Journal of Organometallic Chemistry, 397 (1990) 21–28
Elsevier Sequoia S.A., Lausanne
JOM 21023

ansa-Metallocene derivatives

XX *. An assignment of ^{1}H- and ^{13}C-NMR signals in *ansa*-metallocene complexes with 16-electron and 18-electron configuration

Stephan Gutmann, Peter Burger, Marc-Heinrich Prosenc and Hans-Herbert Brintzinger *

Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz (F.R.G.)

(Received April 6th, 1990)

Abstract

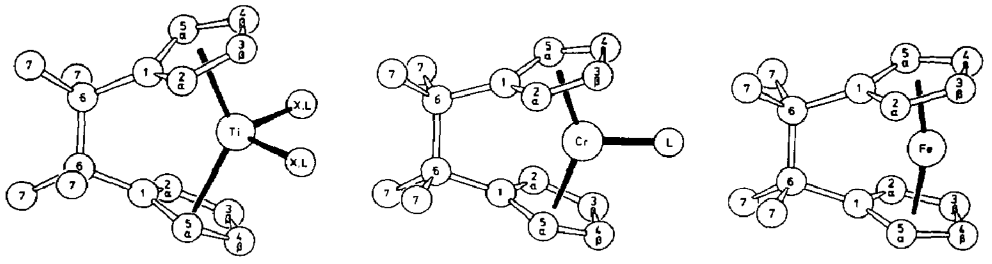
The NMR signals of cyclopentadienyl ring protons and C atoms in *ansa*-metallocene derivatives of general type $(CH_3)_4C_2(C_5H_4)_2M(X,L)_n$, with a 16-electron configuration, i.e. with $MX_n = TiF_2$, $TiCl_2$, $TiBr_2$, TiI_2 or $Ti(CH_3)_2$, and with an 18-electron configuration, i.e. with $ML_n = Ti(CO)_2$, $Ti(P(CH_3)_3)_2$, $Cr(CO)$ or Fe, have been assigned to the α- and β-ring positions by nuclear Overhauser effect and selective decoupling studies. Whereas the α-proton resonances appear at higher fields than those for the β-protons in all the complexes with the 16-electron configuration, the opposite is the case for the 18-electron *ansa*-metallocene derivatives studied.

Introduction

There have been many recent reports on the syntheses, structures and reactions of ring-bridged metallocene complexes. Some of these compounds are of interest as catalysts, e.g. for α-olefin polymerisation [1–3]. In characterization of such compounds, ^{1}H-NMR spectra, in particular the conspicuous cyclopentadienyl proton signals, are especially useful. The differences in the chemical shifts between cyclopentadienyl protons α- and β- to the bridgehead atom, for example, have been reported to correlate with the tilt angle between the two C_5H_5 ring ligands [4,5]. Frequently it is unclear, however, which of the two signals are to be assigned to the α- and β-ring positions. In *ansa*-ferrocene derivatives, e.g., the high-field signals are

---

* For part XIX see ref. 3.



1a X = F
b Cl
c Br
d I
e CH_3

2a L = CO
b $P(CH_3)_3$

3 L = CO

4

Scheme 1

usually assigned to the set of ring protons α to the bridgehead atom [6,7], while assignment of the high-field signals to the β protons is usual for Group IV *ansa*-metallocene derivatives [8,9]. In a study of chirally-substituted *ansa*-metallocenes we have encountered results incompatible with such an assignment [10,11]. We present here results of a systematic study of ^1H- and ^{13}C-NMR assignments in a series of tetramethylethano-bridged metallocene derivatives comprising the 16-electron species **1a–e** and the 18-electron species **2–4**.

Experimental

Complexes **1b** [12], **2a** [13] and **3** [14] were prepared by published procedures. Complex **4** [6,7] was obtained by reaction of $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$ [12] with $FeCl_2$ in THF. The dichloride **1b** was converted into **1a**, **1c–e**, and **2b**, respectively, by reaction with KF in CH_3OH, with BBr_3 or BI_3 in CH_2Cl_2, with CH_3Li in diethylether, and by reduction of **1b** with Mg metal in a THF solution of $P(CH_3)_3$, as previously described for the corresponding unbridged titanocene species [15–18]. All compounds were obtained pure as indicated by ^1H-NMR spectroscopy. Their ^1H- und ^{13}C-NMR spectra were recorded on Bruker WM 250 and Jeol FX 90Q NMR spectrometers, and the ^{31}P-NMR spectrum of **2b** was recorded on a Jeol JNM-GX 400 FT NMR spectrometer.

Results and discussion

1. ansa-*Titanocene complexes with 16-electron configurations*

In the ^1H-NMR spectra of compounds **1a–e** (see Tab. 1), the cyclopentadienyl protons give rise to a pair of pseudo triplets; this indicates that a fast interconversion of the δ and λ conformers of the ethano bridge creates equivalent sets of four α- and four β-protons, respectively. For all the compounds in this series, the pseudo triplet at higher field is selectively enhanced in intensity by a factor of up to 1.4 upon irradiation at the CH_3 resonance frequency of the tetramethylethano bridge. The strong distance dependence of this nuclear Overhouser effect (NOE) enhancement thus identifies the high-field signals as being due to the set of protons α to the

Table 1

^{1}H- and ^{13}C-NMR data for 16-electron *ansa*-titanocene species $(CH_3)_4C_2(C_5H_4)_2TiX_2$ in $CDCl_3$ solution (δH values in C_6D_6 solution given in italics) (J in Hz)

TiX_2	δH(2,5)	δH(3,4)	δH(7)	δC(1)	δC(2,5)	δC(3,4)	δC(6)	δC(7)	^1J(C-α-H)	^1J(C-β-H)
TiF_2	6.17 (4,m) [a] *5.80*	6.38 (4,m) [a] *6.38*	1.54 (12,2) *1.04*	145.3	110.3 [b]	126.9 [b]	45.0	28.1	172.4	177.3
$TiCl_2$	6.21 (4,pt) [c] *5.75*	6.86 (4,pt) [c] *6.78*	1.44 (12,2) *0.88*	145.3	112.8	128.7	45.5	28.1	174.3	179.3
$TiBr_2$	6.22 (4,pt) [c] *5.66*	7.18 (4,pt) [c] *7.05*	1.39 (s) *0.76*	144.7	113.2	128.0	45.7	28.0	174.0	184.0
TiI_2	6.15 (4, pt) [c] *5.55*	7.74 (4,pt) [c] *7.58*	1.29 (12,s) *0.64*	143.6	113.2	125.3	45.9	27.9	174.9	180.7
$Ti(CH_3)_2$ [d]	5.63 (4,pt) [c] *5.31*	6.87 (4,pt) [c] *6.76*	1.14 (12,s) *0.85*	135.0	108.4	118.9	43.8	27.9	170.0	173.3

[a] Broadened due to unresolved H–F coupling. [b] Pseudotriplets due to C–F coupling with J(C-α–F) = 1.8 and J(C-β–F) = 3.4 Hz. [c] Pseudotriplets with apparent J(HH) = 2.5 to 2.6 Hz. [d] Data for $Ti(CH_3)_2$ groups: δH = −0.19 ppm (s) in $CDCl_3$, 0.15 ppm in C_6D_6, δC = 42.8 ppm, ^1J(CH) = 122.7 Hz.

bridgehead atom. This assignment is the opposite of that previously proposed for a number of related ansa-titanocene derivatives [8,9] *.

Variation of coligands in complexes **1a**–**e** causes only minor changes in the chemical shifts of the high-field α-set of protons, but substantial changes of those of the low-field β-set. The chemical shift difference $\Delta\delta$ is smallest (0.58 ppm in C_6D_6) for the difluoro and largest (2.03 ppm in C_6D_6) for the diiodo derivative. These changes are practically identical with those reported by Köpf et al. for the corresponding series of dimethylsilyl-bridged *ansa*-titanocene derivatives [8]. This indicates that the ordering of α-H and β-H resonances is the same for these two series of *ansa*-metallocenes, as expected from their closely related geometries [20].

The mean values of α-H and β-H shifts for each of the dihalogenide complexes **1a**–**d** reveal the same trend, i.e. the greatest shielding for the difluoro and the greatest deshielding for the diiodo species, as the (rotationally averaged) ring-H shifts measured for the corresponding unbridged titanocene dihalides, $(C_5H_5)_2TiX_2$ [16,21,22]. The apparent H(α,β) coupling constants of 2.5–2.7 Hz are comparable with those observed in unbridged substituted titanocene derivatives [23]. In the difluoro derivative **1a**, both ring proton signals are broadened, presumably by an unresolved coupling to the fluoride ligands; this effect is more pronounced for the β-H than for the α-H resonances.

In the ^{13}C-NNR data obtained for complexes **1a**–**e** in $CDCl_3$ solution (see Tab. 1), the C(1) and C(6) signals are identified by their relatively low intensities and the absence of any direct C–H coupling; the other signals can be assigned to the respective C atoms in view of the collapse of their direct-neighbour proton splitting with $^1J(CH) \approx 170$–185 Hz upon selective irradiation at the corresponding H-atom frequency. Each of these complexes has its α-C atom signals at higher fields than its β-C signals; this ordering coincides with that of the respective ring proton NMR signals. A C–F coupling observed in the broad-band decoupled ^{13}C spectrum of the difluoro derivative has a coupling constant $^2J(CF)$ about twice as large for the low-field (β) as for the high-field (α) signal, as expected from the closer proximity of the β-C atoms to the fluoride ligands **.

2. ansa-*Metallocene complexes with 18-electron configurations*

For the ^{1}H-NMR spectra of compounds **2a**, **2b**, **3** and **4** (C_6D_6 solution, see Tab. 2), assignment of the α- and β- ring proton signals is based on the observation that irradiation at the resonance frequency of the CH_3 groups at the ethano-bridge causes a selective NOE enhancement of the low-field pseudo-triplets. For all of these four 18-electron species the ordering of α and β ring protons is thus the reverse of that observed for the 16 electron species **1a**–**e** discussed above. The present assignment of the β-ring hydrogen atoms to the high-field set of signals is again the opposite of that previously proposed for ring-bridged ferrocene derivatives [6,7] ***.

---

* An analogous assignment of high- and low-field signals to α- and β-protons, respectively, has been proposed for $CH_2(C_5H_4)_2TiCl_2$ [19].

** The value of $^2J(CF) = 2.4$ Hz reported for $(C_5H_5)_2TiF_2$ [22] is the approximate mean of ^2J(C-α–F) and ^2J(C-β–F).

*** An assignment in accord with the present one has been reported for the phosphane-bridged ferrocene species $(C_6H_5)P(C_5H_4)_2Fe$ [24].

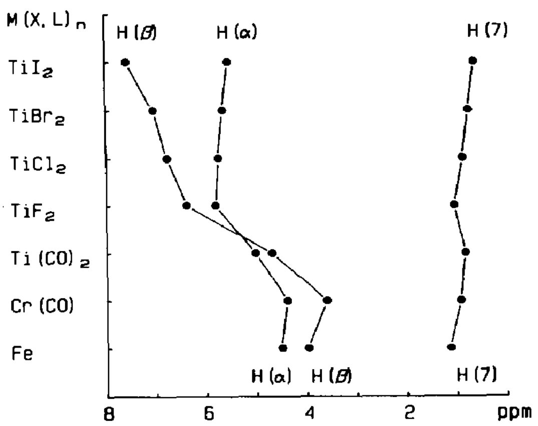


Fig. 1. ^{1}H-NMR shifts for α and β cyclopentadienyl and tetramethylethano protons in various $(CH_3)_4C_2(C_5H_4)_2M(X,L)_n$ complexes.

In the ^{13}C-NMR spectra for this series of 18-electron species, α- and β-ring positions are again assigned on the basis of the disappearance of their direct C–H coupling upon irradiation of the respective ring-hydrogen resonance frequency. In all cases, α- and β-C signals are rather close to each other, the β-C signals appearing at slightly lower fields for the titanium and chromium complexes, but at slightly higher fields for the iron complex **4**.

A marked intensity enhancement of the CO ^{13}C signals observed in the carbonyl complexes **2a** and **3** upon selective irradiation at the respective high-field (but not at the low-field) ring proton frequency is in accord with the assignment of the high-field signals to the β hydrogen atoms, as these are in closest proximity to the CO ligands.

Conclusions

The changes in relative shifts of α- and β-protons with changing coligands X in the series $(CH_3)_4C_2(C_5H_4)_2TiX_2$ (Fig. 1) must evidently be connected with changes in the electronic structure of these compounds. The high-field shift of the cyclopentadienyl protons in the related 16-electron series $(C_5H_5)_2TiX_2$ from $X = I^-$ to $X = F^-$, which is opposite to that expected from the associated electronegativity changes, has been ascribed to an increasing tendency of the lighter halogens to transfer electrons to the metal centre by $\pi_{p,d}$ back donation [16,21,22]. This view is not supported, however, by a series of Extended Hückel Molecular Orbital calculations that we conducted on complexes **1a**, **1b** and **1d** *, which yield positive charges of 2.28, 1.66 and 0.56 units on the Ti centre of the difluoro, dichloro and diiodo derivatives, respectively, wholly in accord with the expected electronegativity effects. Changes in π-electron density between α and β ring positions are also not a likely source of the observed changes in ^{1}H- and ^{13}C-NMR shifts: negative charges of 0.16–0.18 and 0.11–0.14 units were invariably obtained in our EHMO study for the α and β C atoms, respectively, in all *ansa*-titanocene halides studied.

---

* EHMO calculations were performed as described in ref. 25.

Table 2

^{1}H- and ^{13}C-NMR data for 18-electron *ansa*-metallocene species $(CH_3)_4C_2(C_5H_4)_2ML_n$ in C_6D_6 solution

ML_m	δH(2,5)	δH(3,4)	δH(7)	δC(1)	δC(2,5)	δC(3,4)	δC(6)	δC(7)	^1J(C-α–H)	^1J(C-β–H)
$Ti(CO)_2$ [a]	5.02 (4,pt) [b]	4.69 (4,pt) [b]	0.82 (12,s)	128.1	89.4	93.4	44.2	27.7	172.8 Hz	173.6 Hz
$Ti(PMe_3)_2$ [c]	4.97 (4,m) [d]	4.66 (4,m) [d]	1.04 (12,s)	123.9	86.9	93.6	43.0	27.9	170.3	173.5
Cr(CO) [e]	4.39 (4,pt) [f]	3.60 (4,pt) [f]	0.92 (12,s)	109.4	74.9	76.4	44.5	27.9	176.9	177.6
Fe	4.51 (4,pt) [g]	3.98 (4,pt) [g]	1.13 (12,s)	96.5	69.8	68.7	49.4	27.6	173.3	175.1

[a] Carbonyl ^{13}C signal at 262.9 ppm. [b] Pseudo triplets with apparent J(HH) = 2.6 Hz. [c] PMe_3 data: $\delta_P = 37.4$ ppm vs. 85% H_3PO_4 (ext. standard), $\delta_C = 23.4$ ppm, $\delta_H = 0.84$ ppm. [d] Broadened due to unresolved H–P coupling. [e] Carbonyl ^{13}C signal at 261 ppm. [f] Pseudo triplets with apparent *J*(H) = 2.2 Hz. [g] Pseudo triplets with apparent *J*(HH) = 1.9 Hz.

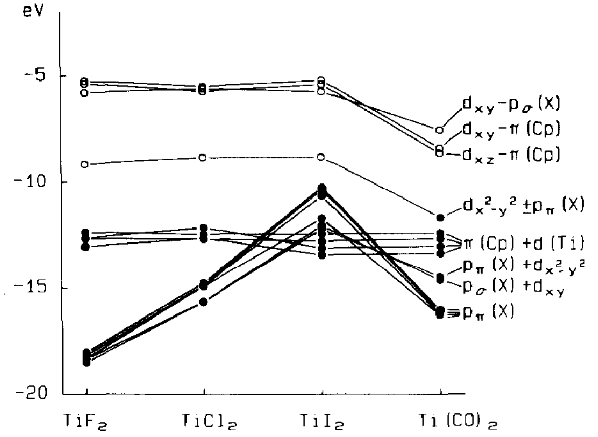


Fig. 2. Orbital energy diagram for filled (●) and empty (○) MOs calculated for $H_4C_2(C_5H_4)_2Ti(X,L)_2$ complexes with X = F, Cl and I and L = CO (C_{2v} symmetry assumed).

An orbital energy correlation diagram derived from our EHMO study (Fig. 2) is in qualitative agreement with earlier reports [26–30]. It indicates, as the most marked change in this series, a rise in energy of the essentially nonbonding halogen *p* orbitals from $MX_2 = TiF_2$ to TiI_2. This trend makes these halogen *p* orbitals the uppermost occupied orbitals in $(CH_3)_4(C_5H_4)_2TiI_2$ *, thus greatly diminishing the energy gap between the highest occupied *p* levels and the lowest unoccupied MO, which is an antibonding combination of $d_{x^2-y^2}$ and ligand p_π orbitals. This decrease in $\Delta E_{p,p^\star}$ in the series **1a–d** indicates that an increased magnetic anisotropy of the heavier halogen atoms X is the origin of the low-field shift of the β-protons in this series, since these protons are situated almost directly above and below the two X ligands, perpendicular to the TiX bond axis. The reversal in the positions of α- and β-proton resonances in an 18-electron complex such as **2a** is likely to arise from the occupation of the $d_{x^2-y^2}$ orbital by the two additional *d* electrons of the Ti^{II} centre, which will cause a similar change of the magnetic anisotropy of the metal centre, as suggested before for related zirconocene derivatives [31].

The NMR signal assignments presented here are clearly in accord with our earlier observations on substituted Group IV metallocene dichloride derivatives [10,11]. Introduction of a substituent at the α position of a cyclopentadienyl ring must be associated with loss of one of the high-field proton resonances, while a β substituent can be recognised by loss of one of the low-field proton signals.

Acknowledgements

Financial support of this work by Deutsche Forschungsgemeinschaft (grant Br 510), by Fonds der Chemischen Industrie and by funds of the University of Konstanz is gratefully acknowledged.

---

* An analogous MO ordering was reported for $(C_5H_5)_2TiI_2$ in ref. 28 and 29.

References

1 J.A. Ewen, J. Am. Chem. Soc., 106 (1984) 6355.

2 W. Kaminsky, K. Külper, H.H. Brintzinger and F.R.W.P. Wild, Angew. Chem., 97 (1985) 507.

3 W. Röll, H.H. Brintzinger, B. Rieger and R. Zolk, Angew. Chem., 102 (1990) 339.

4 T.H. Barr and W.E. Watts, Tetrahedron, 24 (1968) 6111.

5 M. Hillman and A.J. Weiss, J. Organomet. Chem., 42 (1972) 123.

6 K.L. Rinehart, Jr., A.K. Frerichs, P.A. Kittle, L.F. Westman, D.H. Gustafson, R.L. Pruett and J.E. McMahon, J. Am. Chem. Soc., 82 (1960) 4111; K.L. Rinehart, Jr., D.E. Bublitz and D.H. Gustafson, ibid., 85 (1963) 970.

7 R.R. McGuire, R.E. Cochoy and J.A. Winstead, J. Organomet. Chem., 84 (1975) 269.

8 H. Köpf and W. Kahl, J. Organomet. Chem., 64 (1974) C37; H. Köpf and N. Klouras, Z. Naturforsch. B, 38 (1983) 321; N. Klouras and H. Köpf, Monatsh. Chem., 112 (1981) 887.

9 J.A. Smith, J. von Seyerl, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 173 (1979) 175.

10 S. Gutmann, P. Burger, H.U. Hund, J. Hofmann and H.H. Brintzinger, J. Organomet. Chem., 469 (1989) 343.

11 H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz and H.H. Brintzinger, J. Organomet. Chem., 369 (1989) 359.

12 H. Schwemlein and H.H. Brintzinger, J. Organomet. Chem., 254 (1983) 69.

13 H. Schwemlein, W. Tritschler, H. Kiesele and H.H. Brintzinger, J. Organomet. Chem., 293 (1985) 353.

14 H. Schwemlein, L. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 256 (1983) 285.

15 E. Samuel, Bull. Soc. Chim. Fr., (1966) 3548.

16 P.M. Druce, B.M. Kingston, M.F. Lappert, T.R. Spalding and R.C. Srivastava, J. Chem. Soc. (A), (1969) 2106.

17 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.

18 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Wolf, Angew. Chem., 97 (1985) 425.

19 U. Dämmgen and H. Bürger, J. Organomet. Chem., 101 (1975) 307.

20 C.S. Bajgur, W.R. Tikkanen and J.L. Petersen, Inorg. Chem., 24 (1985) 2539; C.S. Bajgur, S.B. Jones and J.L. Petersen, Organometallics, 4 (1985) 1929.

21 H.C. Beachell and S.A. Butter, Inorg. Chem., 4 (1965) 1133.

22 A.N. Nesmeyanov, O.V. Nogina, E.I. Fedin, V.A. Dubovitskii, B.A. Kvasov and P.V. Petrovskii, Dokl. Akad. Nauk SSSR, 205 (1972) 857. A.N. Nesmeyanov, E.I. Fedin, P.V. Petrovskii, V.A. Dubovitskii, O.V. Nogina and N.S. Kochetkova, Zh. Strukt. Khim., 16 (1975) 759.

23 J.H. Davis, H.N. Sun, D. Redfield and G.D. Stucky, J. Magn. Reson., 37 (1980) 441.

24 A.G. Osborne, R.H. Whiteley and R.E. Meads, J. Organomet. Chem., 193 (1980) 345.

25 G. Calzaferri, L. Forss and I. Kamber, J. Phys. Chem., 93 (1989) 5366.

26 J.L. Petersen, D.L. Lichtenberger, R.F. Fenske and L.F. Dahl, J. Am. Chem. Soc., 97 (1975) 6433.

27 J.W. Lauher and R. Hoffmann, J. Am. Chem. Soc., 98 (1976) 1729.

28 M.R.M. Bruce and D.R. Tyler, Organometallics, 4 (1985) 528; M.R.M. Bruce, A. Kenter and D.R. Tyler, J. Am. Chem. Soc., 106 (1984) 639.

29 C. Cauletti, J.P. Clark, J.C. Green, S.E. Jackson, I.L. Fragala, E. Ciliberto and A.W. Coleman, J. Electron Spectrosc., 18 (1980) 61.

30 T. Vondrák, K. Mach and V. Varga, J. Organomet. Chem., 367 (1989) 69.

31 R. Benn and A. Rufinska, Angew. Chem., 98 (1986) 851.