

Fulvalenediyl-bridged heterobimetallic complexes consisting of sandwich and half-sandwich compounds with early–late transition metals

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A B S T R A C T

A straightforward synthesis methodology for the preparation of heterobimetallic $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{M}]$ (**3a**, M = Fe; **3b**, M = Ru) and $[(\eta^5\text{-C}_5\text{H}_5)((\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{TiCl}_3)\text{M}]$ (**4a**, M = Fe; **4b**, M = Ru) in which early and late transition metals are connected by a fulvalenediyl bridge is reported.

The structures of molecules **3b** and **4a** in the solid state are discussed. Most noteworthy in **4a** is the *exo* arrangement of the iron and titanium atoms coordinated by the fulvalenediyl unit which itself is twisted with a dihedral angle between the joined cyclopentadienyl rings of 19.33(9)°. Electrochemical, UV/Vis/NIR spectroscopic and spectroelectrochemical experiments on **4a** and Cp*TiCl₃, for comparison, provide evidence for some transfer of electronic information between the conjoined ferrocene and half-sandwich titanocene trichloride subunits of **4a**. Evidence comes from systematic potential shifts and the presence of a fairly intense Fe → Ti charge-transfer absorption band that vanishes upon oxidation and reduction of **4a**.

Keywords:

Ferrocene
Ruthenocene
Titanium
Heterobimetallic
Spectroelectrochemistry

1. Introduction

Homo- and heterobimetallic compounds in which two metal atoms are interconnected by conjoined cyclopentadienyl ligands have been studied in relation to metal–metal interactions because the appropriate transition metal centers are kept in close proximity by the organic linking group [1]. Such molecules are promising redox-active candidates with applications, for example, in multimetal catalysis and energy storage devices [2]. They also serve as starting compounds for the preparation of organometallic-based polymers and heteropolymetallics [3]. Many examples of metallocene-based homo- and heterobimetallic systems exist in which the two transition metals are linked by fulvalenediyl, fluorenediyl or indacenediyl moieties [4]. An example of a chiral heterobimetallic bis(fulvalenediyl) complex featuring early (Zr) and late (Fe) metal atoms from bis(cyclopentadienyl)- and bis(indenyl)-substituted ferrocenes was reported by Brintzinger and coworkers [5]. Therefore, we set out to explore the possibility of synthesizing fulvalenediyl-based heterobimetallic complexes with titanium(IV) and iron(II) or ruthenium(II) metal ions.

We describe here a straightforward synthesis methodology for the preparation of molecules of type $[(\eta^5\text{-C}_5\text{H}_5)((\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{TiCl}_3)\text{M}]$ (M = Fe, Ru). The electrochemical and UV/Vis/NIR

spectroelectrochemical behavior of **4a** and Cp*TiCl₃, for comparison, is reported as well.

2. Results and discussion

The synthesis strategy to prepare the title compounds is shown in Scheme 1. Our approach includes the reaction of monolithiated metallocenes $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{M}]$ (**1a**, M = Fe; **1b**, M = Ru) with 2,3,4,5-tetramethylcyclopent-2-enone (**2**) in a 1:1 molar ratio in tetrahydrofuran at –80 °C followed by acidic work-up and dehydration with *para*-toluenesulfonic acid. After appropriate work-up, the corresponding 2,3,4,5-tetramethylcyclopentadienyl-functionalized metallocenes **3a** (M = Fe) and **3b** (M = Ru), respectively, could be isolated as orange (**3a**) or yellow (**3b**) solids in 78% yield. Molecules **3a** and **3b** were prepared in analogy to the synthesis route reported by Plenio [6] and Wan [4b].

Molecules **3a** and **3b** are the starting materials for the preparation of metallocene-based fulvalenediyl-bridged Fe–Ti and Ru–Ti complexes **4a** and **4b**, respectively. Reaction of these compounds with ^tBuLi produced **Li-3** which on further treatment with TiCl₄ in tetrahydrofuran at ambient temperature gave, after filtration through Celite and crystallization from dichloromethane/*n*-hexane mixtures (1/10, v/v) at –30 °C, the heterobimetallic compounds $[(\eta^5\text{-C}_5\text{H}_5)((\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{TiCl}_3)\text{M}]$ (**4a**, M = Fe; **4b**, M = Ru) in 33% or 50% yield. Compounds **4a** and **4b** were obtained as intense green (**4a**) or purple (**4b**) solids, which are stable under inert gas atmosphere but decompose slowly on exposure to

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Table 1
Crystal and intensity collection data for **3b** and **4a**.

	3b	4a
Formula weight	351.44	459.46
Chemical formula	C ₁₉ H ₂₂ Ru	C ₁₉ H ₂₁ Cl ₃ FeTi
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P $\bar{1}$
a (Å)	14.0392(3)	6.8296(6)
b (Å)	11.3396(3)	11.0008(11)
c (Å)	9.5540(2)	12.3892(12)
α (°)	—	83.369(8)
β (°)	96.665(6)	83.792(7)
γ (°)	—	88.820(8)
V (Å ³)	1510.71(6)	919.13(15)
ρ_{calc} (g cm ⁻³)	1.545	1.660
F(0 0 0)	720	468
Crystal dimensions (mm)	0.48 × 0.48 × 0.34	0.3 × 0.2 × 0.2
Z	4	2
Maximum and minimum transmission	1.00000, 0.75168	1.00000, 0.94954
Absorption coefficient (λ , mm ⁻¹)	1.025	1.657
Scan range (°)	2.92–26.00	3.00–26.00
Index ranges	–17 ≤ h ≤ 16, –10 ≤ k ≤ 13, –10 ≤ l ≤ 11	–8 ≤ h ≤ 8, –13 ≤ k ≤ 13, –15 ≤ l ≤ 15
Total reflections	7900	9218
Unique reflections	2945	3616
R _{int}	0.0246	0.0190
Data/restraints/parameters	2945/0/181	3616/0/217
Goodness-of-fit on F ²	1.077	1.047
R ₁ ^a , wR ₂ ^a [I 2 σ (I)]	0.0356, 0.0975	0.0333, 0.0890
R ₁ ^a , wR ₂ ^a (all data)	0.0470, 0.1024	0.0421, 0.0941
Largest difference in peak and hole peak in final Fourier map (e Å ⁻³)	1.404, –0.591	0.694, –0.649

^a $R_1 = [\sum(|F_o| - |F_c|) / \sum|F_o|]$;
 $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(wF_o^2)]^{1/2}$. $S = [\sum(w(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$. N , number of reflections, p , parameters used.

bands exhibit positive solvatochromism and shift to 678 and 459 nm in the more polar 1,2-C₂H₄Cl₂/[ⁿBu₄N]PF₆ supporting electrolyte of spectroelectrochemical experiments. This is indicative of a more polar excited state. Molar extinction coefficients ϵ of 1060 and 1850 l mol⁻¹ cm⁻¹ were measured in dichloromethane. The band at 446 (dichloromethane) or 459 nm (1,2-C₂H₄Cl₂/[ⁿBu₄N]PF₆) is characteristic of a CpTiCl₃-type chromophore (c.f., $\lambda_{\text{max}} = 445$ nm for (η^5 -C₅Me₄Ph)TiCl₃ [15]). The low-energy band, however, has neither precedence in Cp^RTiCl₃ (Cp^R = η^5 -C₅H₄R, R = single bonded organic group) systems nor in ferrocenes. We therefore assign this band to a charge-transfer absorption from the electron-rich ferrocene to the electron-poor half-sandwich titanium site.

In order to probe for this assignment the changes of the electronic spectra of **4a** upon reduction to its associated radical anion **4a⁻** and upon oxidation to its radical cation **4a⁺** were investigated.

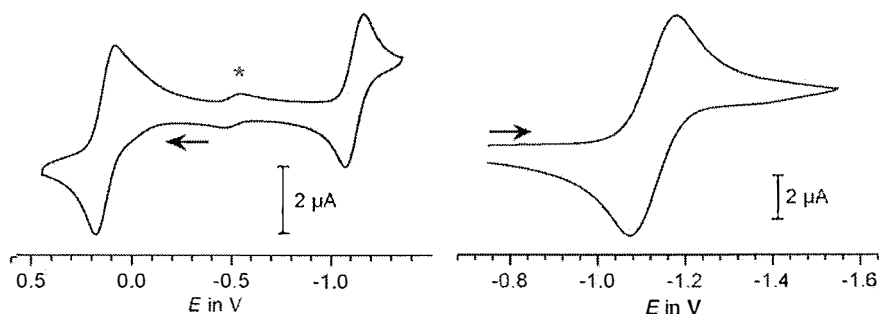


Fig. 3. Cyclic voltammogram of **4a** (left) and Cp^RTiCl₃ (right), for comparison, (10⁻³ M solution in dichloromethane at 25 °C with [ⁿBu₄N]PF₆ (0.1 M) as supporting electrolyte, scan rate 0.10 V s⁻¹); the asterisk marks an impurity. All potentials are referenced to the [Fch/Fch⁺] redox couple (Fch = (η^5 -C₅H₅)₂Fe) with $E_0 = 0.00$ V [13].

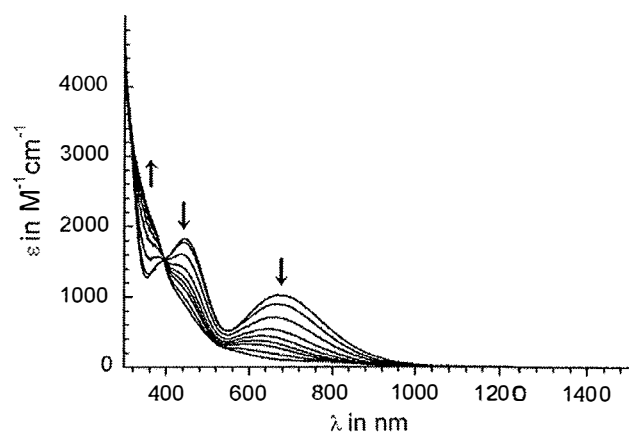


Fig. 4. Spectroscopic changes upon reduction of **4a** (1,2-C₂H₄Cl₂/[ⁿBu₄N]PF₆) in an OTTE cell.

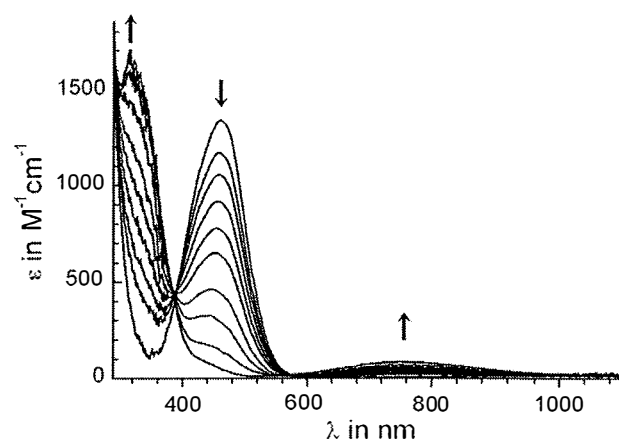


Fig. 5. Spectroscopic changes upon reduction of Cp^RTiCl₃ (1,2-C₂H₄Cl₂/[ⁿBu₄N]PF₆) in an OTTE cell.

Upon reduction the low-energy charge-transfer band and the 459 nm absorption assigned to the CpTiCl₃ chromophore disappeared and were replaced by a very weak band at 774 nm ($\epsilon = 65$ l mol⁻¹ cm⁻¹, Fig. 4). Very similar results were obtained for the *in situ* reduction of Cp^RTiCl₃ (Fig. 5). In particular, the 460 nm band vanished and was replaced by a weak low-energy band at 751 nm ($\epsilon = 60$ l mol⁻¹ cm⁻¹) and a more intense band at 320 nm ($\epsilon = 1650$ l mol⁻¹ cm⁻¹). The low-energy feature in the electronic spectrum of **4a⁻** is thus a genuine absorption of the reduced Cp^RTiCl₃⁻ system.

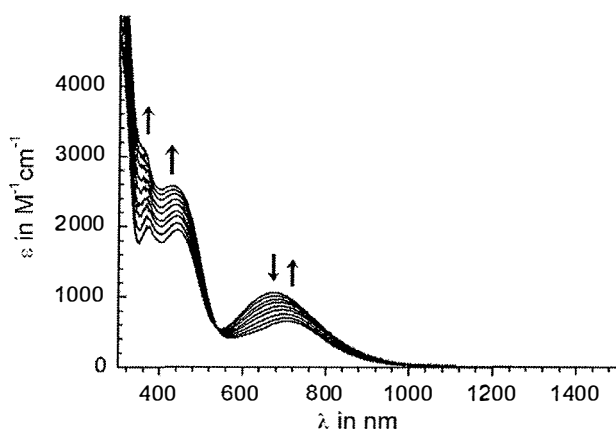


Fig. 6. Spectroscopic changes upon oxidation of **4a** ($1,2\text{-C}_2\text{H}_4\text{Cl}_2/[\text{Bu}_4\text{N}]\text{PF}_6$) in an OTTLE cell.

Oxidation of **4a** to **4a⁺** causes the emergence of a new absorption at 710 nm ($\epsilon = 650 \text{ l mol}^{-1} \text{ cm}^{-1}$) that we ascribe to the oxidized ferrocenium chromophore (Fig. 6). A further, more intense band is observed at 430 nm and can be deconvoluted into separate absorptions at 450 and 371 nm, respectively. The 450 nm component with an estimated ϵ of $2300 \text{ l mol}^{-1} \text{ cm}^{-1}$ is most probably due to the half-sandwich titanium subunit of **4a⁺**. The blue shift of this band by 9 nm upon oxidation is a token of the decreasing electron density at the half-sandwich titanocene site upon oxidation of the attached ferrocene building block [15]. Along with the disappearance of the low-energy charge-transfer band in **4a** upon oxidation and reduction provides further evidence for some transmittance of electronic information between the joined ferrocene and CpTiCl_3 subunits of **4a** via the fulvalenediyl bridge.

3. Conclusion

The consecutive preparation of fulvalenediyl-bridged early-late heterobimetallics has been achieved by treatment of monolithiated metallocenes (ferrocene, ruthenocene) with 2,3,4,5-tetramethylcyclopent-2-enone followed by addition of $^n\text{BuLi}$ and TiCl_4 , respectively. In molecules $[(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{TiCl}_3\text{M}]$ ($\text{M} = \text{Fe, Ru}$) early and late transition metals are brought in close proximity to each other as it could be demonstrated by single X-ray structure determination (Fe–Ti separation of $5.3076(8) \text{ \AA}$). Electrochemical studies revealed the mutual influence of the subunits by the anodic shift of the ferrocene-based half-wave potential, when compared to those of ferrocene itself and biferrocene, respectively. Further evidence for such interactions comes from the fairly intense low-energy band of **4a** and **4b** that has no precedent in the isolated mononuclear counterparts and is assigned as a $\text{Fe} \rightarrow \text{Ti}$ charge-transfer absorption. In keeping with this assignment, it disappears when the ferrocene moiety is oxidized or the cyclopentadienyl TiCl_3 building block is reduced. A weak low-energy absorption of reduced **4a⁻** can be traced to the reduced $\text{CpTiCl}_3^{\cdot-}$ subunit as is shown by the comparison with electro-generated $\text{Cp}^*\text{TiCl}_3^{\cdot-}$.

4. Experimental

4.1. General data

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Toluene, tetrahydrofuran, *n*-pentane and *n*-hexane were purified by distillation from sodium/

benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

4.2. Instruments

^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: CDCl_3 (99.8%), $\delta = 7.26$. $^{13}\text{C}\{^1\text{H}\}$ NMR: CDCl_3 (99.8%), $\delta = 77.16$). The abbreviation *pt* in the ^1H NMR spectra corresponds to pseudo-triplet. Microanalyses were performed with the C,H,N analyzer FLASHEA 1112 Series (Thermo company). The equipment for voltammetric and spectroelectrochemical studies and the conditions employed in this work were described elsewhere [16]. UV/Vis/NIR spectra were recorded on an Omega20 spectrometer of Bruins Instruments.

4.3. Reagents

1-Bromoferrocene [17a], 1-iodoruthenocene [17b], and **3a** [4b,5] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

4.3.1. Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{Ru}]$ (**3b**)

To 2.68 g (7.51 mmol) of iodoruthenocene dissolved in 40 mL of tetrahydrofuran were added 3 mL (7.52 mmol) of $^n\text{BuLi}$ at -80°C in a single portion. After 1 h of stirring at this temperature, 1.12 mL (7.53 mmol) of **2** were added in a single portion by syringe. The reaction solution was warmed to ambient temperature and stirred for 1 h. Afterward, 20 mL of a concentrated aqueous solution of $[\text{NH}_4]\text{Cl}$ was used for quenching the reaction and stirring was continued for 30 min. The separated organic phase was then treated with 2 g (10.51 mmol) of *para*-toluenesulfonic acid monohydrate and stirred for another 30 min. The reaction mixture was extracted with diethyl ether (4 times, 50 mL each) and all volatiles were removed under reduced pressure. The title compound could be obtained by chromatography on silica gel and *n*-hexane as eluent. Yield: 2.07 g (5.89 mmol, 78% based on iodoruthenocene).

Anal. Calc. for $\text{C}_{19}\text{H}_{22}\text{Ru}$ (351.45): C, 64.93; H, 6.31. Found: C, 65.05; H, 6.36. ^1H NMR (δ , CDCl_3): 1.10 (d, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.90 (d, $^4J_{\text{HH}} = 1.0 \text{ Hz}$, 3H, CH_3), 1.94 (d, $^4J_{\text{HH}} = 1.7 \text{ Hz}$, 3H, CH_3), 2.76 (ddd, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, $^4J_{\text{HH}} = 1.7 \text{ Hz}$, $^4J_{\text{HH}} = 1.0 \text{ Hz}$, 1H, CH_3), 4.50 (s, 5H, C_5H_5), 4.57 (pt, $J_{\text{HH}} = 1.4 \text{ Hz}$, 2H, C_5H_4), 4.65–4.70 (m, 1H, C_5H_4), 4.73–4.78 (m, 1H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3): 11.4 (CH_3), 12.2 (CH_3), 13.3 (CH_3), 16.5 (CH_3), 51.4 ($\text{C}^1/\text{C}_5\text{H}_4$), 69.9 ($\text{C}^2/\text{C}_5\text{H}_4$), 71.2 (C_5H_5), 71.8 ($\text{C}^2/\text{C}_5\text{H}_4$), 87.2 (CHCH_3), 135.3 (CCH_3), 136.8 (CCH_3), 137.8 (CCH_3), 140.0 ($\text{C}^1/\text{C}_5\text{H}(\text{CH}_3)_4$). Mp. 68°C .

4.3.2. Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{Me}_4)\text{TiCl}_3\text{Fe}]$ (**4a**)

To 1.15 g (3.61 mmol) of **3a** dissolved in 50 mL of diethyl ether were added 1.45 mL (3.61 mmol) of $^n\text{BuLi}$ at -30°C in a single portion. After 2 h of stirring at ambient temperature the lithium salt precipitated and a solution of 0.34 mL (3.13 mmol) of titanium tetrachloride in 10 mL of toluene was added dropwise to the reaction mixture, whereby the color changed from orange to dark green. After stirring over night with 8.90 g (3.20 mmol) of PbCl_2 all volatiles were removed in *oil-pump* vacuum and the dark green residue was dissolved in 40 mL of dichloromethane and was filtered through a pad of Celite. The obtained solution was concentrated (10 mL) under reduced pressure and layered with *n*-hexane, whereby a dark green solid crystallized at -30°C . Impurities of

ferrocene could be removed by sublimation in *oil-pump* vacuum. Yield: 730 mg (1.55 mmol, 50% based on **3a**).

Anal. Calc. for $C_{19}H_{21}Cl_3FeTi \times 1/5CH_2Cl_2$ (476.43): C, 48.40; H, 4.53. Found: C, 48.31; H, 4.69. 1H NMR (δ , $CDCl_3$): 2.41 (s, 6H, CH_3), 2.70 (s, 6H, CH_3), 4.19 (s, 5H, C_5H_5), 4.49 (pt, $J_{HH} = 1.8$ Hz, 4H, H^α/C_5H_4), 4.68 (pt, $J_{HH} = 1.8$ Hz, 4H, H^β/C_5H_4), 5.29 (CH_2Cl_2). $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$): 14.8 (CH_3), 16.7 (CH_3), 53.1 (CH_2Cl_2), 68.1 (C^i/C_5H_4), 69.6 (C^j/C_5H_4), 69.9 (C_5H_5), 70.1 (C^k/C_5H_4), 135.1 ($C_5(CH_3)_4$), 140.0 ($C_5(CH_3)_4$), 140.9 ($C^l/C_5(CH_3)_4$).

4.3.3. Synthesis of $[(\eta^5-C_5H_5)(\mu-\eta^5:\eta^5-C_5H_4-C_5Me_4)TiCl_3Ru]$ (**4b**)

Compound **4b** was synthesized by the same reaction protocol as described for the preparation of **4a**. Thus, 1.05 g (2.98 mmol) of **3b** were reacted with 1.19 mL (2.98 mmol) of nBuLi and 0.33 mL (3.04 mmol) of titanium tetrachloride. Please, notice that work-up with $PbCl_2$ is not necessary. The title complex was isolated as a purple solid. Yield: 496 mg (0.98 mmol, 33% based on **3b**).

Anal. Calc. for $C_{19}H_{21}Cl_3RuTi$ (504.67): C, 45.22; H, 4.19. Found: C, 45.46; H, 4.32. 1H NMR (δ , $CDCl_3$): 2.37 (s, 6H, CH_3), 2.60 (s, 6H, CH_3), 4.58 (s, 5H, C_5H_5), 4.75 (pt, $J_{HH} = 1.7$ Hz, 4H, H^α/C_5H_4), 4.99 (pt, $J_{HH} = 1.7$ Hz, 4H, H^β/C_5H_4). $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$): 15.0 (CH_3), 16.7 (CH_3), 70.2 (C^i/C_5H_4), 71.2 (C^j/C_5H_4), 72.2 (C^k/C_5H_4), 72.7 (C_5H_5), 135.7 ($C_5(CH_3)_4$), 139.0 ($C_5(CH_3)_4$), 139.9 ($C^l/C_5(CH_3)_4$).

4.4. Crystal structure determination

The crystal and intensity collection data for **3b** and **4a** are summarized in Table 1. All data were collected on a Oxford Gemini S diffractometer with graphite monochromatized $Mo K\alpha$ radiation ($\lambda = 0.71073$ Å) at 100 K (**3b**, **4a**) using oil-coated shock-cooled crystals [18]. The structures were solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-square procedures on F^2 using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

Supplementary material

CCDC 729388 and 729387 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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References

- [1] (a) H. Hilbig, F.H. Köhler, K. Mörtl, *J. Organometal. Chem.* 627 (2001) 71; (b) E.G. Perevalova, O.A. Nesmeyanova, *Dokl. Akad. Nauk. SSSR* 132 (1960) 1093; (c) M.D. Rausch, *J. Am. Chem. Soc.* 82 (1960) 2080; (d) F.L. Hedberg, H. Rosenberg, *J. Am. Chem. Soc.* 91 (1969); (e) M.D. Rausch, R.F. Kovar, C.G. Kraihanzel, *J. Am. Chem. Soc.* 91 (1969) 1259; (f) G.H. Brown, T.J. Meyer, D.O. Cowan, C. LeVanda, F. Kaufmann, P.V. Riling, M.D. Rausch, *Inorg. Chem.* 14 (1975) 506; (g) E.W. Neuse, H. Rosenberg, *Metalocene Polymers*, Marcel Dekker, New York, 1970 (Chapter 3); (h) D.S. Brown, M.-H. Delville, K.P.C. Vollhardt, D. Astruc, *Organometallics* 15 (1996) 2360; (i) D. Obendorf, H. Schottenberger, C. Rieker, *Organometallics* 10 (1991) 1293.
- [2] (a) R. Boese, J.K. Cammack, A.J. Matzger, K.P. Williams, B. Tolman, K.P.C. Vollhardt, T.W. Weidman, *J. Am. Chem. Soc.* 119 (1997) 6757; (b) L. Zhang, N. Xiao, Q. Xu, J. Sun, J. Chen, *Organometallics* 24 (2005) 5807; (c) M. Mitani, K. Oouchi, M. Hayakawa, T. Yamada, T. Mukaiyama, *Macromol. Chem. Phys.* 197 (1996) 1815.
- [3] (a) J.J. Morris, B.C. Noll, G.W. Honeyman, C.T. O'Hara, A.R. Kennedy, R.E. Mulvey, K.W. Henderson, *Chem. Eur. J.* 13 (2007) 4418; (b) I. Tomita, M. Ueda, *Macromol. Symp.* 209 (2004) 217; (c) J.-C. Lee, A. Nishio, I. Tomita, T. Endo, *Macromolecules* 30 (1997) 5205; (d) R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, *Chem. Eur. J.* 14 (2008) 4948; (e) S. Lanza, F. Loiseau, G. Tresoldi, S. Serroni, S. Campagna, *Inorg. Chim. Acta* 360 (2007) 1929; (f) R. Packheiser, A. Jakob, P. Ecorchard, B. Walfort, H. Lang, *Organometallics* 27 (2008) 1214; (g) A. Cucos, N. Avarvari, M. Andruh, Y. Journaux, A. Müller, M. Schmidtman, *Eur. J. Inorg. Chem.* (2006) 903; (h) R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, *Organometallics* 27 (2008) 3534.
- [4] (a) J.M. Manriquez, M.D. Ward, W.M. Reiff, J.C. Calabrese, N.L. Jones, P.J. Carroll, E.E. Bunel, J.S. Miller, *J. Am. Chem. Soc.* 117 (1995) 6182; (b) S. Wan, M.J. Begley, P. Mountford, *J. Organomet. Chem.* 489 (1995) C28; (c) I.M. Piglosiewicz, S. Kraft, R. Beckhaus, D. Haase, W. Saak, *Eur. J. Inorg. Chem.* (2005) 938; (d) O.Š. Miljanić, K.P.C. Vollhardt, M.J. West, *Synthesis* 19 (2005) 3373; (e) J. Ni, Q. Zhou, D.K. Canseco, T.R. Calhoun, A.R. Graham, K.L. Carreras, C.N. Schultz, *Inorg. Chim. Acta* 309 (2000) 23; (f) T.-Y. Dong, H.-Y. Lin, S.-F. Lin, C.-C. Huang, Y.-S. Wen, L. Lee, *Organometallics* 27 (2008) 555; (g) S. Santi, L. Orian, C. Durante, E.Z. Bencze, A. Bisello, A. Domoli, A. Cecon, F. Benetollo, L. Crociati, *Chem. Eur. J.* 13 (2007) 7933; (h) B. Quillian, Y. Wang, C.S. Wannere, P. Wei, P. Ragué Schleyer, G.H. Robinson, *Angew. Chem., Int. Ed.* 46 (2007) 1836; (i) T.-Y. Dong, M.-C. Lin, S.-W. Chang, C.-C. Ho, S.-F. Lin, L. Lee, *J. Organomet. Chem.* 692 (2007) 2324; (j) S. Santi, L. Orian, C. Durante, A. Bisello, F. Benetollo, L. Crociani, P. Ganis, A. Cecon, *Chem. Eur. J.* 13 (2007) 1955; (k) C.A. Nijhuis, K.A. Dolatowska, B.J. Ravoo, J. Huskens, D.N. Reinhoudt, *Chem. Eur. J.* 13 (2007) 69; (l) S. Köcher, G.P.M. Klink, G. Koten, H. Lang, *J. Organomet. Chem.* 691 (2006) 3319; (m) J. Lin, B. Wang, S. Xu, H. Song, *J. Organomet. Chem.* 691 (2006) 2528; (n) Y. Yu, A.D. Bond, P.W. Leonard, K.P.C. Vollhardt, G.D. Whitener, *Angew. Chem., Int. Ed.* 45 (2006) 179; (o) T.-Y. Dong, S.-W. Chang, S.-F. Lin, M.-C. Lin, Y.-S. Wen, L. Lee, *Organometallics* 25 (2006) 2018; (p) R. Warratz, G. Peters, F. Studt, R.-H. Römer, F. Tuczec, *Inorg. Chem.* 45 (2006) 2531; (q) A. Nafady, T.T. Chin, W.E. Geiger, *Organometallics* 25 (2006) 1654; (r) B. Li, B. Wang, S. Xu, X. Zhou, H. Song, *Organometallics* 25 (2006) 1158; (s) G. Laus, C.E. Strasser, M. Holzer, K. Wurst, G. Pfirnstinger, K.-H. Ongania, M. Rauch, G. Bonn, H. Schottenberger, *Organometallics* 24 (2005) 6085; (t) T. Mochida, K. Takazawa, H. Matsui, M. Takahashi, M. Takeda, M. Sato, Y. Nishio, K. Kajita, H. Mori, *Inorg. Chem.* 44 (2005) 8628; (u) H. Schottenberger, M. Buchmeister, O. Elsner, E. Ernst, J. Reussner, W. Neissl, H. Angleitner, *US 5.521.265*, 1996; (v) D.R. Talham, D.O. Cowan, *Organometallics* 6 (1987) 932; (w) M. Tamm, T. Bannenberg, K. Baum, R. Fröhlich, T. Steiner, T.M. Friedrichsen, J. Heck, *Eur. J. Inorg. Chem.* (2000) 1161.
- [5] P. Scott, U. Rief, J. Diebold, H.H. Brintzinger, *Organometallics* 12 (1993) 3094.
- [6] H. Plenio, *Organometallics* 11 (1992) 1856.
- [7] (a) S. Fortier, M.C. Baird, K.F. Preston, J.R. Morton, T. Ziegler, T.J. Jaeger, W.C. Watkins, J.H. MacNeil, K.A. Watson, K. Hensel, Y.L. Page, J.-P. Charland, A.J. Williams, *J. Am. Chem. Soc.* 113 (1991) 542; (b) F. de Montigny, G. Argouarch, T. Roisnel, L. Toupet, C. Lapinte, S.C.-F. Lam, C.-H. Tao, V. Wing-Wah, *Organometallics* 27 (2008) 1912; (c) C. Bruhn, T. Kügerb, D. Steinborn, *Acta Crystallogr., Sect. C* 64 (2008) m455.
- [8] (a) T.Y. Dong, D.N. Hendrickson, K. Iwai, M.J. Cohn, S.J. Geib, A.L. Rheingold, H. Sano, I. Motoyama, S. Nakashima, *J. Am. Chem. Soc.* 107 (1985) 7996; (b) T. Yuan, D.N. Hendrickson, C.G. Pierpont, M.F. Moore, *J. Am. Chem. Soc.* 108 (1986) 963.
- [9] C. Elschenbroich, J. Plackmeyer, M. Nowotny, A. Behrendt, K. Harms, J. Pebler, O. Burghaus, *Chem. Eur. J.* 11 (2005) 7427.
- [10] C.G. Atwood, W.E. Geiger, *J. Am. Chem. Soc.* 122 (2000) 5477.
- [11] (a) P. Hudeczek, F.H. Köhler, P. Bergerat, O. Kahn, *Chem. Eur. J.* 4 (1999) 70; (b) H. Hilbig, P. Hudeczek, F.H. Köhler, X. Xie, P. Bergerat, O. Kahn, *Inorg. Chem.* 37 (1998) 4246.
- [12] T. Weiß, K. Natarajan, H. Lang, R. Holze, *J. Electroanal. Chem.* 533 (2002) 127.
- [13] (a) G. Gritzner, J. Kuta, *Pure Appl. Chem.* 56 (1984) 461; (b) H. Strehlow, W. Knoche, H. Schneider, *Ber. Bunsenges. Phys. Chem.* 77 (1973) 760.
- [14] T.-Y. Dong, T.-Y. Lee, S.-H. Lee, G.-H. Lee, S.-M. Peng, *Organometallics* 13 (1994) 2337.
- [15] (a) J.W. Kennedy III, D.R. Boone, D.R. Striplin, Y.-H. Chen, K.B. Hamar, *Organometallics* 12 (1993) 3671; (b) J. Pinkas, A. Lyčka, P. Sindelář, R. Gyepes, V. Varga, J. Kubišta, M. Horáček, K. Mach, *J. Mol. Catal. A* 257 (2006) 14.
- [16] J. Maurer, B. Sarkar, B. Schwederski, W. Kaim, R.F. Winter, S. Zális, *Organometallics* 25 (2006) 3701.
- [17] (a) A.N. Nesmeyanow, W.A. Ssazonowa, V.N. Drosd, *Chem. Ber.* 93 (1960) 2717; (b) L. Bednarik, E. Neuse, *J. Organomet. Chem.* 168 (1979) C8.

- [18] (a) T. Kottke, D.J. Stalke, *Appl. Crystallogr.* 26 (1993) 615;
(b) T. Kottke, R.J. Lagow, D.J. Stalke, *Appl. Crystallogr.* 29 (1996) 465;
(c) D. Stalke, *Chem. Soc. Rev.* 27 (1998) 171.

- [19] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467.
[20] G.M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, 1997.