

# Formation of tetrabenzodispiro[4.0.4.3]tridecatetraene by a titanium mediated fluorenyl coupling reaction <sup>☆</sup>

Cornelia Fritze, Gerhard Erker <sup>\*</sup>, Roland Fröhlich

*Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany*

22 February 1995; in revised form 9 March 1995

## Abstract

Treatment of 1,3-propanediol-ditosylate with fluorenyllithium yields 1,3-bis(fluorenyl)propane (**5**). Subsequent addition of methyl-lithium gives the corresponding dilithio compound **6**. Dilithio-1,3-bis(fluorenyl)propane (**6**) was treated with titanium tetrachloride to yield the organic tetrabenzodispiro[4.0.4.3]tridecatetraene product **7**, presumably formed by means of a carbon–carbon coupling reaction involving substituted fluorenyl radicals. The organic compounds **5** and **7** were identified by X-ray crystal structure analyses.

**Keywords:** Titanium; Tetrabenzodispiro(4,3,4)tridecatetraene; Coupling reaction; Metallocenes; Crystal structure

## 1. Introduction

$\eta^5$ -Cyclopentadienyl,  $\eta^5$ -indenyl, and  $\eta^5$ -fluorenyl complexes of the Group 4 transition metals are of great importance in organometallic chemistry and catalysis. Such compounds have found much use as stoichiometric reagents in organic synthesis and there is currently an enormous interest in homogeneous Ziegler-type catalysts derived of such organometallic systems [1]. The  $\eta^5$ -Cp-type ligands usually become attached to the titanium, zirconium or hafnium center by metathetical exchange using the metal halide and the corresponding Cp-anion equivalent. A few cases have become known where the combination of the Group 4 metal halide with an Cp-anion derivative can give rise to an oxidative Cp–Cp coupling reaction. Two mechanistically distinctly different types of Cp-coupling reaction have been described in the literature. One takes place at the already formed cyclopentadienyl metal complex and makes use of the presence of other suitable ligands attached to the early transition metal center to serve as the active reagents for carrying out the formal ligand

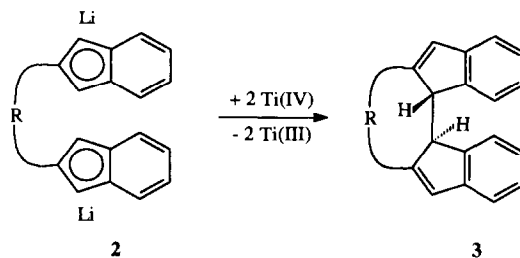
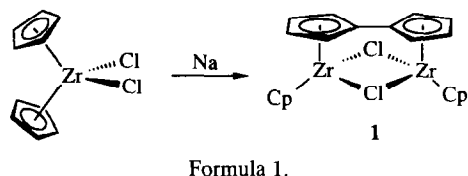
oxidation step in a sequence of two-electron transformations involving only closed-shell intermediates. The formation of a dinuclear pentafulvalene dizirconium complex (**1**), as depicted below, is a typical example [2], and pentafulvalene early transition metal complex chemistry has benefitted enormously by opening up this elegant synthetic entry [3].

There is also the possibility that single-electron transfer is favored over nucleophilic halide displacement when a Cp-anion derivative is treated with a metal halide. In a suitable system this may also lead to Cp coupling, in this case involving Cp radical chemistry, although such a pathway is much less frequently observed. The reaction of a substituted bis-indenyl system (**2**, R = binaphthyl) with  $\text{TiCl}_4$  is a typical although rare example of such a coupling reaction, that in this case gives rise to the formation of the di-indene derivative **3** [4].

We have now found an interesting example of a related oxidative coupling reaction that takes place by treating a fused bis-fluorenyl dianion system with titanium tetrachloride. It is likely that this reaction also involves the intermediate formation of the organic radical systems by means of an electron transfer reaction. In this case the carbon–carbon coupling step proceeds intramolecularly and leads to the formation of a dispiro hydrocarbon product.

<sup>☆</sup> Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

<sup>\*</sup> Corresponding author.



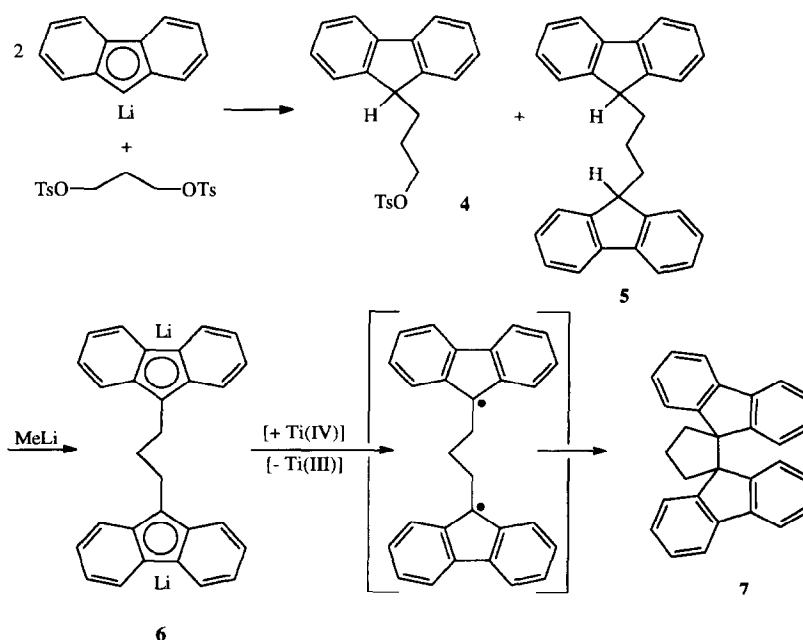
## 2. Results and discussion

Fluorenyllithium was reacted with the ditosylate of 1,3-dihydroxypropane in ether to give a mixture of the monosubstitution and disubstitution products. 1,3-Bis(fluorenyl)propane (**5**) was separated from the monotosylate (**4**) by chromatography and isolated with a 34% yield. Subsequent treatment of **5** with two molar equivalents of methyllithium in ether led to the formation of the corresponding dilithio compound **6**. Dilithio-1,3-bis(fluorenyl)propane (**6**) was characterized by NMR spectroscopy. It exhibits  $^1\text{H}$  NMR resonances at  $\delta = 2.10$  (2H) and 3.24 (4H) ppm of the bridging trimethylene unit ( $^{13}\text{C}$  NMR at  $\delta = 26.5$  (C-2') and 68.5 (C-1', C-3') ppm). In tetrahydrofuran- $d_8$  the  $^{13}\text{C}$  NMR signals of the symmetry equivalent fluorenyl groups of **6** appear at  $\delta = 96.1$  (C-9), 107.1, 114.8 (C-1, C-8, C-4, C5), 118.7, 118.9 (C-2, C-7, C-3, C-6), 122.3 and 136.0 (C-10, C-13, C-11, C-12) ppm.

Dilithio-1,3-bis(fluorenyl)propane (**6**) was treated with titanium tetrachloride at  $-50^\circ\text{C}$  in pentane. The mixture was warmed to room temperature and worked up after 2 days to give the tetrabenzodispiro[4.0.4.3]tridecatetraene (**7**), isolated as a crystalline material with a 23% yield. The organic spiro compound exhibits  $^1\text{H}$

NMR signals of the trimethylene group at  $\delta = 2.40$  (2H) and 2.50 (4H) ppm and the corresponding  $^{13}\text{C}$  NMR resonances at  $\delta = 23.7$  and 35.1 ppm. The  $^{13}\text{C}$  NMR signal of the symmetry equivalent spiro bridgehead carbon atoms appears at  $\delta = 66.4$  ppm.

Both the educt and the final product hydrocarbons **5** and **7** were characterized by X-ray crystal structure analyses. In **5** an extended  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  chain connects the two fluorenyl substituents (Fig. 1). In the crystal the fluorenyl groups are not symmetry equivalent. The C(13)–C(14) (1.530(4) Å) and C(15)–(16) (1.521(4) Å) vectors are oriented in an anti-periplanar manner at the connecting C(14)–C(15) bond (1.516(4) Å), whereas the C(14)–C(15) and C(16)–C(17) (1.543(3) Å) vectors are found in a *gauche* arrangement at the connecting C(15)–C(16) linkage. As often observed, the C–C–C angles of the three carbon bridge in **5** deviate markedly from tetrahedral [5] (e.g. C(13)–C(14)–C(15),  $114.2(2)^\circ$ ; C(14)–C(15)–C(16),  $113.9(2)^\circ$ ; C(15)–C(16)–C(17),  $115.9(2)^\circ$ ; C(18)–C(17)–C(16),  $114.1(3)^\circ$ ; C(12)–C(13)–C(14),  $114.4(2)^\circ$ ). The C–C–C



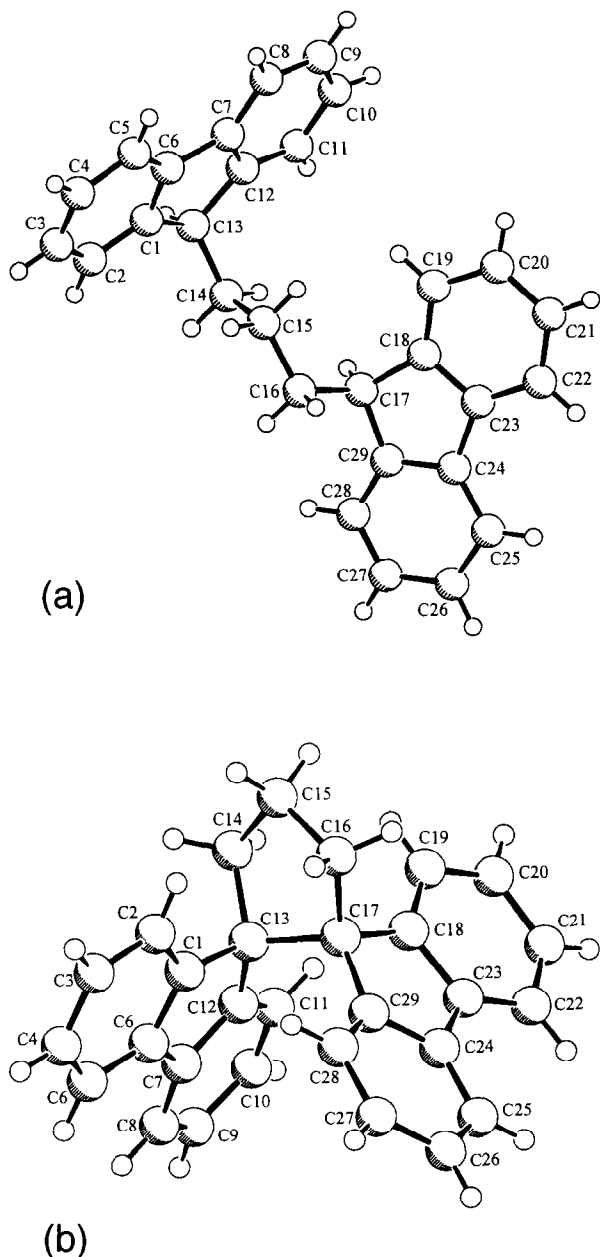


Fig. 1. Views of molecular geometries of (a) **5** and (b) **7**.

bond angles at the  $sp^3$ -hybridized carbon centers inside the five-membered ring are  $101.7(2)^\circ$  ( $C(12)-C(13)-C(1)$ ) and  $102.2(2)^\circ$  ( $C(18)-C(17)-C(29)$ ) respectively.

The crystal structure analysis of **7** shows two independent molecules in the unit cell that are chemically identical. Both are close to  $C_2$  symmetric owing to a twist conformation of the saturated five-membered ring. The central  $C(13)-C(14)$  and  $C(16)-C(17)$  bond lengths ( $1.542(2)$  and  $1.545(2)$  Å (molecule 1);  $1.542(2)$  and  $1.547(2)$  Å (molecule 2)) are typical for unstrained  $C(sp^3)-C(sp^3)$   $\sigma$  bonds [6]. Similar values are found for the  $C(14)-C(15)$  ( $1.540(2)$  and  $1.540(2)$  Å) and  $C(15)-C(16)$  ( $1.543(2)$  and  $1.543(2)$  Å) linkages,

whereas the central  $C(13)-C(17)$  bond of the dispiro framework is markedly longer at  $1.588(2)$  Å (molecule 2:  $1.587(2)$  Å). The  $C(12)-C(13)-C(14)$  angle is  $115.70(12)^\circ$ , whereas the adjacent angle between the spiro components ( $C(1)-C(13)-C(14)$ ) is only  $110.91(12)^\circ$  owing to the  $C_2$  distortion. The C–C–C angles inside the five-membered rings are small (e.g.  $C(1)-C(13)-C(12)$ ,  $101.27(12)^\circ$ ;  $C(14)-C(13)-C(17)$ ,  $101.87(11)^\circ$ ).

A detailed mechanistic description of this titanium-mediated C–C coupling reaction must await further experimental details. However, it is likely that the reaction sequence leading to the formation of the dispiro[4.0.4.3]tridecatetraene framework involves the intermediate generation of a trimethylene-linked fluorenyl radical system. It may be that in this case the electron transfer pathway is favored over the normal double nucleophilic substitution reaction because that would produce a slightly strained ansa-metallocene system [7]. Whether such a titanium-mediated Cp-coupling reaction can be developed into useful general methods for synthesizing organic target compounds containing spiro-annulated five-membered ring systems will be explored in our laboratory.

### 3. Experimental details

#### 3.1. General conditions

All reactions with organometallic reagents were carried out in inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. For characterization the following spectrometers were used: Bruker AC 200 P NMR spectrometer ( $^1H$ , 200.13 MHz;  $^{13}C$ , 50.3 MHz), Bruker ARX 300 NMR spectrometer ( $^1H$ , 300.1 MHz;  $^{13}C$ , 75.5 MHz); Nicolet 5DXC Fourier transform IR spectrometer. The X-ray crystal structure analyses were carried out on an Enraf–Nonius CAD 4 diffractometer.

#### 3.2. Reaction of fluorenyllithium with the ditosylate of 1,3-propanediol

Fluorene (20.3 g, 122 mmol) was dissolved in 200 ml of THF. At  $0^\circ C$ , 97.6 ml of a 1.6 M *n*-butyllithium solution in *n*-hexane was added dropwise. The mixture was stirred over night at room temperature and then the solvent was removed in vacuo. Pentane (150 ml) was added and the precipitated yellow fluorenyllithium reagent collected by filtration (20.6 g; 97% yield;  $^1H$  NMR ([benzene- $d_6$ -THF- $d_8$ ):  $\delta$  6.13 (s, 1H), 6.88 (m, 2H), 7.21 (m, 2H), 7.64 (m, 2H), 8.28 (m, 2H) ppm). A solution of 10.3 g (26.8 mmol) of the 1,3-propanediol-ditosylate was dissolved in 150 ml of ether and added dropwise to a solution of 9.2 g (53.6 mmol) of fluo-

renyllithium in 70 ml of THF at  $-78^{\circ}\text{C}$ . The mixture was allowed to warm to room temperature and stirred over night. It was then cooled to  $0^{\circ}\text{C}$  and hydrolyzed by slowly adding 50 ml of water. The reaction mixture was extracted with ether (100 ml), the organic phase washed with water ( $3 \times 100$  ml) and dried over magnesium sulfate. Solvent was removed in vacuo and the residue chromatographed on a silical gel column (60 cm) which was pre-treated with triethylamine. Elution with pentane:ether (9:1) gave the 1,3-difluorenylpropane product **5**. Subsequent elution with pentane:ether (4:1) gave the monosubstitution product **4**. Remaining 1,3-propanediol-ditosylate starting material was then recovered from the column by elution with ether.

**4**: Yield 2.44 g (24%) isolated; melting point (m.p.),  $91^{\circ}\text{C}$ , Anal. Found: C, 73.00; H, 5.75.  $\text{C}_{23}\text{H}_{22}\text{O}_3\text{S}$  (378.5) Calc.: C, 72.99; H 5.86%  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.27–1.38 (m, 2H), 2.04–2.13 (m, 2H) and 3.87 (t, 2H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OSO}_2\text{R}$ ), 2.41 (s, 3H,  $\text{CH}_3$ ), 3.97 (t, 1H, fluorenyl 9-H), 7.24–7.44 (m, 8H), 7.67–7.73 (m, 4H), fluorenyl and tosyl CH); ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.6 ( $\text{CH}_3$ ), 24.4 and 28.4 ( $\text{CH}_2$ ), 46.5 (fluorenyl C-9), 70.7 ( $\text{CH}_2\text{-OSO}_2\text{R}$ ), 119.8, 124.1, 127.0, 127.1, 127.7, 129.7 (CH), 133.1, 141.2, 144.6, 146.3 (C) ppm. IR (KBr):  $\nu$  3065, 3038, 3016, 1599, 1451, 952, 850, 841, 744 (fluorenyl and aryl), 2990, 2958, 2909, 2876, 2859, 1476 (alkyl), 1351, 1187, 1173, 1097 ( $-\text{OSO}_2\text{-Ar}$ ), 666, 554  $\text{cm}^{-1}$ .

**5**: Yield, 3.43 g (34%) isolated after crystallization from the pentane–ether eluate; m.p.,  $118^{\circ}\text{C}$ . Anal. Found: C, 92.11; H, 6.46.  $\text{C}_{29}\text{H}_{24}$ (372.5) Calc.: C, 93.51; H, 6.49%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.23–1.41 (m, 2H) and 1.93 (m, 4H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 3.88 (t, 2H, fluorenyl 9-H), 7.22–7.43 (m, 12H, fluorenyl CH), 7.69 (m, 4H, fluorenyl CH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  29.7 and 33.3 (double intensity,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 47.1 (fluorenyl C-9), 119.8, 126.8 (double intensity, fluorenyl CH), 141.0 and 147.4 (fluorenyl C) ppm. IR (KBr):  $\nu$  3063, 3038, 3013, 1448, 740, 739 (fluorenyl), 2937, 2909, 2898, 2867, 2853, 2837, 1477  $\text{cm}^{-1}$ , X-ray crystal structure analysis of **5**: crystal size,  $0.7 \times 0.3 \times 0.2$  mm; monoclinic space group,  $P2_1/n$ ;  $a = 11.829(2)$ ,  $b = 5.2081(5)$  and  $c = 33.515(4)$  Å;  $\beta = 90.97(1)^{\circ}$ ;  $V = 2064.4(5)$  Å<sup>3</sup>; graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å); temperature,  $293(2)$  K;  $\theta$  range for data collection,  $2.43\text{--}23.98^{\circ}$ ; 3621 reflections collected; 3211 independent reflections; 3206 reflections observed; 262 refined parameters; goodness of fit on  $F^2$ , 1.018;  $\rho(\text{calc.}) = 1.198$  g  $\text{cm}^{-3}$ ;  $R = 0.049$ ;  $wR^2 = 0.124$ ; programs used, SHELX 86 and 93, SCHAKAL.

Details of the X-ray crystal structure analyses of the **5** and **7** (see below) are available upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-401616, 401617, the names of the authors and the journal citation.

### 3.3. Dilithio-1,3-bis(fluorenyl)propane (**6**)

1,3-Bis(fluorenyl)propane (2.46 g, 6.60 mmol) was dissolved in 50 ml of ether. At  $0^{\circ}\text{C}$ , 8.25 ml of a 1.6 M solution of methylolithium (13.2 mmol) in ether was added dropwise with stirring. The mixture was stirred over night, then the solvent was removed in vacuo to give 2.49 g (98%) of the dilithio compound that was characterized by NMR spectroscopy.  $^1\text{H}$  NMR ( $\text{THF-}d_8$ ):  $\delta$  2.10 (br m, 2H), 3.24 (m, 4H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 6.29 (m, 4H), 6.76 (m, 4H), 7.38 (m, 4H), 7.83 (m, 4H, fluorenyl CH), ppm  $^{13}\text{C}$  NMR ( $\text{THF-}d_8$ ):  $\delta$  26.5 ( $\text{CH}_2$ ), 68.5 (double intensity,  $\text{CH}_2$ ), 96.1 (fluorenyl C-9), 107.1, 114.8, 118.7, 118.9 (CH), 122.3, 136.0 (C) ppm.

### 3.4. 1,2,3,4,7,8,9,10-Tetrabenzodispiro [4.0.4.3] trideca-1,3,7,9-tetraene (**7**)

Titanium tetrachloride (615 mg, 3.24 mmol) was added to a suspension of 2.49 g (6.49 mmol) of dilithio-1,3-bis(fluorenyl)propane (**6**) in 50 ml of pentane at  $-50^{\circ}\text{C}$ . The mixture was allowed to warm to room temperature and stirred for a period of 2 days. It was then filtered through ca. about 1 g of silicalgel. Upon concentration of the filtrate in vacuo the organic product **7** crystallized. The crystals were collected by filtration to give 558 mg (23%) of **7**; m.p.,  $214^{\circ}\text{C}$ .  $^1\text{H}$  NMR (benzene- $d_8$ ):  $\delta$  2.40 (m, 2H) and 2.50 (m, 4H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 6.95–7.05 (m, 12 H, fluorenyl CH), 7.18–7.24 (m, 4H, fluorenyl CH) ppm,  $^{13}\text{C}$  NMR (benzene- $d_8$ ): see text. IR (KBr):  $\nu$  3064, 3032, 1444, 769, 749 (fluorenyl), 2966, 2926, 2878, 1477 (alkyl), 624  $\text{cm}^{-1}$ . X-ray crystal structure analysis of **7**: crystal size,  $0.6 \times 0.4 \times 0.3$  mm; triclinic space group,  $P1$ :  $a = 7.582(1)$ ,  $b = 15.793(1)$  and  $c = 17.271(2)$  Å,  $\alpha = 102.30(1)$ ,  $\beta = 92.46(1)$  and  $\gamma = 91.03(1)^{\circ}$ ;  $V = 2018.0(4)$  Å<sup>3</sup>; graphite-monochromated Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.54178$  Å); temperature,  $293(2)$  K;  $\theta$  range for data collection,  $2.62\text{--}74.23^{\circ}$ ; 8981 reflections collected; 8232 independent reflections; 7072 reflections observed; 524 refined parameters; goodness of fit on  $F^2$ , 1.032;  $\rho(\text{calc.}) = 1.219$  g  $\text{cm}^{-3}$ ;  $R = 0.058$ ;  $wR^2 = 0.165$ .

### Acknowledgments

Financial support from the Fonds der Chemischen Industrie and the Alfred Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

### References

- [1] M. Aulbach and F. Küber, *Chem. Unserer Zeit*, 28 (1994) 197 and references cited therein.
- [2] T. Cuenca and P. Royo, *J. Organomet. Chem.*, 293 (1985) 61; T.V. Ashworth, T. Cuenca, E. Herdtweck and W.A. Herrmann,

- Angew. Chem.*, 98 (1986) 278; *Angew. Chem., Int. Edn. Engl.*, 25 (1986) 289, S. Gambarotta and M.Y. Chiang, *Organometallics*, 6 (1987) 897.
- [3] W.A. Herrmann, B. Menjón and E. Herdtweck, *Organometallics*, 10 (1991) 2134, and references cited therein.
- [4] W.W. Ellis, T.K. Hollis, W. Odenkirk, J. Whelan, R. Ostrander, A.L. Rheingold and B. Bosnich, *Organometallics*, 12 (1993) 4391.
- [5] R. Boese, D. Bläser, N. Niederprüm, M. Nüsse, W.A. Brett, and P.v.R. Schleyer, *Angew. Chem.*, 104 (1992) 356; *Angew. Chem., Int. Edn. Engl.*, 31 (1992) 314.
- [6] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans., II*, (1987) S1.
- [7] For representative examples see G. Erker, C. Mollenkopf, M. Grehl, R. Fröhlich, C. Krüger, R. Noe and M. Riedel, *Organometallics*, 13 (1994) 1950, and references cited therein.