EXCEPTIONALLY SYMMETRIC CRYSTAL STRUCTURE OF (PENTABENZYLCYCLOPENTADIENYL)(CYCLOOCTATETRAENE)TITANIUM(III)

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Complex [Ti(III)(η^8-C_8H_8)(η^5-C_5Bn_5)] (**1**) was prepared by salt metathesis reaction of [TiCl(η^8-C_8H_8)(thf)]$_2$ with LiC_5Bn_5 and characterized by ESR and UV-near-IR spectra. Its crystal structure is symmetric with respect to a mirror plane involving the titanium atom and one of the benzyl groups.

Keywords: Metallocenes; Titanocenes; Titanium; Sandwich complexes; Cyclooctatetraene; X-ray diffraction; ESR spectroscopy; Conformation analysis.

Transition metal complexes bearing one pentabenzyl-η^5-cyclopentadienyl (η^5-$C_5Bn_5^-$) auxiliary ligand (C_5Bn_5) are known for a limited number of metals although their synthesis can in many cases follow protocols for obtaining pentamethyl-η^5-cyclopentadienyl analogs. The C_5Bn_5 ligand has been used to stabilize the metal complexes due to its bulkiness which effectively exceeds that of the widely used pentamethyl-η^5-cyclopentadienyl[1,2]. Furthermore, the coordination behavior of the ligand is versatile because two conformations of the benzyl groups can occur, with the phenyl group declined away from the metal (up) or inclined to the metal (down). Generally, a crown-like conformer with all Bn groups up (I) arises when the other coordination hemisphere of the metal is occupied by other ligands. In the case of coordination vacancy, conformers with one Bn group down (II) or with two Bn groups down (III) are obtained. Crystal structures of the crown-like conformers I are known for [Ti{(μ-Cl)$_2$AlCl$_2$}$_2$(C_5Bn_5)] [3], [Fe{η^2-S_2CNMe_2}$_2$(C_5Bn_5)]$^+$[PF_6]$^-$ (lit.[4]), [$MoCl_3$(η^2-$COCH_3$)(C_5Bn_5)] and

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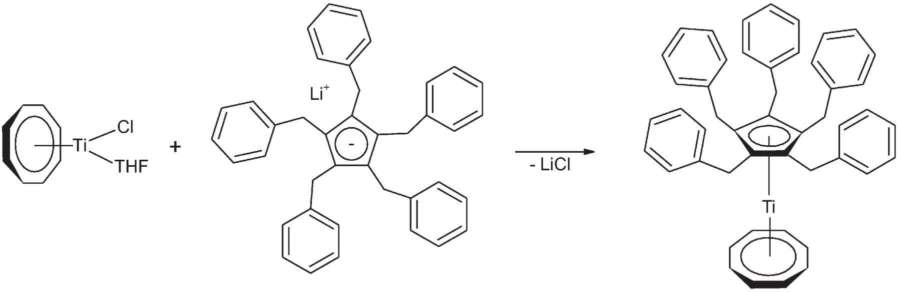
$[WCl_4(C_5Bn_5)]$ [5]. The most abundant conformers II were found in the complexes $[TiCl_2(\eta^5\text{-}C_5H_5)(C_5Bn_5)]$, $[Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5H_5)(C_5Bn_5)]$ [6], $[\{Ti(\mu\text{-}Cl)Cl(C_5Bn_5)\}_2]$ [7], $[Co(CO)_2(C_5Bn_5)]$ [8], $[Mn(CO)_3(C_5Bn_5)]$ [9], $[Mo(Me)(CO)_3(C_5Bn_5)]$, $[W(Me)(CO)_3(C_5Bn_5)]$, $[MoCl(CO)_3(C_5Bn_5)]$ [5a], and $[MoI(CO)_3(C_5Bn_5)]$ [5b]. Conformer III was found only in the trigonally coordinated Ti complex $[TiCl(\eta^5\text{-}C_5H_5)(C_5Bn_5)]$ where the benzyl group above the chlorine atom is up and its neighbours on both sides are down[6]. Of the complexes containing two C_5Bn_5 ligands, only decabenzylferrocene is known, prepared by reaction of $FeCl_2$ with lithium cyclopentadienide. Its crystal structure proved the staggered cyclopentadienyl rings and the up-orientation of all phenyl groups with respect to the metal, oriented in a propeller fashion. The crystallographically asymmetrical molecule crystallizes in monoclinic space group $P2_1/c$ with two molecules of toluene[9,10]. It is of interest that its ferrocenium cation is centrosymmetric with the iron atom lying on an inversion centre, and fits the D_{5d} symmetry[11].

For titanium, there is little chance to prepare decabenzyltitanocene in a conventional way: an attempt to synthesize the parent compound $[TiCl_2(C_5Bn_5)_2]$ failed while the synthesis of the less bulky $[TiCl_2(\eta^5\text{-}C_5H_5)(C_5Bn_5)]$ appeared to be feasible[6]. Except a few stable monomeric titanocenes bearing tetramethyl(triorganylsilyl)-substituted cyclopentadienides $[Ti\{\eta^5\text{-}C_5Me_4(SiR^1R^2{}_2)\}_2]$ (R^1 = t-Bu, R^2 = Me [12a]; R^1 = R^2 = Me [12b]; R^1 = CH_2CH_2Ph, R^2 = Me; R^1 = Me, R^2 = Ph [12c]), for which crystal structures were determined, only decamethyltitanocene was obtained although not crystallographically characterized due to inherent contamination with a product of rearrangement, $[TiH(\eta^5\text{-}C_5Me_5)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)]$ [13]. With respect to the stable titanocene formation, the Bn group is less suitable substituent than Me group because it is a weaker electron donor[3] and shows even higher propensity to hydrogen abstraction by the titanium centre than the methyl group[14]. In our effort to prepare titanocene with the C_5Bn_5 ligand we have undertaken a synthesis of a mixed titanocene bearing cyclooctatetraene dianion $\eta^8\text{-}C_8H_8{}^{2-}$ (cot) as the other aromatic ring[15]. In this case the central Ti(III) atom shows no tendency to abstract hydrogen from either of the ligands. Below, we report the synthesis, crystal structure and some spectroscopic properties of the $[Ti(III)(cot)(C_5Bn_5)]$ complex.

RESULTS AND DISCUSSION

Compound $[Ti(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Bn_5)]$ (**1**) was obtained by the reaction of half equivalent of dimeric $[TiCl(cot)(thf)]_2$ (lit.[16]) with one equivalent of LiC_5Bn_5 (lit.[17]) (Eq. (*1*)), affording thus a complementary method to the two known methods for preparing [Ti(cot)(Cp*)] (Cp* = η^5-C_5Me_5) which consist in the reduction of [$TiCl_3$(Cp*)] by magnesium in the presence of cyclooctatetraene in tetrahydrofuran[18] or the reaction between [$TiCl_3$(Cp*)] and K_2(cot)[19]. Using equimolar quantities of the reagents the yield was nearly quantitative, some loss occurred in purification of **1** from LiCl because **1** is nearly insoluble in hexane and low-soluble in toluene, slightly better than LiCl only.



Eq. (*1*)

1

Compound **1** is thermally very robust, pale green solid crystallizing from toluene with one toluene molecule of crystallization. In spite of the presence of toluene, the crystals of **1** melt as high as 230 °C. Its EI-MS spectrum shows the molecular ion isotopic pattern as the base peak and a similar isotopic pattern of the fragment peak at *m/z* 282. The light green paramagnetic d^1 complex **1** dissolves in toluene to give a pale blue solution; this color change is reversible upon evaporation. The electronic absorption spectrum in toluene displays a low-intensity absorption band at 10 640 cm^{-1} and absorption band of medium intensity at 17 300 cm^{-1}. These bands were found somewhat closer in [Ti(cot)(Cp)] (Cp = η^5-C_5H_5) (11 360 and 13 980 cm^{-1}) and assigned to $A_1 \rightarrow {}^3E_1$ and ${}^1E_2 \rightarrow A_1$ transitions, respectively. The ground level a_1 bearing the unpaired electron is essentially $d_z{}^2$ whereas the lower-energy $1e_2$ consists of metal-cot orbital combination and the upper level $3e_1$ of metal-Cp orbital combination[20a]. A series of high intensity shoulders at 24 510, 26 040, 27 625, and 30 303 cm^{-1} resemble the vibronic structure observed in electronic transition of aromatic compounds. The ESR spectrum of **1** in toluene solution affords a well discernible septuplet with a_H = 0.32 mT at g = 1.983 due to the interaction of the d^1 electron with 8 equivalent protons of the cot ligand (the weakest, outermost resonances of the nonet pattern are overlapped by wing spectra due to Ti isotopes (I_N = 5/2 and 7/2, and are not observable). The spectrum intensity decreases with increasing magnetic field so that the up-field wing spectra due to Ti isotopes are poorly observable (Fig. 1a). In toluene glass, the splitting due to the $C_8H_8^{2-}$ protons and Ti isotopes are observable, depending on the quality of glass. In the freshly frozen glass, $A_\perp \approx 0.24$ mT, $A_{||} \approx 0.38$ mT and the features of A(Ti) spectra were poorly observed on both sides of the anisotropic ESR spectrum (Fig. 1b). All these superhyperfine splittings were disappearing during ageing of the glass at –140 °C. The axial $\boldsymbol{g}$-tensor ($g_\perp = 2.002$, $g_{||} = 1.975$) remained virtually unaffected by these changes in the toluene glass. The ESR spectra resemble the solution ESR spectra of [Ti(cot)(Cp*)] reported by Teuben et al.[18b] and solid state spectra of [Ti(cot)(Cp)] in toluene glass described by Samuel et al.[20a] who also gave interpretation of ESR parameters for compounds of this type[20].

*Crystal Structure of Compound **1***

Compound **1** shows the sandwich structure with parallel cyclooctatetraene and cyclopentadienyl ring planes (within e.s.d.'s) as it is common for [Ti(cot)(Cp)][21] and [Ti(cot)(Cp*)][19] complexes. The C_5Bn_5 ligand bears all the benzyl groups up, farther away from the metal (Fig. 2). The molecule of **1** resides on a crystallographic mirror plane containing the Ti atom, the C1 and C5 atoms of the cot ring, C6 atom of the cyclopentadienyl ring and all

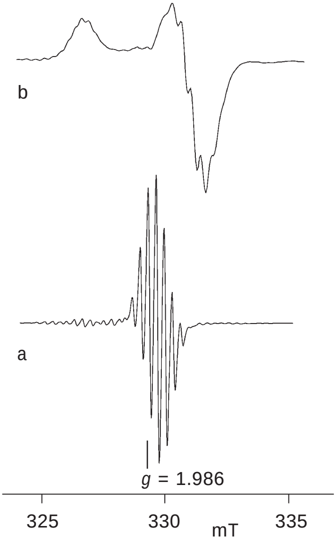


FIG. 1
a ESR spectrum of a toluene solution of **1** at 292 K; b ESR spectrum of fresh toluene glass of **1** at 133 K

carbon atoms of the C9–C15 benzyl group. The mirror plane bisects only the C8–C8′ bond in the cyclopentadienyl ring (Fig. 3). It is of interest that both the above mentioned molecules are symmetric with respect to the mirror plane. However, in [Ti(cot)(Cp)] [21] the mirror plane bisects the bonds in cot, and in [Ti(cot)(Cp*)] [19] two crystallographically different molecules are present with mirror plane containing carbon atoms or bisecting

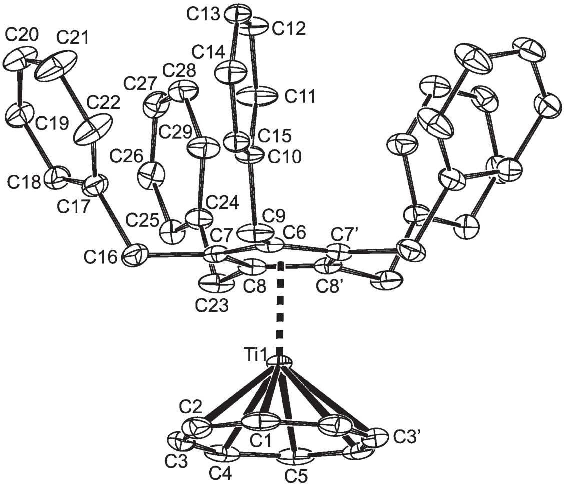


FIG. 2
The molecular structure of compound **1** drawn at the 30% probability level showing the atom labeling scheme. Prime-labeled equivalent positions are generated by the symmetry operation (–*x*, *y*, *z*). All hydrogen atoms are omitted for clarity

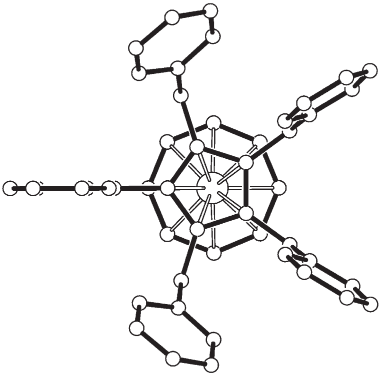


FIG. 3
View of the molecule of **1** in the direction of the Cg2, Ti, Cg1 vector

the C–C bonds. The geometric parameters for **1** vary only little; the ranges of bond and angle values are given in Table I. The pairs of phenyl rings outside the mirror plane and the least-squares plane of the cyclopentadienyl ring subtend angles of 62.5(1)° (C17–C22) and 82.3(1)° (C24–C29). The methylene carbon atoms are very slightly declined from the cyclopentadienyl plane toward the metal (C9 0.055(6) Å, C16 0.083(4) Å, and C23 0.066(5) Å).

The structure of **1** is exceptional because the benzyl groups do not introduce asymmetry into the molecular structure. This is probably induced by the tendency of [Ti(cot)(Cp′)] (Cp′ = Cp, Cp* or C_5Bn_5) compounds to crystallize in orthorhombic space groups which impose the mirror plane into their molecules. In the present case, the rigid positions of benzyl groups are somewhat surprising in view of the fact that toluene of crystallization is positionally disordered.

EXPERIMENTAL

General Data and Methods

Preparation, isolation, handling, and spectroscopic measurements of solutions of **1** were performed in vacuo. An all-sealed glass device equipped with breakable seals, an EPR sample tube and a pair of quartz cuvettes (*d* = 1.0 and 10 mm; Hellma) was used for the measurement of ESR and UV-VIS spectra. The adjustment of single crystals into Lindemann glass capillaries for X-ray analysis and preparation of KBr pellets for IR measurements were performed in a glovebox (mBraun) under purified nitrogen. Mass spectra were measured on a VG 7070E spectrometer at 75 eV (only important mass peaks and peaks of intensity ≥5% are

TABLE I
Bond lengths (in Å) and selected bond angles (in °) for complex **1**

Ti–C (1–5)	2.313–2.325(3)	Ti–C (6–8)	2.340–2.345(2)
Ti–Cg1[a]	1.435(1)	Ti–Cg2[b]	2.004(1)
C–C (cot ring)	1.385–1.403(5)	C–C (Cp ring)	1.419–1.434(4)
C(Cp)–C_{CH2}	1.507–1.513(4)	C_{CH2}–C_{ipso}	1.522–1.524(4)
C–C(Ph)	1.378–1.395(5)		
Cg1–Ti–Cg2	180.0(1)	C–C–C (cot)	134.5–135.3(3)
C–C–C (Cp)	107.7–108.7(3)	C–C_{CH2}–C	116.0–116.5(3)
C–C–C (Ph)	117.6–121.9(3)		

[a] Cg denotes the centroid of the cyclooctatetraene ring (C1–C5 and symmetry-related carbon C2′–C4′ atoms). [b] Cg denotes the centroid of the cyclopentadiene ring (C6–C8 and symmetry-related carbon C7′ and C8′ atoms).

reported) using a direct inlet. Crystalline samples in capillaries were opened and inserted into the direct inlet under argon. ESR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) equipped with a magnet controlling and data acquisition CU1 unit (Magnettech, Berlin, Germany) in the X-band. *g*-Values were determined using an Mn^{2+} (M_I = –1/2 line) standard at $g = 1.9860$. An STT-3 variable temperature unit was used for the measurement in the range from –130 to +22 °C. UV-near-IR spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra of KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{-1}.

Chemicals

Hexane, toluene, and tetrahydrofuran were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[\{Ti(\mu\text{-}H)(C_5H_5)\}_2\text{-}(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]$ [22]. Butyllithium (1.6 M solution in hexanes) was purchased from Aldrich. Pentabenzylcyclopentadiene was prepared by an improved method of Hirsch and Bailey[23], as reported in[3]. The salt LiC_5Bn_5 was obtained by mixing equimolar quantities of BuLi in hexanes with the cyclopentadiene in tetrahydrofuran[9]. $[TiCl(cot)(thf)]_2$ prepared in[16b] was used.

Preparation of **1**

$[TiCl(cot)(thf)]_2$ (0.259 g, 1.0 mmol) was stirred with tetrahydrofuran (20 ml) under argon and $Li^+[C_5Bn_5]^-$ prepared from C_5Bn_5H (0.516 g, 1.0 mmol) in tetrahydrofuran (20 ml), and BuLi (1.04 mmol, 0.65 ml, 1.6 M solution in hexanes) was slowly added from the reaction vessel. The reaction mixture was stirred for 1 h, finally under reflux. Then, all volatiles were evaporated in vacuum and the dry reaction residue was repeatedly extracted with toluene (30 ml). The toluene was evaporated and the residue was extracted with hexane (30 ml). The hexane extracts were discarded and the residue was again extracted with toluene (30 ml). The solution was cooled in a refrigerator for 2 days to precipitate practically all dissolved LiCl and some product. The solution was further concentrated and crops of light green brilliant-like crystals were subsequently obtained by cooling. Yield 0.39 g (58%).

Compound **1**. M.p. 230 °C. EI-MS (210 °C), *m/z* (rel. abundance): 670 (9), 669 (25), 668 (60), 667 ($M^{\bullet+}$; 100), 666 (18), 665 (13), 284 (7), 283 (14), 282 (26), 281 (6), 280 (5), 91 (12), 57 (15). HR MS analysis of $M^{\bullet+}$: 667.28442, error 0.2 mmu for $^{12}C_{48}H_{43}{}^{48}Ti$. ESR (toluene, 22 °C): $g = 1.983$, $a_H = 0.32$ mT (observable septuplet), $a_{Ti} = 1.22$ mT; (toluene, –140 °C): $g_\perp = 2.002$, $g_{||} = 1.975$, $g_{av} = 1.984$. UV-near-IR (toluene, 22 °C): 30 303 sh > 27 624 sh > 24 510 sh > 17 300 > 10 640 cm^{-1}. IR (KBr, cm^{-1}): 3083 w, 3056 m, 3022 s, 2916 m, 2848 vw, 1949 vw, 1887 vw, 1812 vw, 1693 vw, 1601 m, 1582 w, 1494 vs, 1451 s, 1439 m, 1322 vw, 1297 vw, 1181 w, 1152 w, 1074 m, 1030 m, 910 w, 812 w, 756 vs, 733 vs, 697 vs, 622 vw, 612 w, 594 vw, 581 w, 482 m, 460 w, 432 m.

X-ray Crystal Structure Determination

A pale green crystal of **1** grown from toluene was inserted into a Lindemann glass capillary in nitrogen atmosphere in a glovebox and the capillary was sealed with wax. Diffraction data were collected on a Nonius KappaCCD diffractometer at 150(2) K and analyzed using the HKL program package[24]. The structure was solved by direct methods (SIR97)[25] followed by consecutive Fourier syntheses and refined by full-matrix least squares on F^2 (SHELXL97)[26]. All non-hydrogen atoms of **1** were refined anisotropically; all hydrogen atoms were included into calculated positions. The toluene molecule of crystallization was disordered, and was not refined.

Crystal data for **1**: $C_{48}H_{43}Ti$. C_7H_8, M = 759.84 g mol^{-1}, orthorhombic, $Pmn2_1$ (No. 31), a = 16.9210(1), b = 11.9800(3), c = 10.0030(4) Å; V = 2027.74(10) Å^3, Z = 2, ρ_c = 1.241 g cm^{-3}, μ(MoKα) = 0.249 mm^{-1}, F(000) = 802, number of parameters 246, crystal dimensions 0.5 × 0.4 × 0.3 mm^3, θ-range: 1.0–27.5°, 4539 unique and 4265 observed [$I > 2\sigma(I)$] diffractions, final R = 0.0526, wR = 0.1434 for observed diffractions, R = 0.0566 for all data, GOF = 1.055, largest difference peak and hole on the final difference electron density map 0.569 and –0.608 e Å^{-3}. CCDC 246465 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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REFERENCES AND NOTES

1. Okuda J.: *Top. Curr. Chem.* **1992**, *160*, 97.
2. Janiak C., Schumann H.: *Adv. Organomet. Chem.* **1991**, *33*, 291.
3. Schmid G., Thewalt U., Troyanov S. I., Mach K.: *J. Organomet. Chem.* **1993**, *453*, 185.
4. Delville-Desbois M.-H., Mross S., Astruc D., Linares J., Varret F., Rabaa H., Le Beuze A., Saillard J.-Y., Culp R. D., Atwood D. A., Cowley A. H.: *J. Am. Chem. Soc.* **1996**, *118*, 4133.
5. a) Martins A. M., Branquinho R., Cui J., Dias A. R., Duarte M. T., Fernandes J., Rodrigues S. S.: *J. Organomet. Chem.* **2004**, *689*, 2368; b) Song L.-C., Zhang L.-Y., Hu Q.-M., Huang X.-Y.: *Inorg. Chim. Acta* **1995**, *230*, 127.
6. Schmid G., Thewalt U., Polášek M., Mach K., Sedmera P.: *J. Organomet. Chem.* **1994**, *482*, 231.
7. Schmid G., Thewalt U., Sedmera P., Hanuš V., Mach K.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 636.
8. For Co, Rh, see: Chambers J. W., Baskar A. J., Bott S. G., Atwood J. L., Rausch M. D.: *Organometallics* **1986**, *5*, 1635.
9. Rausch M. D., Tsai W.-M., Chambers J.-W., Rogers R. D., Alt H. G.: *Organometallics* **1989**, *8*, 816.
10. For Fe, Lu, see: Schumann H., Janiak C., Köhn R. D., Loebel J., Dietrich A.: *J. Organomet. Chem.* **1989**, *365*, 137.
11. Zanello P., Cinquantini A., Mangani S., Opromolla G., Pardi L., Janiak C., Rausch M. D.: *J. Organomet. Chem.* **1994**, *471*, 171.
12. a) Hitchcock P. B., Kerton F. M., Lawless G. A.: *J. Am. Chem. Soc.* **1998**, *120*, 10264; b) Horáček M., Kupfer V., Thewalt U., Štěpnička P., Polášek M., Mach K.: *Organometallics*

1999, *18*, 3572; c) Lukešová L., Horáček M., Štěpnička P., Fejfarová K., Gyepes R., Císařová I., Kubišta J., Mach K.: *J. Organomet. Chem.* **2002**, *659*, 186.

13. a) Bercaw J. E., Brintzinger H. H.: *J. Am. Chem. Soc.* **1971**, *93*, 2046; b) Bercaw J. E., Marvich R. H., Bell L. G., Brintzinger H. H.: *J. Am. Chem. Soc.* **1972**, *94*, 1219; c) Bercaw J. E.: *J. Am. Chem. Soc.* **1974**, *96*, 5087.
14. Kupfer V., Thewalt U., Tišlerová I., Štěpnička P., Gyepes R., Kubišta J., Horáček M., Mach K.: *J. Organomet. Chem.* **2001**, *620*, 39.
15. Sandwich metal complexes with two aromatic ligands, e.g., M(cot)$_2$ are also named metallocenes. Seyferth D.: *Organometallics* **2004**, *23*, 3562.
16. a) van der Wal H. R., Overzet F., van Oven H. O., de Boer J. L., de Liefde Meijer H. J., Jellinek F.: *J. Organomet. Chem.* **1975**, *92*, 329; b) Horáček M., Hiller J., Thewalt U., Štěpnička P., Mach K.: *J. Organomet. Chem.* **1998**, *571*, 77.
17. Dohmeier C., Baum E., Ecker A., Koppe R., Schnöckel H.: *Organometallics* **1996**, *15*, 4702.
18. a) Demerseman B., Bouquet G., Bigorgne M.: *J. Organomet. Chem.* **1975**, *101*, C24; b) Blenkers J., Bruin P., Teuben J. H.: *J. Organomet. Chem.* **1985**, *297*, 61.
19. Kool L. B., Rausch M. D., Rogers R. D.: *J. Organomet. Chem.* **1985**, *297*, 289.
20. a) Samuel E., Labauze G., Vivien D.: *J. Chem. Soc., Dalton Trans.* **1979**, 956; b) Samuel E., Labauze G., Vivien D.: *J. Chem. Soc., Dalton Trans.* **1981**, 2353.
21. Kroon P. A., Helmholdt R. B.: *J. Organomet. Chem.* **1970**, *25*, 451.
22. Antropiusová H., Dosedlová A., Hanuš V., Mach K.: *Transition Met. Chem. (London)* **1981**, *6*, 90.
23. Hirsch S. S., Bailey W. J.: *J. Org. Chem.* **1978**, *43*, 4090.
24. a) Otwinowski Z., Minor W.: *HKL Denzo and Scalepack Program Package*. Nonius BV, Delft 1997; b) For a reference, see: Otwinowski Z., Minor W.: *Methods Enzymol.* **1997**, *276*, 307.
25. Altomare A., Burla M. C., Camalli M., Cascarano G., Giacovazzo C., Guagliardi A., Polidori G.: *J. Appl. Crystallogr.* **1994**, *27*, 435.
26. Sheldrick G. M.: *SHELXL97, Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1997.