ELSEVIER

Journal of Organometallic Chemistry 572 (1999) 125–129

Journal of Organometallic Chemistry

Synthesis and crystal structure of decaphenyltungstenocenium triiodide

Wen-Yann Yeh [a,]*, Shi-Ming Peng [b], Gene-Hsiang Lee [b]

[a] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, 804 Taiwan*
[b] *Department of Chemistry, National Taiwan University, Taipei, 106 Taiwan*

Received 7 August 1998; received in revised form 18 August 1998

Abstract

Oxidation of $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) with I_2 affords $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1}^+\mathbf{I}_3^-$), which is reconverted to **1** upon treatment with Cp_2Co. Compound $\mathbf{1}^+\mathbf{I}_3^-$ crystallizes in the space group $P2_1/c$ with $a = 14.5258(8)$, $b = 18.6515(9)$ and $c = 15.5185(8)$ Å; $\beta = 111.512(1)°$; $V = 3911.5(4)$ Å^3; $Z = 2$; and $R_1/wR_2 = 0.050/0.091$. The structure of $\mathbf{1}^+$ reveals that the two cyclopentadienyl groups are planar, staggered and exactly parallel. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Decaphenyltungstenocenium triiodide; Tungsten

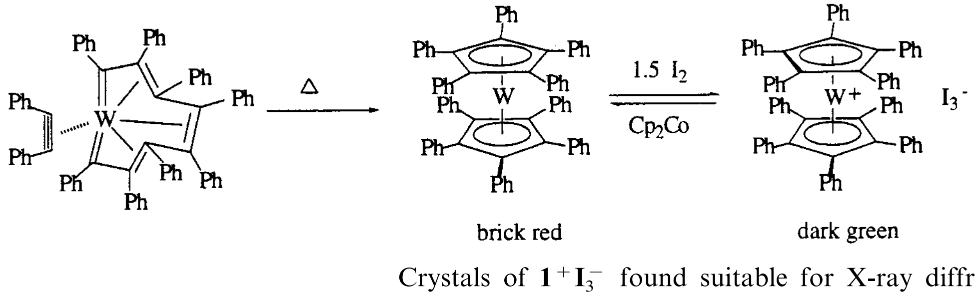
---

1. Introduction

Since the first discovery of ferrocene in 1951 [1–3], at least one cyclopentadienyl derivative of every main group and d-block transition metals has been prepared and characterized, though not all of them are subject to isolation [4–6]. For example, chromocene is stable [7–10], while the analogous molybdenocene and tungstenocene were only identified in low temperature matrices [11]. Previous attempts to synthesize $(\eta^5\text{-}Cp)_2Mo$ and $(\eta^5\text{-}Cp)_2W$, and their derivatives containing alkyl and arylcyclopentadienyls, have been unsuccessful [12–15]. One exception is $(C_5Ph_5)_2Mo$ [16], but with no extensive characterization. Herein, the authors wish to report the first structurally characterized tungstenocenium complex.

2. Results and discussion

The authors recently described [17] that the thermolysis of $W(C_2Ph_2)(\eta^8\text{-}C_8Ph_8)$ might yield $[(C_5Ph_5)_2W]_n$, and treating the latter species with I_2 in refluxing benzene afforded dark green crystals, previously identified as $(\eta^5\text{-}C_5Ph_5)_2W(I)_2$. This green compound, however, has now been shown to be a tungstenocenium salt, $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1}^+\mathbf{I}_3^-$). Furthermore, on the basis of its spectroscopic data and physical properties, $[(C_5Ph_5)_2W]_n$ should actually be monomeric tungstenocene, $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) (see Eq. ((1))).



(1)

Crystals of $\mathbf{1}^+\mathbf{I}_3^-$ found suitable for X-ray diffraction studies were grown from dichloromethane/benzene

---

* Corresponding author. Fax: + 886-7-525-3908.

PII: S0022-328X(98)00919-X

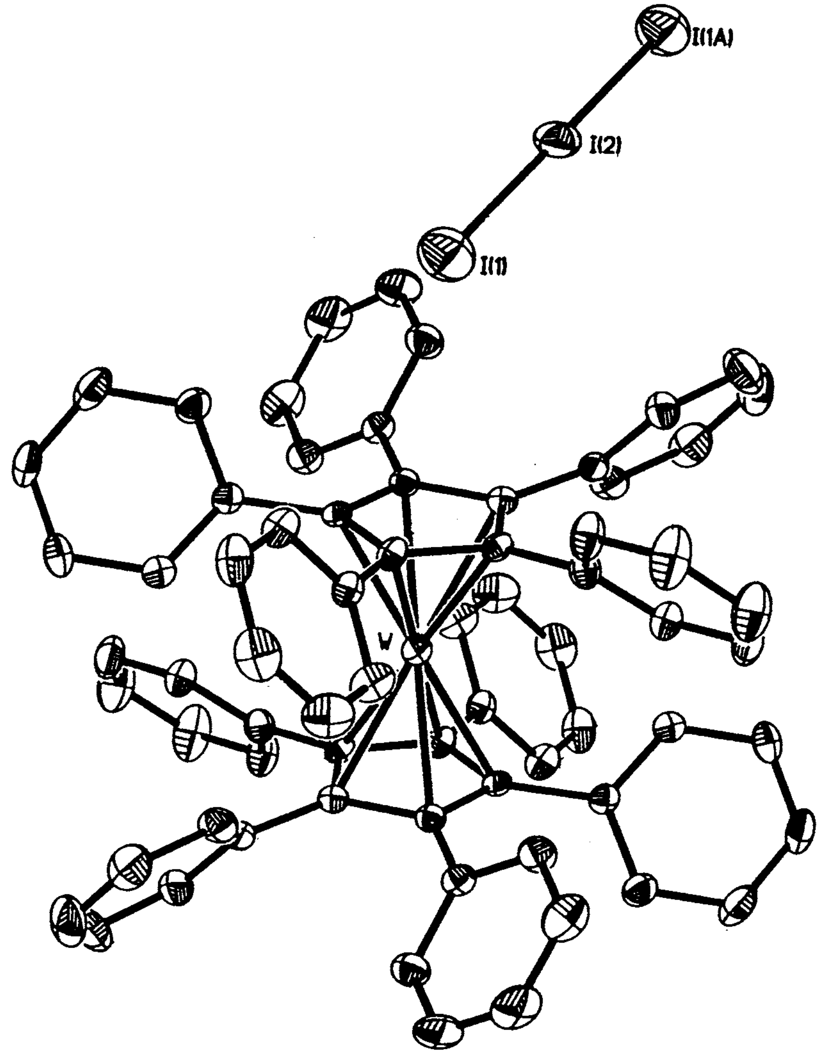


Fig. 1. ORTEP diagram of $\mathbf{1}^+\mathrm{I}_3^-$. The phenyl groups are canted to each Cp ring oppositely in a double-opposed paddlewheel fashion.

at 25°C with four molecules of benzene in the crystal lattice. The ORTEP diagrams (Figs. 1 and 2) consist of discrete molecules with each formally W(III) atom bonded to two pentaphenylcyclopentadienyl groups on a crystallographic center of symmetry. The selected bond distances and bond angles are presented in Table 1. The two cyclopentadienyls are planar, staggered and exactly parallel. The attached phenyl groups are canted to each cyclopentadienyl ring in a paddlewheel fashion to give molecules of S_{10} symmetry. The phenyl *ipso* carbon atoms are bent away from the cyclopentadienyl rings and *exo* to the tungsten atom by averaging 6.2°. The cyclopentadienyl ring carbons are coplanar to within 0.01 Å and about equally bonded to the central tungsten atom, with the W–C distances in the range 2.344(5)–2.370(5) Å. For comparison, it is noted that the cyclopentadienyl groups in $(C_5Ph_5)_2W(=O)$ are severely distorted and display an unusual, bent η^3,η^2-bonding mode, where the W–C distances range from 2.355(6) Å to 2.646(6) Å [17].

Compounds **1** and $\mathbf{1}^+$ form air-stable, paramagnetic solids. The electron impact mass spectra of **1** and $\mathbf{1}^+$ give the molecular ion peak at $m/z = 1074$ (^{184}W). The IR spectrum of **1** in a KBr pellet closely resembles that of $\mathbf{1}^+$, suggesting that their structures are similar. Compound **1** presents remarkably thermal stability in air but is insoluble to all common solvents. In contrast, $\mathbf{1}^+$ is soluble in polar solvents, such as dichloromethane and acetone, but it is susceptible to decomposition in solution upon exposure to air. The observed insolubility of **1** parallels that of $(\eta^5\text{-}C_5Ph_5)_2Fe$ [18,19] and $(\eta^5\text{-}C_5Ph_5)_2Ni$ [20]. Metallocenes of the general formula $(C_5Ph_5)_2M$ are expected to be highly insoluble due to very restricted rotation of the phenyl groups. This would result in greatly reduced molecular motion, and therefore, poor solubility of the complexes.

Apparently, the pentaphenylcyclopentadienyl ligand plays an important role in the stabilization of **1** and **1**$^+$. It has been shown that electronic withdrawal and steric bulk of the phenyl groups are capable of conferring novel steric and electronic properties on metal centers [21], such that the two parallel C_5 planes of (η^5-C_5Ph_5)$_2$Sn contrast with the bent structure of (η^5-C_5H_5)$_2$Sn and (η^5-C_5Me_5)$_2$Sn [22–24], diamagnetic (η^5-C_5Ph_5)$_2$Ni contrasts with paramagnetic (η^5-C_5H_5)$_2$Ni [20,25,26], and the dimer [(η^5-C_5R_5)$_2$Ni(μ-Br)]$_2$ is unknown for R = H but it is stable up to 200°C when R = Ph [27].

Oxidation of **1** with equimolar of $AgPF_6$ or $NOPF_6$ in CH_2Cl_2 at 25°C also produces [(η^5-C_5Ph_5)$_2$W]$^+PF_6^-$ (**1**$^+$**PF**$_6^-$). The reversed process is achieved by treating **1**$^+$**I**$_3^-$ with cobaltocene in CH_2Cl_2 solvent or Na/Ph_2CO in THF solvent at 25°C to yield **1** as a microcrystalline solid, but the quality is poor for an X-ray diffraction study point of view. Cyclic voltammetric investigations confirm that **1**$^+$**I**$_3^-$ is reversibly reduced to **1** in CH_2Cl_2 solvent; the redox potential for the one-electron reduction is −14 mV versus Ag/AgCl (Fig. 3).

In summary, the authors have prepared the unprecedented monomeric tungstenocene complexes (η^5-C_5Ph_5)$_2$W (**1**) and [(η^5-C_5Ph_5)$_2$W]$^+I_3^-$ (**1**$^+$**I**$_3^-$) originally from coupling of five diphenylacetylene ligands on a W(0) center. The results present in this work can fill in the missing link in the series of transition metallocenes and provide comparisons with the chromocene analogs.

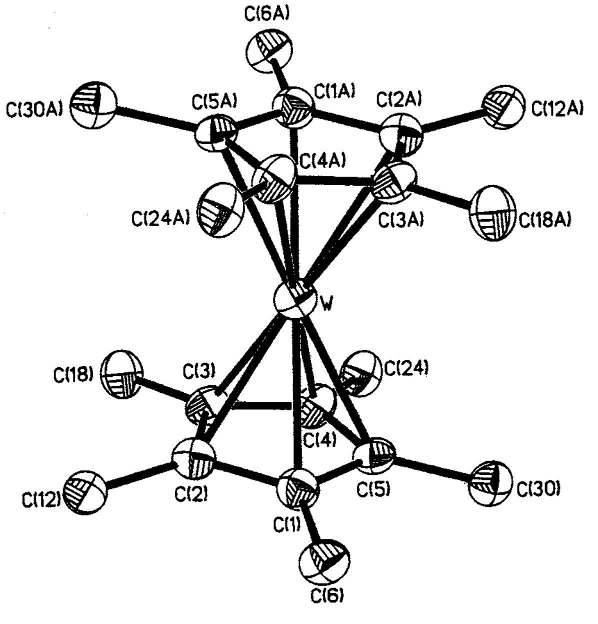


Fig. 2. Simplified molecular structure of **1**$^+$**I**$_3^-$, showing the atomic labeling scheme used in the text. The phenyl groups and the triiodide ion have been artificially omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **1**$^+$**I**$_3^-$

Bond lengths (Å)			
W–C(1)	2.352(5)	W–C(2)	2.370(5)
W–C(3)	2.358(5)	W–C(4)	2.357(5)
W–C(5)	2.344(5)	I(1)–I(2)	2.9292(6)
C(1)–C(2)	1.422(7)	C(1)–C(5)	1.425(7)
C(1)–C(6)	1.505(7)	C(2)–C(3)	1.444(7)
C(2)–C(12)	1.492(7)	C(3)–C(4)	1.434(6)
C(3)–C(18)	1.489(7)	C(4)–C(5)	1.431(7)
C(4)–C(24)	1.497(7)	C(5)–C(30)	1.501(7)
Bond angles (°)			
C(1)–W–C(2)	35.1(2)	C(1)–W–C(3)	59.2(2)
C(1)–W–C(4)	59.0(2)	C(1)–W–C(5)	35.3(2)
C(2)–W–C(3)	35.6(2)	C(2)–W–C(4)	58.7(2)
C(2)–W–C(5)	58.4(2)	C(3)–W–C(4)	35.4(2)
C(3)–W–C(5)	59.0(2)	C(4)–W–C(5)	35.4(2)
C(1)–C(2)–W	71.8(3)	C(1)–C(2)–C(3)	108.5(4)
C(1)–C(2)–C(12)	125.7(4)	C(1)–C(5)–W	72.6(3)
C(1)–C(5)–C(4)	108.5(4)	C(1)–C(5)–C(30)	126.1(4)
C(2)–C(1)–W	73.2(3)	C(2)–C(1)–C(5)	107.9(4)
C(2)–C(1)–C(6)	126.0(4)	C(2)–C(3)–W	72.7(3)
C(2)–C(3)–C(4)	107.1(4)	C(2)–C(3)–C(18)	126.2(4)
C(3)–C(2)–W	71.8(3)	C(3)–C(2)–C(12)	125.3(4)
C(3)–C(4)–W	72.3(3)	C(3)–C(4)–C(5)	108.0(4)
C(3)–C(4)–C(24)	126.8(4)	C(4)–C(3)–W	72.2(3)
C(4)–C(3)–C(18)	126.1(4)	C(4)–C(5)–W	72.8(3)
C(4)–C(5)–C(30)	124.9(4)	C(5)–C(4)–W	71.8(3)
C(5)–C(4)–C(24)	125.0(4)	C(5)–C(1)–C(6)	125.5(4)

3. Experimental

3.1. General procedures

All experimental manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. W(C_2Ph_2)(η^8-C_8Ph_8) was prepared as described in the literature [17]. Iodine, cobaltocene, $AgPF_6$ and $NOPF_6$ were purchased from Aldrich and used as-received. IR spectra were taken on a Hitachi I-2001 spectrometer. MS spectra were obtained on a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Chen-Kung University, Tainan.

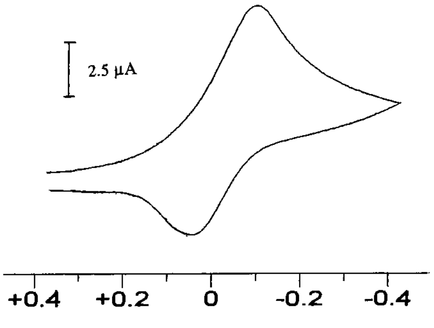


Fig. 3. Cyclic voltammogram of the **1**$^+$**I**$_3^-$/**1** couple.

3.2. Preparation of **1**

$W(C_2Ph_2)(\eta^8\text{-}C_8Ph_8)$ (300 mg, 0.28 mmol) and toluene (20 ml) were added into a 100-ml Schlenk flask equipped with a magnetic stir bar and a reflux condenser connected to an oil bubbler. The solution was heated to reflux for 2 h, forming brick-red precipitates. The solids were washed with toluene and dichloromethane, dried under vacuum and characterized as $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) (264 mg, 0.24 mmol, 86%). MS EI (350°C, 70 eV) *m*/*z*: 1074 ($^{184}W(C_5Ph_5)_2^+$). IR (KBr pellet) 3060, 1602, 1505, 1448, 1072, 1026, 800, 780, 736, 702, 556 cm^{-1}. Elem. Anal. for $C_{70}H_{50}W$: found C, 77.84; H, 4.72; calc. C, 78.21; H, 4.68.

3.3. Preparation of $\mathbf{1^+I_3^-}$

A 100-ml Schlenk flask was equipped with a magnetic stir bar and a reflux condenser connected to an oil bubbler. $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) (236 mg, 0.22 mmol), iodine (89 mg, 0.35 mmol) and benzene (20 ml) were introduced into the flask against a nitrogen flow. The mixture was heated to reflux for 1 h. The dark green precipitates were filtered, washed with benzene and crystallized from dichloromethane/benzene, forming $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3^-}$) $4(C_6H_6)$ (327 mg, 84%). MS FAB *m*/*z*: 1074 ($^{184}W(C_5Ph_5)_2^+$). IR (KBr) 3064, 1604, 1506, 1450, 1408, 1264, 1078, 1028, 968, 906, 800, 778, 740, 710, 700 cm^{-1}. Elem. Anal. for $C_{94}H_{74}WI_3$: found C, 63.63; H, 3.90; calc. C, 63.86; H, 4.19.

3.4. Reduction of $\mathbf{1^+I_3^-}$

A solution of $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3^-}$) (50 mg, 0.034 mmol) and cobaltocene (7 mg, 0.037 mmol) in dichloromethane (10 ml) was stirred at ambient temperature for 1 h, forming microcrystalline solids of **1**, quantitatively.

Table 2
Crystal data and refinement details for $\mathbf{1^+I_3^-}$

Formula	$C_{70}H_{50}I_3W$
T (K)	295(2)
Crystal system	Monoclinic
Crystal solvent	$4C_6H_6$
Space group	$P2_1/c$
Unit cell dimensions:	
a (Å)	14.5258(8)
b (Å)	18.6515(9)
c (Å)	15.5185(8)
β (°)	111.512(1)
V (Å^3)	3911.5(4)
Z	2
D_{calc} (g cm^{-3})	1.501
F(000)	1742
Radiation *λ* (Å)	0.71073
μ (mm^{-1})	2.706
θ range (°)	1.50–24.49
R_1	0.050
wR_2	0.091
GOF on F^2	1.018

Table 3
Selected atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $\mathbf{1^+I_3^-}$

Atom	*x*	*y*	*z*	U_{eq}
W	0	5000	5000	27(1)
I(1)	3677(1)	3776(1)	4810(1)	89(1)
I(2)	5000	5000	5000	64(1)
C(1)	−1738(3)	5069(3)	4414(3)	28(1)
C(2)	−1441(4)	4868(3)	5362(3)	32(1)
C(3)	−852(4)	5442(3)	5923(3)	27(1)
C(4)	−820(4)	6004(3)	5303(3)	29(1)
C(5)	−1361(3)	5769(3)	4377(3)	26(1)
C(6)	−2452(4)	4666(3)	3604(3)	32(1)
C(12)	−1792(4)	4224(3)	5722(4)	34(1)
C(18)	−481(4)	5487(3)	6952(4)	34(1)
C(24)	−388(4)	6737(3)	5565(3)	31(1)
C(30)	−1601(4)	6228(3)	3529(3)	30(1)

3.5. Structure determination for $\mathbf{1^+I_3^-}$

A crystal of $\mathbf{1^+I_3^-}$ with approximate dimensions $0.17 \times 0.15 \times 0.15$ mm^3 was mounted on a glass fiber and aligned to a Simens SMART-CCD diffractometer with graphite monochromated Mo–K_α radiation. Sadabs absorption correction ($T_{min} = 0.746$, $T_{max} = 0.508$) was made. The number of reflections measured was 21 276, and 8917 reflections ($2\theta < 55°$, $R_{int} = 0.0655$) were unique. The structure was solved by the direct method and refined by full-matrix least-square on F^2. The program used was the SHELXTLE package. The data collection and refinement parameters are presented in Table 2. Selected atomic positional parameters are given in Table 3.

3.6. Cyclic voltammetric measurement for $\mathbf{1^+I_3^-}$

Electrochemical measurements were taken with a CV 50 W system. Cyclic voltammetry was performed with a Pt button working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode. The experiments were carried out with 1 mM of $\mathbf{1^+I_3^-}$ in CH_2Cl_2 solvent containing 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte. Potential was scanned at 100 mV s^{-1} at 28°C.

Acknowledgements

The authors are grateful for support of this work by the National Science Council of Taiwan.

References

[1] T.J. Kealy, P.L. Pauson, Nature (London) 168 (1951) 1039.

[2] G. Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, J. Am. Chem. Soc. 74 (1952) 2125.

[3] E.O. Fischer, W. Pfab, Z. Naturforsch. 7B (1953) 377.

[4] G.E. Coates, M.L.H. Green, K. Wade, Organometallic Compounds, 3rd edn, Methuen, London, 1967.

[5] T.J. Marks, Prog. Inorg. Chem. 24 (1978) 51; 25 (1979) 223.

[6] A. Togni, R.L. Halterman, Metallocenes, Wiley-VCH, Weinheim, 1998.

[7] J.L. Robbins, N. Edelstein, B. Spencer, J.C. Smart, J. Am. Chem. Soc. 104 (1982) 1882.

[8] M.P. Castellani, S.J. Geib, A.L. Rheingold, W.C. Trogler, Organometallics 6 (1987) 1703.

[9] D. O'Hare, V.J. Murphy, N. Kaltsoyannis, J. Chem. Soc. Dalton Trans. (1993) 383.

[10] M. Dub, Organometallic Compounds, vol. 1, 2nd ed., Springer, Berlin, 1966.

[11] P. Grebenik, A.J. Downs, M.L.H. Green, R.N. Perutz, J. Chem. Soc. Chem. Commun. (1979) 742.

[12] J.L. Thomas, J. Am. Chem. Soc. 95 (1973) 1838.

[13] J.L. Thomas, H.H. Brintzinger, J. Am. Chem. Soc. 94 (1972) 1386.

[14] M.C. Barral, M.L.H. Green, R. Jimenez, J. Chem. Soc. Dalton Trans. (1982) 2495.

[15] F.G.N. Cloke, J.P. Day, J.C. Green, C.P. Morley, A.C. Swain, J. Chem. Soc. Dalton Trans. (1991) 789.

[16] W. Hübel, R. Merényi, J. Organomet. Chem. 2 (1964) 213.

[17] W.-Y. Yeh, C.-L. Ho, M.Y. Chiang, I.-T. Chen, Organometallics 16 (1997) 2698.

[18] L.D. Field, T.W. Hambley, P.A. Humphrey, C.M. Lindall, G.J. Gainsford, A.F. Masters, T.G. St. Pierre, J. Webb, Aust. J. Chem. 48 (1995) 851.

[19] H. Schumann, A. Lentz, R. Weimann, J. Pickardt, Angew. Chem. Int. Ed. Engl. 33 (1994) 1731.

[20] A. Schott, H. Scott, G. Wilker, J. Brandt, H. Hoberg, E.G. Hoffmann, Justus Liebigs Ann. Chem. (1973) 508.

[21] M.J. Aroney, I.E. Buys, G.D. Dennis, L.D. Field, T.W. Hambley, P.A. Lay, A.F. Masters, Polyhedron 12 (1993) 2051.

[22] M.J. Heeg, C. Janiak, J.J. Zuckerman, J. Am. Chem. Soc. 106 (1984) 4259.

[23] J.L. Atwood, W.E. Hunter, A.H. Cowley, R.A. Jones, C.A. Stewart, J. Chem. Soc. Chem. Commun. (1981) 925.

[24] P. Jutzi, F. Kohl, P. Hofmann, C. Kruger, Y.H. Tsay, Chem. Ber. 113 (1980) 757.

[25] G. Wilkinson, P.L. Pauson, F.A. Cotton, J. Am. Chem. Soc. 76 (1954) 1970.

[26] K.W. Barnett, J. Organomet. Chem. 78 (1974) 139.

[27] W. Klaui, L. Ramacher, Angew. Chem. Int. Ed. Engl. 25 (1986) 97.