NMR SPECTROSCOPY ON PARAMAGNETIC COMPLEXES

XXXIV *. PARAMAGNETIC METALLOCENES BEARING Me₃E (E = C, Si, Ge, Sn) SUBSTITUENTS. SYNTHESES AND ¹H/¹³C NMR STUDIES **

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Summary

The metallocenes $(Me_3ECp)_2M$, with M = V, Cr, Co, Ni and E = C, Si, Ge, Sn, have been synthesized starting from Me_3ECp^-. They behave like the parent metallocenes except for those with E = Sn, which show an increased reactivity of the E–C bond. The compounds have been fully characterized by their paramagnetic ¹H and ¹³C NMR spectra; analysis of these spectra allows interpretation of the signal splitting in terms of the number of electrons in the metallocene frontier orbitals and the type of Cp π-orbital which dominates the spin delocalization. The NMR results show Me_3C to be electron releasing and all the other Me_3E groups to be electron attracting, in the sequence $Me_3Si > Me_3Ge \approx Me_3Sn$. Because of conjugation between Cp and Me_3E, these influences are also apparent in the paramagnetic NMR data for the substituent.

Introduction

For some time paramagnetic metallocenes were regarded as curious analogues of ferrocene that were difficult to handle. Nowadays their high reactivity towards oxygen (and sometimes moisture) can be coped with in most laboratories, and in earlier members in this series of papers we have shown that unambiguous characterization by NMR spectroscopy is straightforward in most cases. Paramagnetic metallocenes are thus starting materials of considerable synthetic potential, as reflected in a number of recent examples of their use [2]. However, little is known about how the reactivity is influenced by electronic effects on the reactivity of the

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* For parts XXX–XXXIII see refs. 1, 2d, and 4.
** Dedicated to Professor Jean Tirouflet on the occasion of his retirement.

metal centre and by transfer of the reaction centre from the metal to the ligand. Robbins et al. [3] have reported on permethylated derivatives, and we have demonstrated [4] that the reactivity of manganocenes may be varied by modifying the cyclopentadienyl ligand.

As an approach to the study of the influences on reactivity mentioned above we have used Me_3E (with E = C, Si, Ge, and Sn) substituents on the cyclopentadienyl ring [5]. A second aim was to examine the NMR behaviour of the series $(Me_3ECp)_2M$ (with M = V, Cr, Co, and Ni). After having introduced paramagnetic ^{29}Si and ^{119}Sn NMR spectroscopy [6] we now present details of the syntheses and the ^1H and ^{13}C NMR investigations.

Results

Syntheses. A well-known route to 1,1′-disubstituted ferrocenes involves use of the corresponding dilithio precursor. In preliminary experiments we found that for paramagnetic metallocenes this approach is not satisfactory. An alternative route involves preparing the substituted Cp ligand first and then attaching it to a metal. For diamagnetic transition metal Cp derivatives this can be carried out by treatment of compounds containing a metal–halide bond with 5,5′-disubstituted cyclopentadienes [7] or with the anions R_3ECp^- [8]. We chose the latter approach, and synthesized Me_3ECp^-; details are given in a separate paper [9]. For E = Sn a more elegant route would make use of the reaction of a solvated metal(II) halide, $MX_2(THF)_n$ with 5,5′-bis(trimethylstannyl)cyclopentadiene, since this is also the precursor for Me_3SnCp^-. However, the yield was only good for M = Fe [9], for M = V it fell to 7%, and for M = Cr and Ni it was lower. Use of the route shown in Scheme 1 gives compounds 1–16 in acceptable to good yields. All compounds with E = Si, Ge, and Sn were unknown except for 14, which was characterized previously by IR and elemental analysis [10].

Except for the 1,1′-di-t-butylmetallocenes, which we have described earlier [11], all the products are liquids at room temperature. They are mixible with hexane, benzene, and ethers in any ratio, and show high reactivity towards oxygen that is typical for paramagnetic metallocenes. All the $(Me_3SnCp)_2M$ compounds are accompanied by $CpM(Me_3SnCp)$ species; these two products may be separated by distillation for M = V, Cr, and Ni but even though the boiling points must be very different we were unable to separate the mono- and distannylated cobaltocene. Repeated distillation always yielded a similar ratio of products which can be determined by ^1H NMR spectroscopy as shown in Fig. 1.

For heavy elements E the well-known thermal lability is probably increased by the neighbouring paramagnetic center so that at the distillation temperature Sn–C bond cleavage yields the monostannylated metallocene. Attempts to separate the
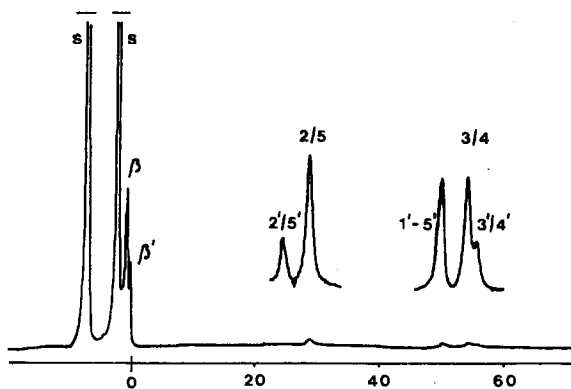

M/E	C	Si	Ge	Sn
V	1	2	3	4
Cr	5	6	7	8
Co	9	10	11	12
Ni	13	14	15	16
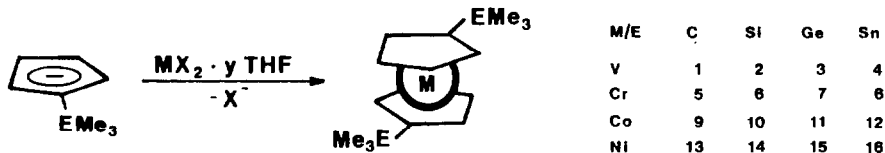
SCHEME 1

Fig. 1. ^{1}H NMR spectrum of (Me$_3$SnCp)$_2$Co and CpCo(Me$_3$SnCp) dissolved in C$_6$H$_5$CH$_3$ at 303 K. For the numbering see Fig. 3; primes denote the mixed sandwich. S = solvent. The scale (in ppm) is linked arbitrarily to SiMe$_4$; it does not provide paramagnetic shifts.

products by crystallization have been unsuccessful so far. In line with these observations the reaction of Me$_3$PbCp$^-$ with NiCl$_2$(THF)$_n$ gives mainly (MeCp)$_2$Ni. This follows from the ^{1}H NMR spectrum, which shows the characteristic Hα signal [11] and only small additional signals in the range of Hβ and H1–5 which could be attributed to (Me$_3$PbCp)$_2$Ni and (MeCp)Ni(Me$_3$PbCp). Since thermal decomposition of R$_4$Pb in benzene yields alkylated benzenes via the radicals R$_3$Pb$^.$ [12], we

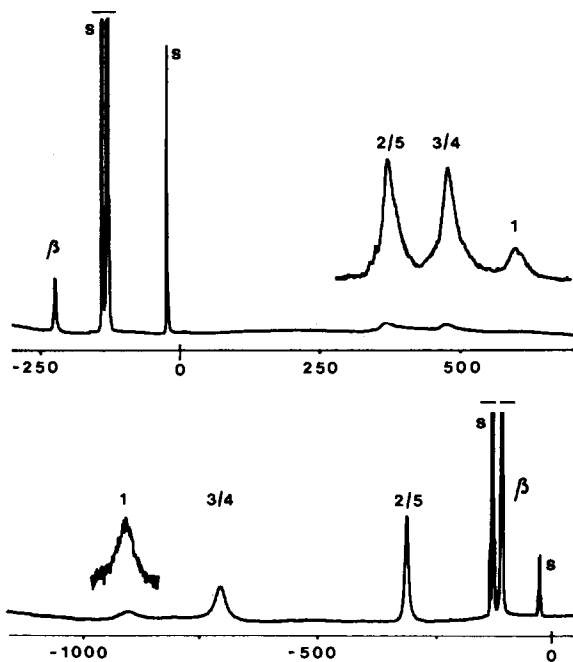Fig. 2. ^{13}C NMR spectra of (Me$_3$SnCp)$_2$V (top) at 320.3 K and (Me$_3$SiCp)$_2$Co (bottom) at 303.1 K, both dissolved in C$_6$H$_5$CH$_3$. For the numbering see Fig. 3, for the scale see Fig. 1. S = solvent.

think that $(Me_3PbCp)_2Ni$ gives $(MeCp)Ni(Me_3PbCp)$ and $(MeCp)_2Ni$ by a similar route.

NMR spectra. The large paramagnetic signal shifts and high solubility permit a "low-cost" NMR characterization of **1–16**. All spectra may be obtained in non-deuterated toluene. In a few cases the signal from nuclei in position β overlaps with the strong peaks from toluene. Such a difficulty can be overcome by changing the temperature and/or the solvent. Because of the line widths (>30 Hz) and the stability of a superconducting magnet, field locking is not necessary. Typical ^{1}H and ^{13}C NMR spectra are shown in Figs. 1 and 2. Numerical data are given in the experimental part. For $CpCo(Me_3SnCp)$ we obtained the following paramagnetic shifts at the standard temperature 298 K: $\delta_{298}^{para}(^{13}C)$ -892(C1), -239(C2/5), -614 (C3/4), -599(Cp), -29.1(Cβ) ppm and $\delta_{298}^{para}(^{1}H)$ 26.6(H2/5), 60.6 (H3/4), 55.0 (Cp), -0.4 (Hβ) ppm.

For a more reliable comparison of the NMR data we have recorded the ^{13}C NMR spectra of **1, 5** and **9** [11] again at higher field. The δ_{298}^{para} remained essentially the same or showed only slight changes. In the case of **5** we were able to separate the formerly [11] unresolved signals of C1 and C3/4 at higher temperatures.

The signal assignment is based on (i) ^1J(C–H) which can be observed for most of the Cβ resonances, (ii) the shift range, which is very different for the nuclei of the five-membered ring and for Cβ or Hβ, and (iii) the relative intensities which distinguish C1, Cβ, and Hβ. Nuclei in positions 2/5 and 3/4 can be differentiated by use of qualitative MO arguments, as described below.

Discussion

When a hydrogen atom of the cyclopentadienyl ligand is replaced by Me_3Si the corresponding manganocene experiences a remarkable shift of its spin equilibrium towards the high-spin isomer [4]. A change of the spin state, which would be accompanied by a change in reactivity, was not observed for any of the metallocenes in the present study. This follows from the fact that the NMR signal shift ranges, remain much the same on going from E = C to Si, Ge, and Sn, even at high temperature.

There is, however, an appreciable increase in the reactivity for E = Sn. This reactivity is located in the ligand, and is a consequence of the lability of the E–C bond. On one hand it complicates the isolation of the compounds, but on the other substitution of the five-membered ring should be facilitated. Thus, in an attempt to synthesize hetero-trimetallic sandwich compounds of the type $Cp_2V-CpMCp-VCp_2$, we treated Cp_2VCl with $(Me_3SnCp)_2M$ (M = Cr and Fe). However, at ambient temperature no reaction was observed, while on heating slow decomposition occurred, even though at least one of the expected products is stable, as we have demonstrated for $Cp_2V-CpFeCp-VCp_2$ [13]. Furthermore, Eaborn et al. have shown that $(Me_3SnCp)_2Fe$ reacts with $(COD)PtCl_2$ to give $(COD)ClPt-CpFeCp-PtCl(COD)$ [14].

The variations of reactivity of the paramagnetic metallocenes are a rather crude indication of electronic effects brought about by changing the substituents. NMR spectroscopy should be a more subtle probe. Our results provide a complete set of ^{1}H and ^{13}C data which are depicted in Figs. 3 and 4. There are several interesting features to which we draw attention below.
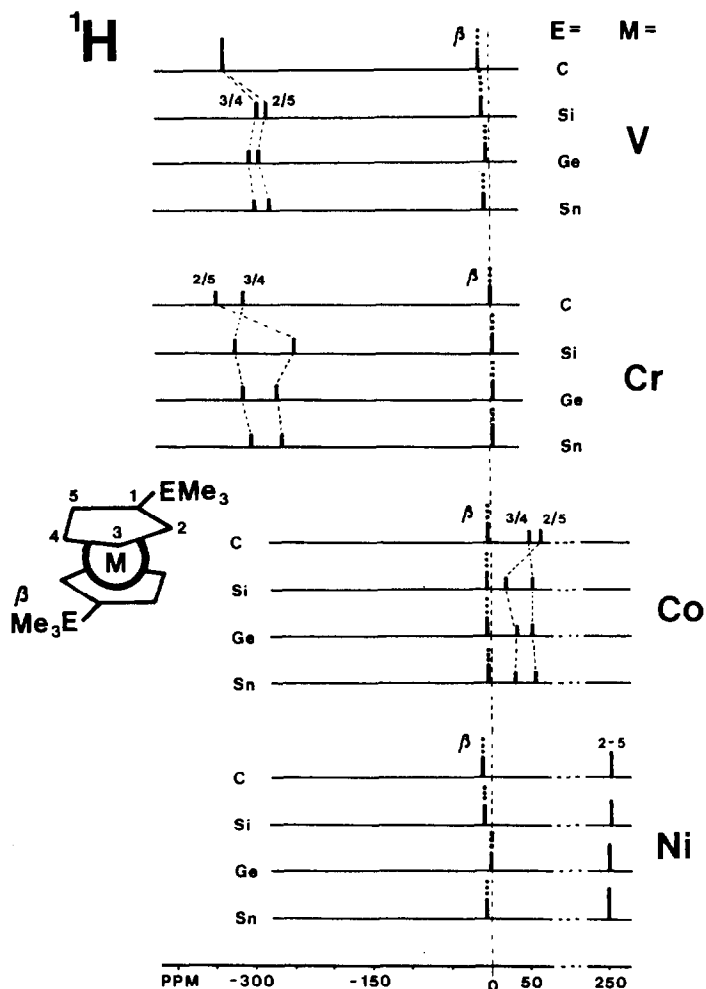
Fig. 3. ^{1}H NMR of $(Me_3ECp)_2M$; Systematic representation of the paramagnetic shifts and relative intensities.

The δ^{para} have different signs, depending on the metal M, the nucleus under study (^{1}H or ^{13}C), and its position relative to the five-membered ring. This can be understood in terms of different electron spin delocalization mechanisms which have been thoroughly discussed [11,15,16]. A more accurate treatment by Eicher makes use of the hole formalism on passing from V and Cr to Co and Ni [17]. There is also a striking crossover of the relative signal positions for C1–5 and H2–5 when E = C is replaced by E = Si, Ge, at Sn. No splitting of the signals of H2–5 has been observed so far for monosubstituted vanadocenes. Surprisingly, such a splitting is found for 2–4. For nickelocenes, in contrast, the corresponding splitting of the signals C1–5 is absent for 14–16 (apart from the artificial splitting introduced by the referencing procedure; see Table 1). We finally note that for a given metal M $\delta^{para}(H\beta)$ and $\delta^{para}(C\beta)$ hardly change, except in the case of 13.
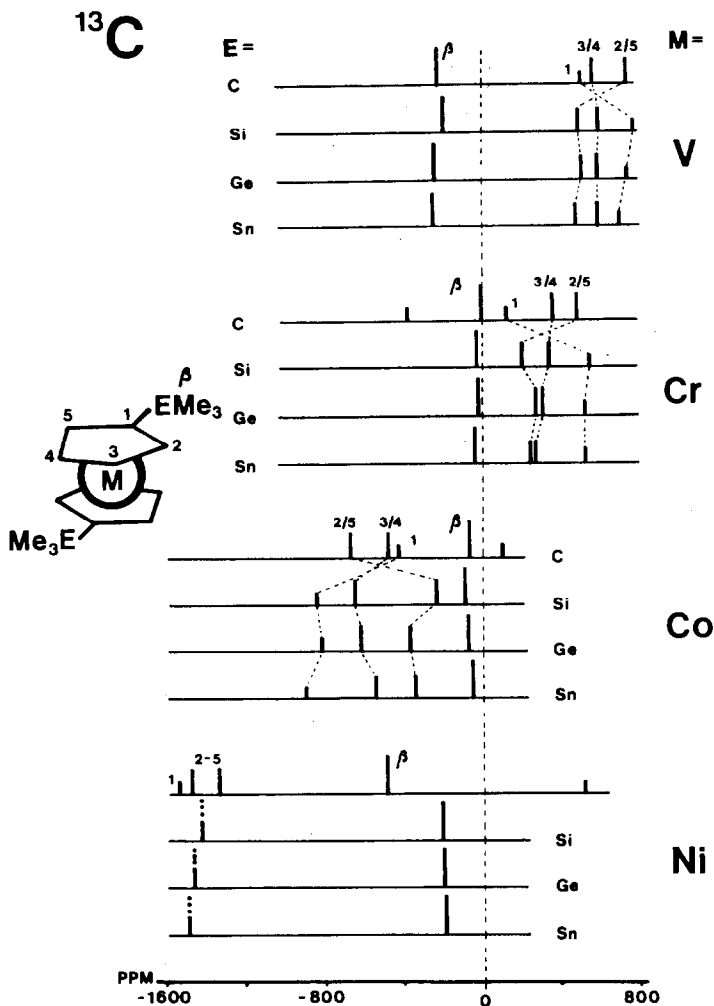
Fig. 4. ^{13}C NMR of $(Me_3ECp)_2M$: Systematic representation of the paramagnetic shifts and relative intensities.

A simple approach to the understanding of these findings is the perturbation of the metallocene frontier orbitals by the substituents, as we have shown for silylated [4] and methylated [18] derivatives. An even simpler approach involves neglect of the sign of δ^{para} (as a metal-specific label), singling out the ligand, and treating it as a cyclopentadienyl radical with reduced spin density. We could then make use of the considerable body of information which has been accumulated by ESR studies [19]. The experimental hyperfine coupling constants of the protons, A(H), are related to the spin density on the neighbouring carbon atom of the five-membered ring. This in turn is proportional to the square of the coefficient of the atomic orbital at that carbon. For the Cp orbitals the relative sizes of the carbon p_z-coefficients are shown in Fig. 5A. Both the symmetric, π_s, and the antisymmetric, π_a, molecular orbitals accomodate the unpaired electron because they are degenerate (neglecting

Jahn–Teller distortion). All the A(H) values are equal in this case. Going back to Cp$_2$M and taking note only of scalar coupling, with $\delta^{\text{para}} \sim -A$(H), we observe one ^{1}H and one ^{13}C NMR signal [11]. When an electron-repelling substituent such as Me$_3$C is introduced (cf. Fig. 5B) the degeneracy of π_a and π_s is lifted, the latter orbital carries the spin, and A(H3/4) > A(H2/5) [19n].

An important difference must be considered when we compare with (Me$_3$CCp)$_2$Co (9). While Cp radicals have three electrons in π_a/π_s, 9 has only one (cf. Fig. 5C) and the A(H) values should be inverted. Convincing evidence comes from the ^{13}C NMR spectrum of 9 (cf. Fig. 4): $|\delta^{\text{para}}(\text{C1})| < |\delta^{\text{para}}(\text{C2–5})|$. On the basis of our MO arguments, this implies $|\delta^{\text{para}}(\text{X3/4})| < |\delta^{\text{para}}(\text{X2/5})|$, with X = ^{1}H, ^{13}C. This is the basis for the assignment of the resonances of H2–5 and C2–5. For the metallocenes it is generally accepted that the ligand content of the MOs that are engaged in the spin delocalization is derived mainly from the Cp e_1''-set. Hence, for chromocenes with an $^3E_{2g}$ ground state the behaviour should be the same as that of cobaltocenes except that the sign of δ^{para} is inverted. It is gratifying that (Me$_3$CCp)$_2$Cr (5) has $|\delta^{\text{para}}(\text{C1})| < |\delta^{\text{para}}(\text{C2–5})|$, and we conclude that $|\delta^{\text{para}}(\text{X3/4})| < |\delta^{\text{para}}(\text{X2/5})|$, with X = ^{1}H, ^{13}C. Conversely, we can argue that, without knowing anything about the disputed [17d] spin delocalization by π-polarization [20], the experiment points to π_a as the dominant ligand orbital.

Next we consider nickelocenes. They have two unpaired electrons, so that both orbitals in Fig. 5C are now engaged in the spin delocalization. At first glance the signal splitting should be removed for H2–5 and C2–5 (similar to Cp$_2$M), and we
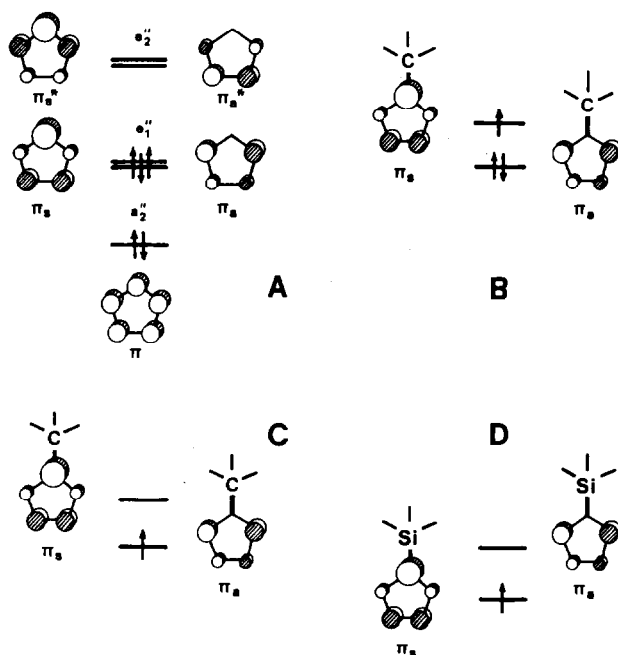

Fig. 5. Selection of the spin-carrying orbitals in (A): the cyclopentadienyl radical, (B): the t-butylcyclopentadienyl radical, (C): (Me$_3$CCp)$_2$Co, and D: (Me$_3$SiCp)$_2$Co (C and D show the ligand content in the MO only).

do, in fact, observe only one signal for the H2–5 of monosubstituted nickelocenes. However, at a given temperature these signals are much broader than for Cp_2Ni and $(Me_3CCp)_2Ni$ (13) shows a 1/2/2-pattern for C1–5. The origin of this may be found in the energy gap between the ligand π_a- and π_s-orbitals; their interaction with the appropriate e-orbitals of the metal will be different, and one unpaired electron will be delocalized more efficiently than the other. The experiment tells us that in 13, for example, more spin is transferred to π_s than to π_a. The effect is, of course, much smaller than for cobaltocenes and chromocenes, so that sometimes the NMR signal spitting is not resolved.

Vanadocenes, with an $^4A_{2g}$ ground state, should behave like nickelocenes in the same way as chromocenes correspond to cobaltocenes. It is therefore not surprising that monoalkylated vanadocenes have only one broad signal for H2–5, or that the difference between $\delta^{para}(H2/5)$ and $\delta^{para}(H3/4)$ is small in the case of 2–4. On the other hand, the signal splitting of C1–5 is much the same for vanadocenes and chromocenes. This shows that our approach is rather crude, especially for vanadocenes; limiting factors are defined below. The ^{13}C NMR data for 1 are in accord with spin delocalization dominated by a π_a-orbital of the ligand. On this basis the signals are assigned as shown in Figs. 3 and 4.

It is easy now to see why there is a signal crossover for C1–5 and H2–5 when we pass from $(Me_3CCp)_2M$ to $(Me_3SiCp)_2M$. Whereas Me_3C releases electrons, Me_3Si is known to be electron attracting. Figure 5D shows that the energies of π_a and π_s are inverted compared to those in Fig. 5C. Whenever, the NMR signals are resolved this inversion is found experimentally; such behavior is found also for Me_3Ge and Me_3Sn.

The above analysis will be more acceptable, but also more complicated, when the following points are included: (i) The paramagnetic shifts may in part originate from a dipolar coupling between the nuclear and the electron spin; (ii) σ-type orbitals are mixed into the π-orbitals of the cyclopentadienyl; (iii) in a substituted metallocene the energy between the π_a- and the π_s-orbital is much smaller than that in a substituted Cp radical because the frontier orbitals are made up mainly of metal orbitals. Hence, in Fig. 5C/D, the π_s or π_a orbitals are populated thermally, and for chromocenes and cobaltocenes π_a and π_s contribute to the spin delocalization. This is one reason why $\delta^{para}(C1) \neq 0$ for 1, 5 and 9. Another consequence is that the temperature dependence of δ^{para} no longer obeys the Curie law. We have demonstrated this for 6 and 10 with paramagnetic ^{29}Si NMR [6]. (iv) $\delta^{para}(^{13}C)$ is determined by the spin density not only on the carbon atom under observation but also on the neighbouring nuclei [21]. This is another reason why $\delta^{para}(C1) \neq 0$ for 1, 5 and 9.

For a metallocene containing a given metal the energy gap between π_a and π_s depends on the electron attracting power of the Me_3E substituent (E = Si, Ge, Sn). If it is weak, the populations of π_a and π_s are similar, and the signal splitting of C1–5 or H2–5 will be small, or vice versa. On this basis, and taking account of the results in Fig. 3 and 4, the order of electron acceptor ability is $Me_3Si > Me_3Ge \approx Me_3Sn$. Me_3Ge comes out to be distinctly electron attracting, whereas Davies et al. [19n] have presented ESR evidence that in $Me_3GeCp^.$ it is electronically neutral. ESR data for the benzene radical anion $Me_3GeC_6H_5^{-}$ show Me_3Ge to be electron attracting [22], in agreement with our results.

The electronic classification of substituents depends on the molecule and the

probe used. Transition metal π-complexes are especially interesting because they may allow experimental resolution of the electronic effect of a substituent into its components. For instance, Elschenbroich and Koch have shown that in the radical cations of silylated bis(η^6-benzene)chromium complexes σ-delocalization dominates [23]. This selects out the inductive effect of Me_3Si, which is positive according to the electron-nuclear coupling $A(^1H)$ and $A(^{53}Cr)$. In our case π-delocalization dominates for the paramagnetic metallocenes. The conjugative effects of Me_3E which are thus probed are negative for E = Si, Ge and Sn. Pitt has given a detailed treatment of these effects [24]. Several contributions must be taken into account, among them hyperconjugation and participation of the d-orbitals of E.

The efficiency of the combined π-effects should be reflected in the spin transmission from the Cp π-orbitals to $C\beta$ and $H\beta$. ESR cannot provide a probe for this effect in most cases because $A(^1H\beta)$ is not resolved and the ^{13}C satellites are hard to detect. In the NMR spectra the value of $\delta^{para}(C\beta)$ and $\delta^{para}(H\beta)$ are easily obtained. As can be seen from Fig. 3 and 4 or Table 1 the $\delta^{para}(X\beta)$ values are small but show a distinct dependence on the spin density at C(1). We take $(Me_3ECp)_2Co$ as an example. Substituting E = Si for C brings the π_s-orbital (cf. Fig. 5C/D) into play. The increase in spin density on C1 is reflected in $\delta^{para}(C\beta)$ and $\delta^{para}(H\beta)$. Further change to Ge and Sn gradually lowers both shifts. The trend does not perfectly parallel the electron attracting power of Me_3E as revealed by the signal splitting of C1–5 and H2–5; changes in the interaction between Cp and Me_3E may be responsible for this [24]. Separation of these effects does not seem to be feasible, however.

Experimental

All experiments were carried out under dry oxygen-free argon by use of standard Schlenk techniques. For the final distillation of the products the apparatus described in ref. 25 was used. Elemental analyses were carried out in the microanalytical laboratory of this institute.

The THF-solvated metal(II) chlorides of vanadium * [25] chromium [25], cobalt [27], and nickel [28], and also the 1,1-di-t-butylmetallocenes **1, 5, 9**, and **13** [11], were prepared as described previously. The formation of the anions Me_3ECp^- will be described in a separate publication. The procedures described below are very similar for a given substituent.

Bis(trimethylsilyl-η^5-cyclopentadienyl)vanadium (2), -chromium (6), -cobalt (10), and -nickel (14)

To a stirred slurry of 22 mmol of $MCl_2(THF)_n$ in 25 ml of THF at room temperature were added slowly 25 ml of a 1.6 molar solution of trimethylsilylcyclopentadienyllithium. The colour changed to deep violet (**2**), red (**6**), dark brown (**10**) or green (**14**) and the precipitate disappeared. After overnight stirring the THF was removed under reduced pressure and the residue extracted twice (50 and 10 ml portions) with pentane. The combined pentane extract was evaporated and the

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* The crude reaction mixture behaves as though it were $VCl_2(THF)_x$; crystallisation yields $[V_2Cl_3(THF)_6][Zn_2Cl_6]$ [26].

TABLE 1

PARAMAGNETIC ^{1}H AND ^{13}C NMR SHIFTS AT 298 K OF THE METALLOCENES (Me$_3$ECp)$_2$M DISSOLVED IN TOLUENE

(Me$_3$ECp)$_2$M			^{13}C-position [a]				^{1}H-position [a]		
E	M		1	2/5	3/4	β	2/5	3/4	β
C [b]	V	1	498	734	548	−225	−335 [c]	−335 [c]	−10.0 [c]
Si	V	2	758	495	586	−205	−280	−293	−10.2
Ge	V	3	733	520	582	−231	−290	−298	−3.8
Sn	V	4	706	471	582	−242	−280	−297	−3.1
C [b]	Cr	5	130	483	368	−2.2	−344 [c]	−312 [c]	0.0 [c]
Si	Cr	6	554	192	337	−24.9	−246	−318	2.6
Ge	Cr	7	517	271	298	−12.4	−268	−310	3.1
Sn	Cr	8	516	253	275	−40.4	−261	−298	2.8
C [b]	Co	9	−421 [e]	−667 [e]	−491 [e]	−79 [e]	64.0 [c,d]	50.2 [c,d]	−2.7 [c]
Si	Co	10	−864	−241	−657	−103.8	25.9	59.3	−3.6
Ge	Co	11	−822 [f]	−348 [f]	−628 [f]	−85.2 [f]	35.7	58.7	−1.3
Sn	Co	12	−892 [g]	−328 [g]	−539 [g]	−59.1 [g]	33.1	59.4	−0.7
C [b]	Ni	13	−1547 [h]	−1470 [d,h]	−1332 [d,h]	−487.4 [h]	255 [c]	255 [c]	−7.5 [c]
Si	Ni	14	−1432	−1432	−1432	−209	251	251	−6.5
Ge	Ni	15	−1466 [k]	−1468 [k]	−1468 [k]	−196	254 [i]	254 [i]	−1.9 [i]
Sn	Ni	16	−1497 [k]	−1492 [k]	−1492 [k]	−197	256	256	−5.9

[a] Cf. numbering in Fig. 3. [b] δ_{298}^{para}(Cα) = −557 (1), −390 (5), 97 [e] (9), 522.8 [h] (13). [c] Data taken from ref. 11. [d] Assignment revised (cf. text). [e] Mean value calculated from measurements at 355.3 and 374 K (cf. text). [f] Solvent: diglyme. [g] Solvent: benzene. [h] Data taken from ref. 29. [i] Solvent: toluene-d_8. [k] One signal for C1–5; splitting introduced by referencing to the corresponding signals of (Me$_3$ECp)$_2$Fe.

residue distilled under vacuum (bath temperature 85°C, cooling finger 15°C). At first a thin colourless to yellow film sometimes formed on the cooling finger, and this was removed mechanically after interrupting the distillation either mechanically or by washing it into a separate flask with the first drops of coloured product. The metallocenes **2, 6, 10** and **14** were then obtained as oils.

$C_{16}H_{26}Si_2V$: yield 43%. Found: C, 58.78; H, 7.94. Calcd.: C, 59.04; H, 8.05%.
$C_{16}H_{26}CrSi_2$: yield 31%. Found: C, 58.39; H, 8.01. Calcd.: C, 58,85; H, 8.03%.
$C_{16}H_{26}CoSi_2$: yield 28%. Found: C, 57.52; H, 7.95. Calcd.: C, 57.63; H, 7.86%.
$C_{16}H_{26}NiSi_2$: yield 26%. Found: C, 57.38; H, 7.83. Calcd.: C, 57.66; H, 7.86%.

Bis(trimethylgermanyl-η^5-cyclopentadienyl)vanadium (3), -chromium (7), -cobalt (11), and nickel (15)

In a procedure similar to that described above, a solution of trimethylgermanyl-cyclopentadienyllithium in THF was added to a slight excess of $MCl_2(THF)_n$ in THF. Colour changes and work-up were as described for the silylated analogues, except that the bath temperature for the distillation was raised to 90°C. Compounds **3, 7, 11** and **15** were obtained as oils.

$C_{16}H_{26}Ge_2V$; yield 52%. Found: C, 46.26; H, 6.52. Calcd.: C, 46,36; H, 6.32%.
$C_{16}H_{26}CrGe_2$: yield 66%. Found: C, 46.63; H, 6.56. Calcd.: C, 46.24; H, 6.31%.
$C_{16}H_{26}CoGe_2$: yield 59%. Found: C, 42.20; H, 6.22; Co, 13.60. Calcd.: C, 45.49; H, 6.20; Co, 13.95%.
$C_{16}H_{26}Ge_2Ni$: yield 37%. Found: C, 45.83; H, 6.41. Calcd.: C, 45.51; H, 6.21%.

Bis(trimethylstannyl-η^5-cyclopentadienyl)vanadium (4), -chromium (8), -cobalt (12), and -nickel (16)

The procedure described above was slightly modified. A solution of trimethyl-stannylcyclopentadienyllithium in THF was added to the stirred slurry of $MCl_2(THF)_n$ in THF at −78°C. The temperature was raised to ca. 25°C and the mixture stirred another 12 h. The colours were as expected, except for **12** and **16**, for which the solutions were green and brown, respectively. The crude product which is obtained as described previously was distilled in two steps. First, with an oilbath temperature of < 80°C, colourless by-products were removed before 5–7% yield of the η^5-cyclopentadienyl(trimethylstannyl-η^5-cyclopentadienyl) derivative was collected. The temperature of the oilbath was then raised to 120 and subsequently to 140°C. Compounds **4, 8, 12,** and **16** were obtained as oils all now of the expected colour. Compound **12** contained some monostannylated product even after repeated distillation.

$C_{16}H_{26}Sn_2V$: yield 33%. Found: C, 37.79; H, 5.13. Calcd.: C, 37.93; H, 5.17%.
$C_{16}H_{26}CrSn_2$: yield 54%. Found: C, 38.74; H, 5.70. Calcd.: C, 37.84; H, 5.16%.
$C_{16}H_{26}CoSn_2$: yield 38% after correction (^{1}H NMR integration) for monostanny-lated cobaltocene.
$C_{16}H_{26}NiSn_2$: yield 71%. Found: C, 35.90; H, 5.68. Calcd.: 37.35; H, 5.09%.

The NMR spectra were recorded with a Bruker CXP 200 spectrometer equipped with a B VT 1000 variable temperature unit. Samples containing 30–40 vol.% of the metallocene in a solvent were placed in 10 mm diameter NMR tubes; use of ground

glass stoppers assured long-term stability of the metallocene. The experimental shifts, δ^{exptl} (ppm), were measured relative to the solvent signals ($C_6D_5CD_2H$: $\delta(^{13}C)$ 19.2, $\delta(^1H)$ 2.3; $C_6H_5CH_3$: $\delta(^{13}C)$ 20.3, $\delta(^1H)$ 2.3; C_6H_6: $\delta(^{13}C)$ 128.0; diglyme: $\delta(^{13}CH_3)$ 57.0. Changes relative to the corresponding signal shifts of isostructural ferrocenes [9] gave the paramagnetic shifts δ^{para}, which are negative when shifted to high frequency. The experimental temperatures were calibrated with a Lauda R42 resistance thermometer placed in a NMR tube containing toluene. For comparison all the δ^{para} values were normalized to 298 K by use of the Curie law. For some metallocenes, δ^{para} is not strictly proportional to $1/T$. Errors due to this effect were kept small by using spectra at $301.8 < T < 305.7$. The shift errors were determined mainly by the line width, which in turn increased with δ^{exptl}; $0 < \delta^{\text{exptl}} < 20$: ± 0.1 ppm, $20 < \delta^{\text{exptl}} < 200$: ± 0.5 ppm, $200 < \delta^{\text{exptl}} < 500$: ± 1–2 ppm, $500 < \delta^{\text{exptl}} < 1000$: ± 2–5 ppm, $\delta^{\text{exptl}} > 1000$: ± 5–10 ppm. For the value of $\delta^{\text{para}}(^{13}C)$ for **9** the error may be larger, since separation of C1 and C3/4 occurred above 355 K.

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