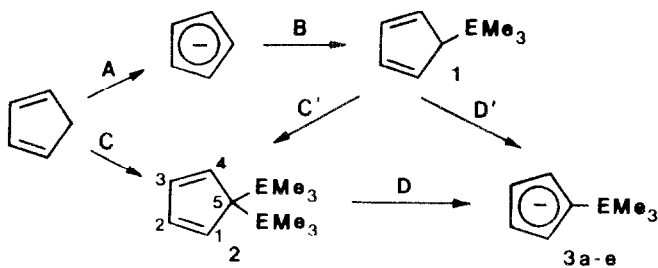
Following the discovery of many major differences in the behavior of cyclopentadienyl- and pentamethylcyclopentadienyl-metal compounds, increasing attention has been paid to the functionalization of Cp [1]. Obviously, there are two simple strategies: variation of the number or the type of a given substituent. The first has been restricted to methyl substituents; examples are the gradual change of the NMR and ESR parameters of ferrocenes and ferricenium ions [2] or the tuning of the spin state of manganocenes [3]. Ferrocene has a rich “aromatic” chemistry and many substituents have been introduced, but systematic variation of the central atom of the substituent over a whole group of the periodic table seems not to have been achieved up to now. We have now prepared ferrocenes bearing the substituents

Me_3E ($\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$). They fill in the gaps in several series of molecules, that have been designed to illuminate the various effects of Me_3E groups by different techniques; e.g. the study of $\text{Me}_3\text{EC}_6\text{H}_5$ by NMR [4], the study of the $\text{Me}_3\text{EC}_6\text{H}_5^-$ [5] and Me_3Ecp^- [6] by ESR, and the study of $(\text{Me}_3\text{Ecp})_2\text{M}$ by paramagnetic NMR [7]. Since we wished to establish a general route to Me_3E -substituted Cp derivatives that are dia- or paramagnetic and since it has been reported that Me_3Pbcp^- could not be made [6] some emphasis had to be placed on the synthesis. Our central concern is the NMR characterization of $(\text{Me}_3\text{Ecp})_2\text{Fe}$ including the isotope effect $^1\Delta^{13}\text{C}(^{13}\text{C})$ and the couplings $^1J(^{13}\text{C}-^{13}\text{C})$, $^2J(\text{E}-^{13}\text{C})$, and $^2J(\text{E}-^1\text{H})$. The data were also needed as a basis for interpreting the NMR signal shifts of the corresponding paramagnetic metallocenes [7].

Results and discussion

A. Synthesis

It has been shown previously that ferrocene may be substituted by Me_3Si and Me_3Sn using 1,1-dilithioferrocene as an intermediate [8,9]. This approach is not applicable to more labile Cp derivatives such as paramagnetic metallocenes [7], which decompose under the reaction conditions. A reliable and versatile synthesis is shown in Scheme 1. For $\text{E} = \text{C}, \text{Si}, \text{Ge}$ steps A, B, and D' lead to the substituted anions **3a–3c**. In step B the chlorides are sufficiently reactive [10] except for $\text{E} = \text{C}$, where the bromide may be necessary depending on the reaction conditions [11]. Owing to facile metal–metal exchange step D' is not applicable for $\text{E} = \text{Sn}$ or Pb . For the alternative route via **2** we have carried out a comparative study of steps C [12] and C': additional purification procedures in route A, B, C' reduce the yield by ca. 5% compared to that obtained through step C. A one-pot synthesis of **3** via C and D cannot be recommended because **2** is always accompanied by some **1**. Surprisingly, the hitherto unknown bis(trimethylplumbyl)cyclopentadiene, **2e**, can be obtained in 83% yield, whereas earlier synthetic approaches [6] failed. Since **2e** decomposes slowly we converted it immediately to the corresponding anion **3e** and the ferrocene **4e**. The intermediate compounds **2d**, **2e** and the anions **3a**, **3b**, **3d** have been characterized by ^{13}C NMR spectroscopy (see Experimental section). The synthesis of the ferrocenes **4a–4e** from **3a–3e** and iron(II) chloride is simple. It should be mentioned that following a literature procedure [13] we obtained $\text{FeCl}_2(\text{THF})_{1.45}$ instead of $\text{FeCl}_2(\text{THF})_2$; the composition of the first product is in



Scheme 1. $\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb} = \text{a}, \text{b}, \text{c}, \text{d}, \text{e}$. A: NaH/THF ; B: Me_3EX ; C = C': Et_2NEMe_3 ; D: $^n\text{BuLi}/\text{THF}$; D': KH/THF or $^n\text{BuLi}/\text{THF}$.

agreement with the $\text{Fe}_4\text{Cl}_8(\text{THF})_6$ [14] which has been structurally characterized. We have prepared the stannylated ferrocene **4d** also by the reaction of $\text{FeCl}_2(\text{THF})_{1.45}$ with **2d** in 36% yield.

B. NMR investigation

Assignment. Monosubstituted cyclopentadienyl ligands give NMR signals which can be readily assigned except for those from nuclei in positions 2/5 and 3/4. There are several ways in which this problem may be overcome [15]. The signal pattern for H(2/5) and H(3/4) should be different because ${}^3J(\text{}^1\text{H}-\text{}^1\text{H}) \approx 2{}^4J(\text{}^1\text{H}-\text{}^1\text{H})$ [15a]. This is not true for **4a–4e**, which show only pseudo-triplets even in the 270 MHz spectra. Whenever the substituent has protons next to the five-membered ring, C(2–5) can be assigned because ${}^3J(\text{C}(2/5)-\text{H}(\alpha))$ leads to a characteristic multiplet for C(2/5) [15b,c]. In the absence of H(α), for example in our case for **4a–4e**, second-order splitting of the ${}^{13}\text{C}$ NMR signals should lead to different pattern for C(2/5) and C(3/4) if ${}^2J(\text{}^{13}\text{C}-\text{}^1\text{H}) \neq {}^3J(\text{}^{13}\text{C}-\text{}^1\text{H})$ [15c]. In the present series these couplings must be similar for **4c** and **4e** because a doublet of quartets is observed at a spectrometer frequency of 50.31 MHz for both C(2/5) and C(3/4). More general methods for the signal assignment are specific deuteration [15d,e] and heteronuclear NOE difference spectroscopy [15f]. In this study we make use of the couplings ${}^1J(\text{}^{13}\text{C}-\text{}^{13}\text{C})$ [15g], which yield two pairs of satellites for C(2/5) and only one for C(3/4). A typical example including the satellites of ${}^{119}\text{Sn}$, ${}^{117}\text{Sn}$, and ${}^{115}\text{Sn}$ is shown for **4d** in Fig. 1. Selective proton decoupling of the ${}^{13}\text{C}$ NMR spectra confirmed the assignment of H(2–5). The NMR data are listed in Table 1.

Signal shifts. There is a considerable scatter of $\delta({}^{13}\text{C}(1))$ values in the series, and relative to the other ${}^{13}\text{C}$ NMR signals of the five-membered ring all possible positions are found: i.e. to high (**4a**, **4c**, **4e**) or to low (**4d**) frequency, or between $\delta({}^{13}\text{C}(2/5))$ and $\delta({}^{13}\text{C}(3/4))$ (**4b**). The scatter is actually a gross trend, which is also observed for $\delta({}^{13}\text{C}(\beta))$ and ${}^1J(\text{}^{13}\text{C}(1)-\text{}^{13}\text{C}(2/5))$ of **4a–4e**, for the paramagnetic signal shift of C(1) of the corresponding cobaltocenes [7] and for the hyperfine coupling to an imaginary proton H^* at C(1) of the corresponding cyclopentadienyl radicals [6]. This is illustrated in Fig. 2.

It is well known that all these data are influenced by the electron distribution in the molecule. In comparison with the unsubstituted Cp derivatives a redistribution

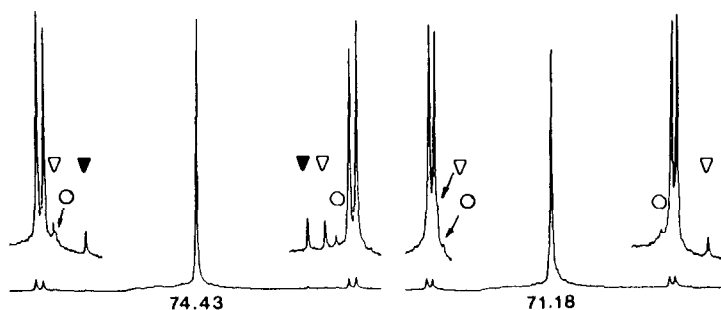


Fig. 1. Part of the 67.8 MHz ${}^{13}\text{C}$ NMR spectrum of **4d**, showing the signals from C(2/5) and C(3/4). Besides the satellites of ${}^{119/117}\text{Sn}$ those due to ${}^1J(\text{}^{115}\text{Sn}-\text{}^{13}\text{C})$ (O) ${}^1J(\text{}^{13}\text{C}(2/5)-\text{}^{13}\text{C}(3/4))$ (∇), and ${}^1J(\text{}^{13}\text{C}(1)-\text{}^{13}\text{C}(2/5))$ (\blacktriangledown) are visible.

Table 1

Multinuclear NMR shifts (ppm), coupling constants (Hz), reduced coupling constants (nm^{-3}), and one-bond ^{13}C isotope shifts for the ferrocenes $(\text{Me}_3\text{Ecp})_2\text{Fe}$

	E				
	^{13}C	^{29}Si	Ge	^{119}Sn	^{207}Pb
$\delta(^1\text{H}(2/5))$	4.04	4.13	4.10	4.07	4.11
$\delta(^1\text{H}(3/4))$	4.08	4.33	4.28	4.28	4.23
$\delta(^1\text{H}(\beta))$	1.25	0.29	0.40	0.29	0.94
$\delta(^{13}\text{C}(1))$	102.06	72.71	74.90	69.22	78.53
$\delta(^{13}\text{C}(2/5))$	65.71	73.27	72.60	74.43	75.17
$\delta(^{13}\text{C}(3/4))$	68.06	71.24	70.98	71.18	70.88
$\delta(^{13}\text{C}(\beta))$	31.96	0.16	-0.52	-8.56	-1.91
$\delta(\text{E})$	31.06	-3.96		-4.20	3.69
$\Delta\text{C}(1)(\text{C}(2/5))$ ^a	0.018	0.020	^c	0.020	0.019
$\Delta\text{C}(2/5)(\text{C}(1))$	0.013	0.015	^c	0.015	0.016
$\Delta\text{C}(2/5)(\text{C}(3/4))$	0.016	0.017	0.017	0.015	0.017
$\Delta\text{C}(3/4)(\text{C}(2/5))$	0.017	0.017	0.016	0.018	0.018
$^2J(\text{E}-^1\text{H}(2/5))$	^c	1.2		10.5	12.2
$^3J(\text{E}-^1\text{H}(3/4))$	^c	0.6		5.6	6.6
$^4J(\text{E}-^1\text{H}(\beta))$	^c	6.7		56.0	66.3
$^1J(^{13}\text{C}(2/5)-^1\text{H})$	171.5	173.8	173.8	174.1	174.8
$^1J(^{13}\text{C}(3/4)-^1\text{H})$	173.6	173.4	173.8	173.8	173.7
$^1J(^{13}\text{C}(1)-^{13}\text{C}(2/5))$	47.0	36.3	37.8	36.0	36.2
$^1J(^{13}\text{C}(2/5)-^{13}\text{C}(3/4))$	46.2	44.8	44.7	44.1	43.8
$^1J(\text{E}-^{13}\text{C}(\beta))$	35.5	52.6		357.8	286.2
$^1J(\text{E}-^{13}\text{C}(1))$	47.7	71.6		492.5	316.0
$^2J(\text{E}-^{13}\text{C}(2/5))$	^c	5.5		51.8	77.5
$^3J(\text{E}-^{13}\text{C}(3/4))$	^c	4.4		40.3	52.9
$^1J(^{57}\text{Fe}-^{13}\text{C}(1))$	5.0	4.5	^c	4.9	4.9
$^1J(^{57}\text{Fe}-^{13}\text{C}(2/5))$	4.7	4.8	4.7	4.7	4.8
$^1J(^{57}\text{Fe}-^{13}\text{C}(3/4))$	4.9	^d	4.6	4.6	4.7
$^2K(\text{E}-^1\text{H}(\beta))$		0.28		1.25	2.64
$^3K(\text{E}-^1\text{H}(2/5))$		0.05		0.23	0.49
$^4K(\text{E}-^1\text{H}(3/4))$		0.03		0.13	0.26
$^1K(\text{E}-^{13}\text{C}(\beta))$	4.68	8.77		31.79	45.31
$^1K(\text{E}-^{13}\text{C}(1))$	6.28	11.94		43.76	50.02
$^2K(\text{E}-^{13}\text{C}(2/5))$		0.92		4.60	12.27
$^3K(\text{E}-^{13}\text{C}(3/4))$		0.73		3.58	8.37

^a Short form for $^1\Delta^{13}\text{C}(1)(^{13}\text{C}(2/5))$ which is the one-bond isotope effect in ppm for ^{13}C isotopes in position 2 or 5 on $\delta(^{13}\text{C})$. Similar notations apply for other carbon atoms. ^b Other one-bond isotope shifts: $\Delta\text{C}(1)(\text{C}(\alpha)) = 0.005$, $\Delta\text{C}(\alpha)(\text{C}(1)) = 0.011$, $\Delta\text{C}(\alpha)(\text{C}(\beta)) = 0.011$, $\Delta\text{C}(\beta)(\text{C}(\alpha)) = 0.006$. ^c Not observed. ^d Obscured by ^{29}Si satellites.

of the electrons is effected by Me_3E groups, and Fig. 2 shows that the electron donating Me_3C is well separated from the other Me_3E groups that are more or less electron accepting. However, the variations of the shifts shown in Fig. 2 do not match very well the variations in the electronegativity of E (see also the discussion of the coupling constants below). This can be expected because various probes were used and the shifts may be influenced differently by more than one factor.

There is a rather close relationship between the $\delta(^{13}\text{C})$ shifts for **4a**–**4e** and those for the substituted benzenes $\text{Me}_3\text{EC}_6\text{H}_5$ [4]. The substituent chemical shifts (SCS)

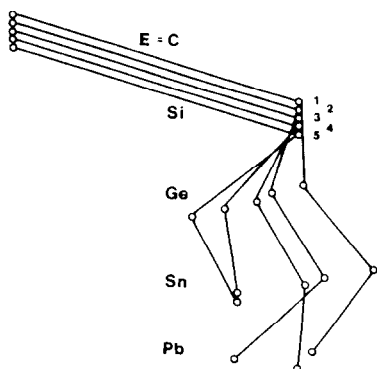


Fig. 2. Comparison of the behavior of $\delta(^{13}\text{C}(\beta))$ (1), $\delta(^{13}\text{C}(1))$ (2), and $^1J(^{13}\text{C}(1)-^{13}\text{C}(2/5))$ (3) for $(\text{Me}_3\text{Ecp})_2\text{Fe}$, the behaviour of $-\delta^{para}(^{13}\text{C}(1))$ for $(\text{Me}_3\text{Ecp})_2\text{Co}$ [7] (4), and the behaviour of $-A(^1\text{H}^*)$. [6] (5) for Me_3Ecp , with E running from top to bottom. The horizontal scale has been chosen such that the data are normalized to the difference of the values for E = C and Si.

based on $\delta(^{13}\text{C}) = 67.80$ for ferrocene show the following correlation coefficients r between the data in the benzene and the ferrocene series: $\text{C}(\beta)$, $r = 0.999$; $\text{C}(1)$, $r = 0.852$; $\text{C}(2/6) \rightarrow \text{C}(2/5)$, $r = 0.995$; $\text{C}(4) \rightarrow \text{C}(3/4)$, $r = 0.960$; $\text{C}(4) + \text{C}(3/5) \rightarrow \text{C}(3/4)$, $r = 0.993$. We note that $\text{C}(3/4)$ of the ferrocenes behave like the sum of $\text{C}(4)$ and $\text{C}(3/5)$ of the benzenes rather than like $\text{C}(4)$ alone. The latter has been noted earlier for other series [16]. Kitching et al. [4] have given a thorough ^{13}C SCS analysis for aryls substituted by Me_3E . They show that the π -interaction between the aromatic ring and Me_3E dominates the electron release of Me_3C (by hyperconjugation) and the electron-withdrawing effects of the other Me_3E groups. It can be seen from the above correlation that the same applies for **4a–4e**. Similarly, our paramagnetic NMR results [7] reveal a distinction of electron releasing and donating substituents, and a molecular orbital account of the different effects of Me_3C and Me_3Si on a cyclopentadienyl ring has been presented for manganocenes [3]. The crossover of $\delta(^{13}\text{C}(2/5))$ and $\delta(^{13}\text{C}(3/4))$ in the series **4a–4e** is further evidence for the change from an electron donating to an electron accepting substituent. There is a similar ^{13}C and ^1H signal crossover for paramagnetic $(\text{Me}_3\text{Ecp})_2\text{M}$ [7], whereas the signals for $\text{H}(2/5)$ and $\text{H}(3/4)$ of **4a–4e** do not change their relative position.

The analysis of the AB-type $^{13}\text{C}/^{13}\text{C}$ -satellite spectra yields the isotope shifts $^1\Delta^{13}\text{C}(i)(^{13}\text{C}(j))$ in Table 1. They display the one-bond effects of the neighbouring nuclei $^{13}\text{C}(j)$ (as compared to $^{12}\text{C}(j)$ on $\delta(^{13}\text{C}(i))$). Little attention has been paid in the literature to this type of isotope effect. In particular, no series which allows the study of substituent effects is listed in a recent review [17]. Table 1 does not show any systematic change of $^1\Delta^{13}\text{C}(i)(^{13}\text{C}(j))$ with Me_3E . On the other hand, data for **4a** confirm that the isotope effect is smaller when sp^3 carbon atoms are involved (cf. the small Δ for $\text{C}(\alpha)$). We note that all the $^1\Delta^{13}\text{C}(2/5)(^{13}\text{C}(3/4))$ values are larger than that for $(\text{MeCp})_2\text{Fe}$ [15g] by a factor of two.

The ^{207}Pb and ^{119}Sn NMR signals of **4e** and **4d** appear at 42.2 and 19.9 ppm to high frequency relative to the corresponding signals of $\text{Me}_3\text{PbC}_6\text{H}_5$ [18] and $\text{Me}_3\text{SnC}_6\text{H}_5$ [19], while the $\delta(^{29}\text{Si})$ and $\delta(^{13}\text{C}(\alpha))$ values of **4b** and **4a** and the analogous phenyl derivatives [4,20] are not very different. This may be due to the

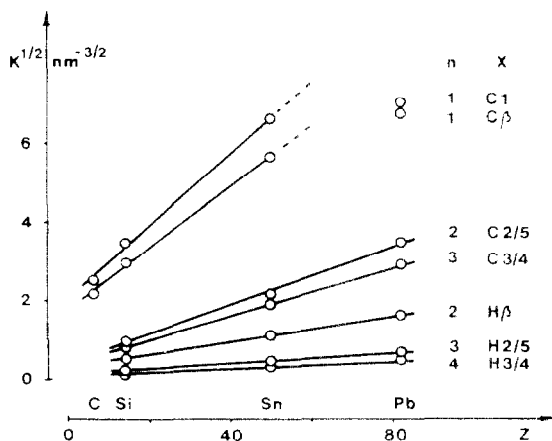


Fig. 3. Plot of the square root of the reduced coupling constant ${}^nK(E-X)$ against the atomic number Z of E in the series $(Me_3Ecp)_2Fe$.

fact that resonances of heavy nuclei are more sensitive to small changes like that from Cp to phenyl. It is more probable that the ${}^{119}Sn$ and ${}^{207}Pb$ signals of **4d**, **4e** experience a characteristic coordination shift to high frequency. Such a shift is observed when $Me_3SnC_6H_5$ is bound to $Cr(CO)_3$ [21].

Coupling constants. The one-bond carbon-carbon coupling is not only important for the signal assignment but also responds to substitution. ${}^1J({}^{13}C(2/5)-{}^{13}C(3/4))$ is less useful because it varies only over a range of 2.4 Hz. For ${}^1J({}^{13}C(1)-{}^{13}C(2/5))$, however, this range extends over 11.0 Hz, and there is a sharp fall-off on going from the electron-donating Me_3C to the attracting Me_3Si group. Wray et al. [22] have demonstrated a good correlation between ${}^1J({}^{13}C(1)-{}^{13}C(2/5))$ of monosubstituted benzenes and the electron-withdrawing power of the substituent. Since nothing but E is changed in the series **4a-4e**, we may simply compare ${}^1J({}^{13}C(1)-{}^{13}C(2/5))$ with the electronegativity of E . The correlation is reasonably good, especially if data for $E = Pb$ are excluded; e.g. $r = 0.982$ or 0.996 with the electronegativities from Mullay [23] or from Allred and Rochow [24].

A special influence of Me_3Pb on the coupling constants is also found when ${}^nJ(E-{}^{13}C)$ values are considered. This is best done by using the reduced coupling constants K shown in Table 1. The square root of ${}^nK(E-{}^{13}C)$ (and of ${}^nK(E-{}^1H)$) should depend linearly on the atomic number Z of E [25] provided the coupling is transmitted by the Fermi contact mechanism. Figure 3 shows the plots of $K^{1/2}$ versus Z for **4a-4e**.

The couplings display a good linear relationship except for ${}^1J({}^{207}Pb-{}^{13}C(1))$ and ${}^1J({}^{207}Pb-{}^{13}C(\beta))$. One-bond ${}^{207}Pb-{}^{13}C$ couplings are known to deviate from the expected values even though the Fermi contact dominates; this can be explained in terms of relativistic effects [26].

The ${}^{57}Fe-{}^{13}C$ couplings should reflect similar variation with the change of substituents as the ${}^{13}C-{}^{13}C$ couplings do, if the same carbon is engaged. In fact, for ${}^1J({}^{57}Fe-{}^{13}C(1))$ also a sharp decrease is observed on going from $(Me_3Ccp)_2Fe$ to $(Me_3Sicp)_2Fe$. However, a reliable substituent effect on ${}^1J({}^{57}Fe-{}^{13}C)$ over the whole series cannot be extracted from the data of Table 1. Most of the ${}^{57}Fe-{}^{13}C$ couplings

lie between 4.6 and 4.9 Hz, a range which has been established for $(\text{Mecp})_2\text{Fe}$ and Cp_2Fe [15g].

In an earlier study use of $^1J(^{13}\text{C}-^1\text{H})$ values seemed to allow the signal assignment of C(2/5) and C(3/4) of monosubstituted ferrocenes [15b] because, throughout, C(3/4) had the larger coupling, but this was the chance result of the particular selection of ferrocenes considered. As Table 1 shows, $^1J(^{13}\text{C}-^1\text{H})$ values have no diagnostic value.

Experimental

Apart from the work-up of the ferrocenes and their further characterization all manipulations were carried out under inert gas. Elemental analyses were performed by the microanalytical laboratory of this institute.

The substituted cyclopentadienes $(\text{Me}_3\text{C})\text{C}_5\text{H}_5$ [11], $(\text{Me}_3\text{Si})\text{C}_5\text{H}_5$ [10], and $(\text{Me}_3\text{Ge})\text{C}_5\text{H}_5$ [10] were prepared by literature procedures. CpNa and $t\text{-BuBr}$ were chosen as starting materials for $(\text{Me}_3\text{C})\text{C}_5\text{H}_5$, $(\text{Me}_3\text{Sn})_2\text{C}_5\text{H}_4$ and $(\text{Me}_3\text{Pb})\text{C}_5\text{H}_5$ were synthesized as described in ref. 12 and 27. The reaction of FeCl_3 with iron powder in THF [13] gave a material which can be formulated as $\text{FeCl}_2 \cdot 1.45 \text{ THF}$. Found: C, 29.63; H, 5.02; Fe, 24.12. Calcd.: C, 30.12; H, 5.05; Fe, 24.14%.

Bis(trimethylplumbyl)cyclopentadiene (2e)

A solution of 10.86 g (33.5 mmol) of diethyl(trimethylplumbyl)amine [28] in 25 ml of THF was cooled to -78°C . When 10.99 g (34 mmol) of trimethylplumbyl-cyclopentadiene were added under stirring the yellow solution soon turned red brown. After removal of the cooling bath the mixture was stirred for another 2 h, the solvent was evaporated, and the product was purified by distillation in an apparatus described previously [29] ($8 \cdot 10^{-6}$ Pa, oilbath $60\text{--}70^\circ\text{C}$). 15.83 g (83%) of a yellow green oil was obtained. ^1H NMR: $\delta = 6.89$ (H(1/4)), 6.61 (H(2/3)), 0.84 (H(β)) (numbering cf. Scheme 1, assignment analogous to **2d** [20]). ^{13}C NMR: $\delta = 136.8$ (C(1/4)), 125.5 (C(2/3)), 60.8 (C(5)), 0.6 (C(β)) (assignment analogous to **2d** [31]).

Preparation of the anions Me_3Ecp^- (3a–3e)

A solution of Me_3CcpK or Me_3SicpK in THF was prepared by slowly adding a solution of **1a** or **1b** in THF to a stirred suspension of KH (in excess) in THF. After the evolution of hydrogen ceased the solution was decanted and stored for further use. ^{13}C NMR of the potassium salts of **3a/3b** in THF, $^1J(^{13}\text{C}-^1\text{H})$ in Hz in brackets: $\delta = 131.92/111.25$ (C(1)), 101.01(155)/112.54(156.3) (C(2/5)), 103.22(155)/108.07(156.3) (C(3/4)), 33.48(124.5)/1.17(117.2) (C(β)); 31.03(C(α)); the assignment follows **4a/4b**).

For the preparation of the other cyclopentadienides a solution of **1c** or **2d**, **2e** in THF was stirred and cooled to 0°C . A ca. 3% excess of a solution of *n*-butyllithium in hexane was added dropwise, and the resulting yellow solution was used for the preparation of the metallocenes and ^{13}C NMR spectroscopy. $\delta(^{13}\text{C})$ for **3d**: 103.8 (C(1)), 112.7 (C(2/5)), 106.7 (C(3/4)), -8.2 (C(β)); the assignment follows **4d**.

Preparation of the ferrocenes $(\text{Me}_3\text{Ecp})_2\text{Fe}$ (4b–4e)

The procedure is similar for all ferrocenes; it is exemplified here for **4e**.

A suspension of 1.76 g (7.61 mmol) of $\text{FeCl}_2 \cdot 1.45 \text{ THF}$ in 25 ml of THF was

cooled to -78°C . A solution of Me_3PbcpLi , prepared from 7.05 g (12.4 mmol) of **2e** in 25 ml of THF, and a solution of 12.8 mmol of n-butyllithium in hexane, were added slowly with stirring. After the cooling bath had been removed the red mixture was stirred for 12 h and solvents were removed in vacuo. The residue was extracted twice with 25 ml of pentane, the solvent was removed under reduced pressure and the crude product was distilled in the apparatus described in ref. 29; at 8×10^{-6} Pa and a bath temperature of 90°C about 5% of monoplumbylferrocene were collected. When the temperature was raised to 145°C 3.0 g (70% relative to **2e**) of **4e** were obtained as an orange red oil. The other ferrocenes were distilled at 8×10^{-6} Pa and the following bath temperatures: 85°C (**4a/4b**), 90°C (**4c**), and 120°C (**4d**). Except for **4a**, which has been described previously [15b], the purities of the compounds were confirmed by elemental analysis.

$\text{C}_{16}\text{H}_{26}\text{FeSi}_2$: Found: C, 58.30; H, 7.64. Calcd.: C, 58.16; H, 7.93%.

$\text{C}_{16}\text{H}_{26}\text{FeGe}_2$: Found: C, 44.59; H, 6.27; Fe, 13.33. Calcd.: C, 45.82; H, 6.25; Fe, 13.32%.

$\text{C}_{16}\text{H}_{26}\text{FeSn}_2$: Found: C, 37.21; H, 5.01. Calcd.: C, 37.56; H, 5.12%.

$\text{C}_{16}\text{H}_{26}\text{FePb}_2$: Found: C, 28.00; H, 3.83. Calcd.: C, 27.91; H, 3.81%.

The NMR spectra were recorded on a Bruker CXP 200 and a Jeol JNM GX 270 spectrometer; solutions of **4a–4e** in acetone- d_6 , **2e** in benzene- d_6 , and **3a,3b, 3d** in THF (no field lock) were used. Shifts were measured relative to the following internal standards: ^{13}C : acetone- d_6 with $\delta(^{13}\text{CD}_3) = 29.80$, ^{29}Si : $(\text{Me}_3\text{Si})_2\text{O}$ with $\delta(^{29}\text{Si}) = 6.90$, ^{119}Sn : Me_4Sn with $\delta(^{119}\text{Sn}) = 0$, ^{207}Pb : Me_4Pb with $\delta(^{207}\text{Pb}) = 0$. The resolution in ppm/digit or Hz/digit was $\delta(^1\text{H}) = 0.002$, $\delta(^{13}\text{C}) < 0.0014$, $\delta(^{29}\text{Si}) = 0.006$, $\delta(^{119}\text{Sn}) = 0.007$, $\delta(^{207}\text{Pb}) = 0.002$, $^nJ(\text{E}-^{13}\text{C}) = ^nJ(^{13}\text{C}-^{13}\text{C}) = ^nJ(^{57}\text{Fe}-^{13}\text{C}) < 0.095$, $^1J(^{13}\text{C}-^1\text{H}) = 0.2$, $^nJ(\text{E}-^1\text{H}) < 0.1$.

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