ansa-Metallocene derivatives

XXI *. Syntheses of etheno-bridged *ansa*-titanocene derivatives by the McMurry reaction

Peter Burger and Hans H. Brintzinger *

Fakultät für Chemie, Universität Konstanz, Postfach 5560, W-7750 Konstanz (Germany)

Abstract

Novel olefin-linked biscyclopentadienyl ligands have been prepared by McMurry coupling reactions of benzoyl- and acetyl-cyclopentadienyl sodium. Reactions of the disodium salts with $TiCl_4$ or $TiCl_3 \cdot 3THF$ afford the alkene-bridged *ansa*-titanocene dichlorides. ^{13}C-NMR shifts of the bridge carbon atoms do not indicate any interaction between the olefin π-system and the metal.

Introduction

Chiral *ansa*-metallocenes of Group IV metals (of current interest as Ziegler–Natta catalysts for stereospecific α-olefin polymerisation [2–5]) with various types of interannular bridges X (a–f) (Fig. 1) have been synthesized. *ansa*-Metallocenes with long and flexible bridges, i.e. **a** and **d**, possess low stereorigidity. Increased distances between the bridge-head carbon atoms due to steric requirements of the bridge-atoms give rise to larger centroid-metal-centroid angles than in the corresponding un-bridged metallocenes [4,8,9]. Dimethylsilyl- (**c**) and methylene- (**f**) linked biscyclo-pentadienyl metal dichlorides, on the other hand, are very stereorigid but rather strained [4,6,7,14,15].

The geometry of ethano-bridged metallocenes (**e**) is almost identical to that of their unbridged congeners. The cyclopentadienyl (Cp) rings are staggered owing to an inclination of the C–C bond of the ethano bridge relative to the Cl–M–Cl bisector plane. This gives rise to two enantiomeric forms, δ and λ, both of which have been characterized by X-ray crystallographic studies [13,16,17]. In solution, these ethano-bridged metallocenes yield axially symmetric ^{1}H-NMR spectra, indi-cating a rapid fluctional interconversion between the δ and λ forms [13,16,17]. We were not able to freeze out this conformer interconversion even at $-90°C$ and 250 MHz; this indicates an energy barrier for this process of < 30 kJ/mol. As the disposition of substituents at the Cp rings is changed considerably by such a

---

* For Part XX see Ref. 1.
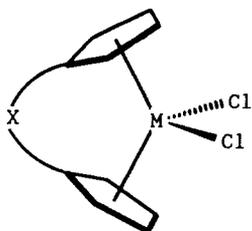
M = Ti, Zr, Hf

Fig. 1. X = −Me$_2$Si(CH$_2$)$_2$SiMe$_2$− [4] (a), −GeMe$_2$− [6] (b), −SiMe$_2$− [4,6,7] (c), −(CH$_2$)$_3$− [8,9] (d), −(CH$_2$)$_2$− [10,11], −(CMe$_2$)$_2$− [12,13] (e), −CH$_2$− [14], −CMe$_2$− [15] (f).

conformational interchange, the latter is likely to affect the stereoselectivity of *ansa*-metallocene catalysts, e.g. in α-olefin polymerisation.

To provide *ansa*-metallocenes with a higher degree of rigidity in their ligand frameworks, we have undertaken a study of novel etheno-bridged metallocenes, in which the five-membered chelate ring (which includes the bridging C atoms, the two bridge-head atoms and the metal centre) is kept planar by an olefinic π-system.

Results and discussion

The McMurry coupling reaction has proved to be useful for the synthesis of symmetric olefins [18,19]. Aldehydes and ketones, both aromatic and aliphatic, can be converted in high yields into symmetric alkenes by treatment with low-valent titanium, which is generated *in situ* by reduction of TiCl$_3$ or TiCl$_4$ with LiAlH$_4$, Li, K, Zn or KC$_8$ in tetrahydrofuran.

In a McMurry-type reaction acetylcyclopentadienyl sodium, prepared in high yield according to eq. 1 [20], was treated with highly reactive "Ti(0)" [21], obtained from the reaction of TiCl$_3$ with potassium-graphite (KC$_8$) in THF.
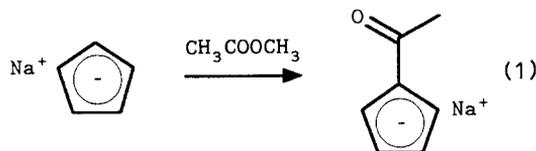
The product, probably a mixture of the *cis* and *trans* isomers of the dianion **1**, was treated, without isolation, with TiCl$_3$ · 3THF and this was followed by oxidation with HCl/O$_2$. From the mixture the alkene-bridged titanocene **2** was isolated analytically pure in 8% overall yield by sublimation *in vacuo* at 150°C (eq. 2).
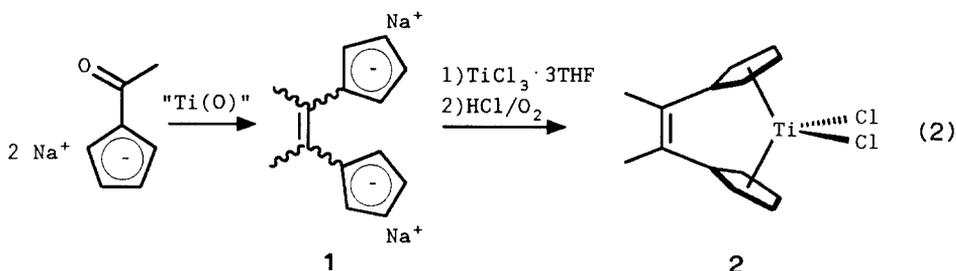
The low yield of **2** is probably attributable to preference of the McMurry coupling reaction for formation of the E isomer of **1** rather than the Z isomer arising from the larger steric demand of the cyclopentadienyl ring than of the methyl substituent. Similar results have been reported for the McMurry coupling of 1-acetyl-1'-ethyl-ferrocene [22], which leads to a mixture of *cis* and *trans* alkene products **3** in a ratio of $1:2.2$ (Z/E) (eq. 3).
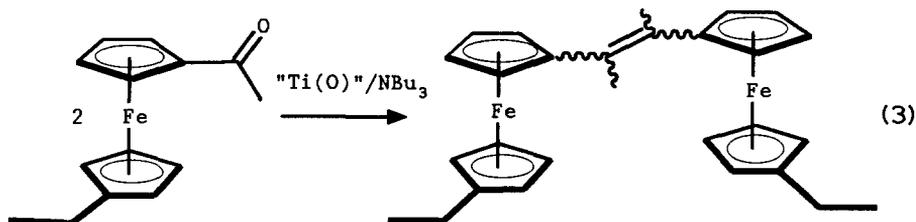

1 : 2.2 mixture of Z and E

The disappointingly low proportion of the *cis* isomer prompted a search for alternative synthetic procedures towards alkene-bridged titanocenes. An attractive possibility would be the closure of a *cis*-disubstituted ring as shown in eq. 4.
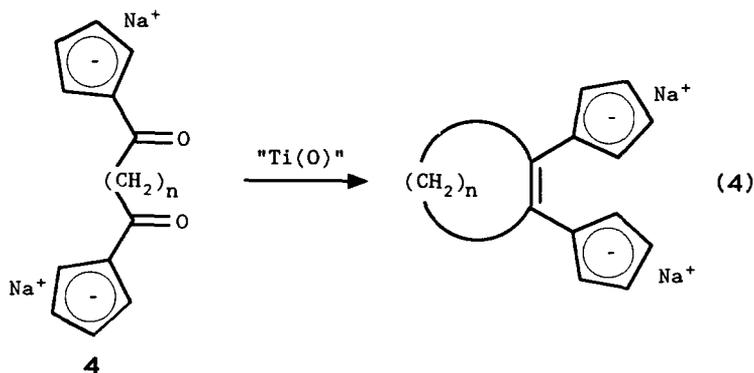

However, the required diketones **4** ($n = 2, 4$) could not be prepared by a route analogous to that in eq. 1; from such reactions only the ester condensation (Dieckmann or Claisen) products were isolated. An alternative possibility, the conversion of 1,1' bisacetyl-titanocene dichloride to the olefin-bridged *ansa*-metal-locene by an intramolecular McMurry reaction, was also ruled out because we were unable to find a reproducible synthesis for this functionalised titanocene dichloride.

Another approach to obtaining better *cis/trans* ratios involved increasing the steric demand of the substituent at the cyclopentadienyl keto-group. The steric requirements of a phenyl substituent would be comparable with that of a cyclo-pentadienyl ring, and hence should produce, in a McMurry reaction, approximately equal amounts of the isomers of the E- and the Z-configurations.

Benzoylcyclopentadienyl sodium **5** was obtained in 82% yield from the reaction of sodium cyclopentadienide with benzoic acid methyl ester. Reductive coupling of **5** with low-valent titanium gives the ligand **6**, which was isolated as an orange solid in 60% yield after recrystallisation (eq. 5).
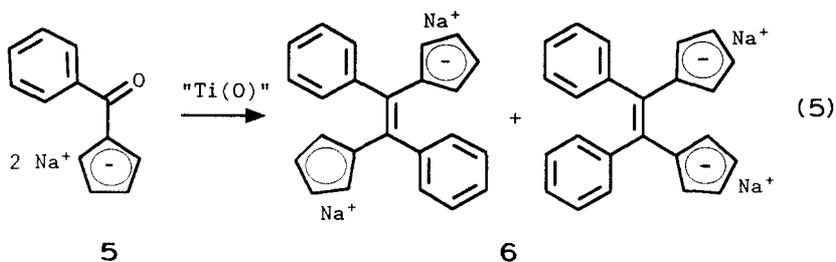
The ^{1}H-NMR spectrum (250 MHz) shows only two pseudotriplets for the cyclopentadienyl protons, and so gives no information about the *cis/trans* ratio. The isolated ligand **6**, probably a mixture of isomers, was used directly for the metathetic reaction with TiCl$_4$ in toluene (eq. 6). Pure complex **7** was obtained after recrystallisation in 25% yield.
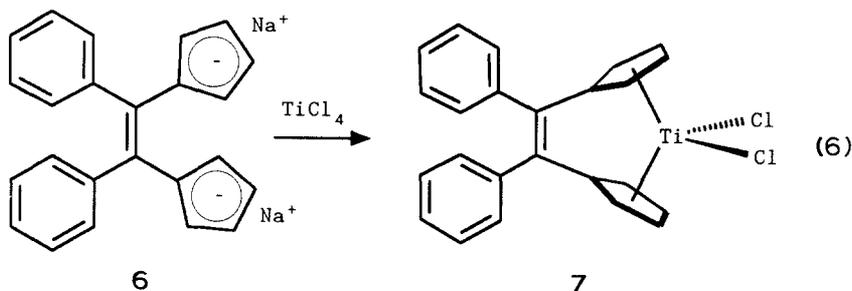
The overall yield of 15% for the two-step synthesis of the *ansa*-metallocene **7** (versus 8% for **2**) is in accord with our expectation that the *cis/trans* ratio of the isomers for the ligand synthesis (eqs. 1 and 5) might be improved by balancing the steric demand of the two substituents.

The ^{1}H-NMR spectra of **2** and **7**, which show two pseudotriplets for the cyclopentadienyl protons, and decoupled ^{13}C-NMR spectra of **2** and **7**, in which the signals from the cyclopentadienyl ring carbon atoms appear as three sharp singlets, indicate that the titanocenes possess C_{2v}-symmetry, at least on the NMR time scale.

The chemical shifts for the olefinic carbon atoms (133 ppm for **2** and 137 ppm for **7**) are comparable with that for free tetraphenylethene (141 ppm) [23] and hence do not reveal any interaction between the π-system of the bridge and the central metal in solution.

The chemical shifts (in CDCl$_3$ solution) for the ring protons in α- (**2**, 5.91; **7**, 5.99 ppm) and in β- (**2**, 6.92; **7**, 6.99 ppm) position are comparable with those found for the $-CH_2CH_2-$ [10] (6.09 and 6.91 ppm) and the $-CMe_2CMe_2-$ [12] (6.21 and 6.86 ppm) bridged titanocene dichlorides. Selective enhancement by Nuclear Overhauser effects of the high field ^{1}H-NMR triplet of **2** upon irradiation at the $C_2(CH_3)$-frequency indicates an assignment of the ^{1}H-NMR signals for the α- and the β-ring protons, which is in agreement with data for other C_2-linked *ansa*-titanocenes [1].

Experimental

Unless otherwise stated, all reactions were carried out under argon by standard Schlenk techniques, with solvents thoroughly dried and degassed.

Acetylcyclopentadienyl sodium was prepared as previously described by Rausch and coworkers [20]. Highly reactive "Ti(0)" was obtained by reduction of $TiCl_3 \cdot 3THF$ with KC_8 [21].

1. Synthesis of $(CH_3)_2C_2(C_5H_4)_2TiCl_2$ (2)

A suspension of 12.2 g (33 mmol) of $TiCl_3 \cdot 3THF$ and 13.5 g (0.1 mol) of KC_8 in 150 ml THF was refluxed for 1.5 h. The mixture was cooled to room temperature, and 3.2 g (16 mmol) of $NaC_5H_4COCH_3 \cdot THF$ was added. The mixture was refluxed for 12 h, then cooled to $-78°C$ and treated with 3 g (8 mmol) of $TiCl_3 \cdot 3THF$. The mixture was allowed to warm to room temperature, then kept for 8 h under reflux. It was then cooled to $-40°C$ and 2.5 ml of 5 M aqueous HCl were added. The mixture was stirred for 6 h under air and evaporated to dryness. The black residue was taken up in 100 ml CH_2Cl_2 and the solution washed three times with 50 ml of 5 M aqueous HCl. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated to dryness. Pure compound 2 was obtained by sublimation *in vacuo* (0.01 torr/150°C). Overall yield: 0.2 g (8%). ^1H- and ^{13}C-NMR data, see Table 1; mass spectrum, ions at m/e 298 (M^+) and 263 (M^+-Cl) with the expected isotope patterns. Elemental analysis: Found: C, 55.83; H, 4.85. $C_{14}H_{14}TiCl_2$ calc.: C, 55.86; H, 4.69%.

2. Synthesis of $NaC_5H_4COC_6H_5 \cdot THF$ (5)

A solution of sodium cyclopentadienide (0.25 mol) and 40.8 g (0.3 mol) of benzoic acid methyl ester in 300 ml THF was refluxed for 24 h. The solvent was removed *in vacuo* and replaced by 300 ml diethyl ether. The solid was filtered off, washed with 100 ml diethyl ether and dried *in vacuo* to give 54.1 g (82% theoretical yield) of a yellow air-sensitive solid. ^1H-NMR, see Table 2.

3. Synthesis of cis / trans $(C_6H_5)_2C_2(C_5H_4Na)_2 \cdot 4THF$ (6)

A procedure essentially analogous to that described in 1. was carried out with 5.3 g (20 mmol) of $C_6H_5COC_5H_4Na \cdot THF$ (5). At the end of the reaction the mixture was filtered through a pad of Celite to give a red filtrate. Removal of the solvent *in vacuo* and recrystallisation at $-78°C$ from diethyl ether/THF (1 : 1) yielded 3.8 g (60%) of 6. ^1H-NMR, see Table 3.

Table 1

^1H-NMR and proton-decoupled ^{13}C-NMR spectra of 2 in $CDCl_3$ at 25°C, δ in ppm (relative to $\delta(CHCl_3)$ 7.24 ppm and $\delta(^{13}CDCl_3)$ 77.0 ppm) at 250 MHz for ^1H and 62.5 MHz for ^{13}C (s, singlet, pt = pseudotriplet with $J(H,H)$ = 2.5 Hz)

6.92	(pt, 4H)	β-C_5H_4
5.91	(pt, 4H)	α-C_5H_4
1.97	(s, 6H)	$C_2(CH_3)_2$
138.1		C(1)
133.1		C(bridge)
129.3		C(3,4)
115.3		C(2,5)
19.4		CH_3

Table 2

^{1}H-NMR spectrum of benzoylcyclopentadienyl sodium (**5**); in THF-d_8 at 25°C, δ in ppm (relative to $\delta(C_4H_8O)$ 3.58 ppm) at 250 MHz (mp = multiplet, ump = unresolved multiplet due to keto-fulvenolate resonance [24–27])

7.76–7.72	(mp, 2H)	C_6H_5
7.28–7.26	(mp, 3H)	C_6H_5
6.38	(ump, 2H) [a]	C_5H_4(H2,5)
5.98	(ump, 2H) [b]	C_5H_4(H3,4)
3.60–3.55	(m, 4H)	C_4H_8O
1.75–1.68	(m, 4H)	C_4H_8O

[a] Half line width of 24 Hz. [b] Half line width of 12 Hz.

Table 3

^{1}H-NMR of **6** in THF-d_8 at 25°C, δ in ppm (relative $\delta(C_4H_8)$ 3.58 ppm) at 250 MHz (ump = unresolved multiplet, pt = pseudotriplet with J(H,H) = 2.4 Hz, mp = multiplet)

7.10	(ump, 10H)	C_6H_5
6.85	(pt, 4H)	C_5H_4
6.10	(pt, 4H)	C_5H_4
3.53–3.47	(m, 16H)	C_4H_8O
1.69–1.62	(m, 16H)	C_4H_8O

4. Synthesis of $(C_6H_5)_2C_2(C_5H_4)_2TiCl_2$ (7)

1 g (5 mmol) of $TiCl_4$ was added from a syringe to a suspension of 3.2 g (50 mmol) **6** in toluene at −78°C. The mixture was kept under reflux for 6 h, then cooled to room temperature. The solvent was removed *in vacuo* and the residue was taken up in 80 ml CH_2Cl_2 and the solution extracted twice with 30 ml of 5 *M* aqueous HCl. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. After recrystallisation from toluene, the pure compound was obtained in 25% yield. Titanocene **7** was identified by its ^{1}H- and ^{13}C-NMR spectra (Tab. 4) and from its mass spectrum (parent ion at m/e 422, m/e 387 M^+ − Cl; with appropriate mass distribution). Elemental analysis: Found: C, 67.09; H, 4.54. $C_{24}H_{18}TiCl_2$ calc.: C, 67.8; H, 4.27%.

Table 4

^{1}H-NMR and proton-decoupled ^{13}C-NMR spectra of **7** in $CDCl_3$ at 25°C, δ in ppm (relative to $\delta(CHCl_3)$ 7.24 ppm and $\delta(^{13}CDCl_3$ 77.0 ppm) at 250 MHz for ^{1}H and 62.5 MHz for ^{13}C (mp = multiplet, pt = pseudotriplet with J(H,H) = 2.5 Hz)

7.16–7.08	(mp, 10H)	C_6H_5
6.99	(pt, 4H)	β-C_5H_4
5.99	(pt, 4H)	α-C_5H_4
137.3		C(1)
137.2		C(bridge)
135.3, 130.1, 128.8, 128.5		C_6H_5
128.4		C(3,4)
116.0		C(2,5)

Acknowledgements

References

1 S. Gutmann, P. Burger, M.-H. Prosenc and H.H. Brintzinger, J. Organomet. Chem., 397 (1990) 21.
2 J.A. Ewen, J. Am. Chem. Soc., 106 (1984) 6355; W. Kaminsky, K. Külper, H.H. Brintzinger and F.R.W.P. Wild, Angew. Chem., 97 (1985) 507.
3 T. Mise, S. Miaya and H. Yamazaki, Chem. Lett., (1989) 1853.
4 W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck and A. Winter, Angew. Chem., 101 (1989) 1536.
5 W. Röll, H.H. Brintzinger, B. Rieger and R. Zolk, Angew. Chem., 102 (1990) 339.
6 H. Köpf and W. Kahl, J. Organomet. Chem., 64 (1974) C37; H. Köpf and W. Klouras, Z. Naturforsch. B, 38 (1983) 321; N. Klouras and H. Köpf, Monatsh. Chem., 112 (1981) 887.
7 H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz and H.H. Brintzinger, J. Organomet. Chem., 369 (1989) 359.
8 W. Röll, L. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 322 (1987) 65; H. Schnutenhaus and H.H. Brintzinger, Angew. Chem., 91 (1979) 837.
9 M. Hillman and A.J. Weiss, J. Organomet. Chem., 42 (1972) 123.
10 J.A. Smith, J. von Seyerl, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 173 (1979) 175.
11 F.R.W.P. Wild, M. Wasiucionek, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 288 (1985) 63.
12 H. Schwemlein and H.H. Brintzinger, J. Organomet. Chem., 254 (1983) 69.
13 S. Gutmann, P. Burger, H.U. Hund, J. Hofmann and H.H. Brintzinger, J. Organomet. Chem., 369 (1989) 343.
14 T.J. Katz and N. Acton, Tetrahedron Lett., 28 (1970) 2497.
15 J.A. Ewen, R.L. Jones and A. Razavi, J. Am. Chem. Soc., 110 (1988) 6255.
16 J. Diebold, Diplomarbeit Universität Konstanz, 1989.
17 J. Diebold, S. Gutmann, H.U. Hund, P. Burger and H.H. Brintzinger, unpublished results.
18 J.E. McMurry, Acc. Chem. Res., 16 (1983) 405.
19 P.C. Auderset, T.C.C. Gartenmann and E.R.F. Gesing, Kontakte (Darmstadt), 3 (1985) 14; Y. Dang and H.J. Geise, Janssen Chim. Acta, Vol. 6, No. 3 (1988) p. 3 and Vol. 7, No. 1 (1989) p. 3; C. Betschart and D. Seebach, Chimia, 43 (1989) 39.
20 R.D. Rogers, J.L. Atwood, M.D. Rausch, D.W. Macomber and W.P. Hart, J. Organomet. Chem., 238 (1982) 79.
21 A. Fürstner and H. Weidmann, Synthesis, (1987) 1071.
22 T.-Y. Dong, T.-J. Ke, S.-M. Peng and S.-K. Yeh, Inorg. Chem., 28 (1989) 2103.
23 T.W. Proulx and W.B. Smith, J. Magn. Reson., 23 (1976) 477.
24 G. Boche, R. Eiben and W. Thiel, Angew. Chem., 94 (1982) 703.
25 W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.
26 M. Arthurs, H.K. Al-Daffee, J. Haslop, G. Kubal, M.D. Pearson, P. Thatcher and E. Curzon, J. Chem. Soc., Dalton Trans., (1987) 2615.
27 M. Arthurs, P. Gross, G. Kubal, L. Paniwnyk and E. Curzon, J. Organomet. Chem., 366 (1989) 223.