

**SYNTHESIS AND CHARACTERIZATION OF ($\eta^1:\eta^5\text{-C}_5\text{H}_4$)-BRIDGED
 GROUP IV METALLOCENE DERIVATIVES. X-RAY STRUCTURE OF
 {Cp($\mu\text{-}[\eta^1:\eta^5\text{-C}_5\text{H}_4]$)Ti[PMe₃]}₂**

L.B. KOOL, M.D. RAUSCH,

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003 (U.S.A.)

H.G. ALT*, M. HERBERHOLD,

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-8580 Bayreuth (F.R.G.)

U. THEWALT and B. HONOLD

Sektion für Röntgen- und Elektronenbeugung der Universität Ulm, Oberer Eselsberg, D-7900 Ulm (F.R.G.)

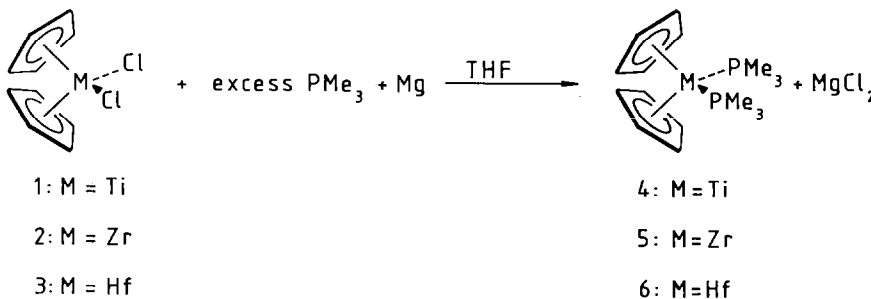
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Summary

Reduction of Cp₂MCl₂ (M = Ti, Zr and Hf) with magnesium in the presence of one equivalent of PMe₃ gives the dimeric ($\eta^1:\eta^5\text{-C}_5\text{H}_4$)-bridged complexes {Cp($\mu\text{-}[\eta^1:\eta^5\text{-C}_5\text{H}_4]$)M[PMe₃]}₂ in excellent yields. The ¹H, ¹³C and ³¹P NMR spectra are presented, together with the results of an X-ray structure determination of the titanium derivative.

Introduction

We recently reported that the reduction of Cp₂MCl₂ (1–3) by magnesium in the presence of excess PMe₃ leads to the complexes Cp₂M(PMe₃)₂ (M = Ti, Zr and Hf) (4–6) [1,2].

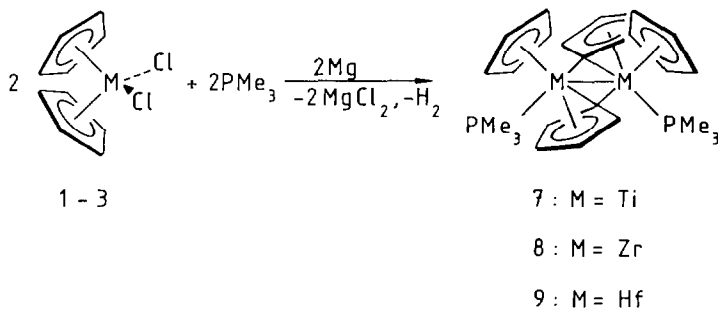


The titanium complex **4** was prepared in quantitative yield, the zirconium analogue **5** in 55% yield, and the hafnium complex **6** in only trace amounts. In order to obtain more information about the reductions which give **4–6** and to identify the side-products, we investigated reductions in the presence of only one equivalent of PMe_3 . This resulted in the formation of the binuclear ($\eta^1 : \eta^5\text{-C}_5\text{H}_4$)-bridged compounds $\{\text{Cp}(\mu\text{-}[\eta^1 : \eta^5\text{-C}_5\text{H}_4])\text{M}[\text{PMe}_3]\}_2$ ($\text{M} = \text{Ti}$ (**7**), Zr (**8**) and Hf (**9**)).

Results and discussion

Syntheses

The reactions of the metallocene dichlorides **1–3** with magnesium in the presence of only one equivalent of PMe_3 resulted in the loss of hydrogen and formation of the diamagnetic ($\eta^1 : \eta^5\text{-C}_5\text{H}_4$)-bridged dimers **7–9** in excellent yields.



Complex **8** was also obtained by heating toluene solutions of **5**. Schwartz and coworkers [3,4] have described similar zirconium complexes obtained by thermal decomposition of Cp_2ZrL_2 ($\text{L} = \text{PMe}_2\text{Ph}$ and PMePh_2). A 16-electron coordinatively unsaturated intermediate, Cp_2ZrL , was suggested to be the active species in C–H bond insertions. Our observations agree with this view, and indicate that a 16-electron intermediate, $\text{Cp}_2\text{M}(\text{PMe}_3)$ can be assumed in the Ti and Hf systems as well. Thus, when **1–3** are reduced in the presence of only one equivalent of ligand, the 16-electron species $\text{Cp}_2\text{M}(\text{PMe}_3)$ are formed initially, and then undergo C–H bond insertion to give the ($\eta^1 : \eta^5\text{-C}_5\text{H}_4$)-bridged products **7–9**.

The reduced yields encountered in the syntheses of the zirconocene and hafnocene bis(phosphine) complexes, **5** and **6**, are presumably due to the greater ease of loss of one PMe_3 ligand from them compared with that from **4**. This is in agreement with the increased reactivity of Group IV metallocene bis(trimethylphosphine) complexes toward ligand displacement on descending the group.

Similarities between the IR and ^1H NMR spectra of ($\eta^1 : \eta^5\text{-C}_5\text{H}_4$)-bridged zirconocene phosphine dimers and “zirconocene” have led to conclusions about the structure of zirconocene [3], and a difference in structure between “zirconocene” and “green titanocene” [5] was implied. The results presented here indicate that the ($\eta^1 : \eta^5\text{-C}_5\text{H}_4$)-bridged structure may also occur in some forms of titanocene and hafnocene.

Spectroscopic characterization

The NMR data for compounds **7–9** are given in Table 1. The spectra contain signals expected for both $\eta^5\text{-Cp}$ and bridging $\eta^1 : \eta^5\text{-C}_5\text{H}_4$ ligands. In the ^1H NMR

TABLE 1
NMR SPECTRA ^a OF {Cp(μ-η¹:η⁵-C₅H₄)M(PMe₃)₂} (7-9)

Compound	¹ H NMR			¹³ C NMR			³¹ P NMR ^b
	δ(Cp) [³ J(P,H) in Hz]	δ(C ₅ H ₄)	δ(PMe ₃) [² J(P,H) in Hz]	δ(Cp)	δ(C ₅ H ₄) ^c	δ(PMe ₃) [¹ J(P,C) in Hz]	
M = Ti (7)	5.02	3.86			103.9		+ 15.9
	[1.5]	4.35	0.89	98.5	106.1	17.3	
		5.40	[5.4]		111.3	[6.8]	
		5.95			115.1		
M = Zr (8)	5.23	3.79			99.0		-0.1
	[1.7]	5.04	1.01	98.5	104.8	16.4	
		5.77	[5.6]		108.9	[13.4]	
		6.16			111.0		
M = Hf (9)	5.10	3.42					-10.4
	[^d]	4.87	0.99	95.7	^d	17.2	
		5.70	[5.9]			[18.8]	
		5.94					

^a Toluene-*d*₈, -20°C. ^b Free PMe₃ (in toluene-*d*₈): -58.5 ppm. ^c Metal-bonded C_α of C₅H₄ not observed. ^d Not resolved.

spectra the η⁵-Cp ligands appear as doublets as a result of coupling to phosphorus, with ³J(P, H) coupling constants in the range observed for other Group IV metallocene complexes containing the PMe₃ ligand, such as Cp₂M(PMe₃)(CO) (M = Ti, Zr and Hf) [6]. The protons of the C₅H₄ bridges are all magnetically inequivalent and appear as broad multiplets. Variable temperature ¹H NMR spectra indicated no fluxionality for 7 up to 90°C. Above this temperature considerable decomposition occurred. The resonances of the methyl groups of the PMe₃ ligands are split into doublets.

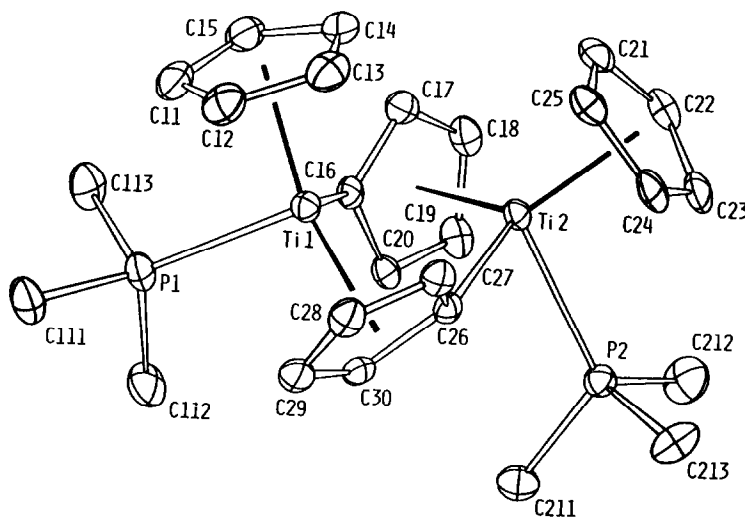


Fig. 1. Molecular structure of {Cp(μ-η¹:η⁵-C₅H₄)Ti(PMe₃)₂} (7).

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) IN $\{\text{Cp}(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}[\text{PMe}_3]\}_2$ (7)

Ti(1)–Ti(2)	3.223(1)	Ti(1)–C(11)	2.435(5)	C(11)–C(12)	1.392(2)
Ti(1)–P(1)	2.589(1)	Ti(1)–C(12)	2.423(5)	C(12)–C(13)	1.403(8)
Ti(1)–C(16)	2.211(4)	Ti(1)–C(13)	2.388(5)	C(13)–C(14)	1.404(8)
Ti(1)–Z(1)	2.099(5) ^a	Ti(1)–C(14)	2.402(4)	C(14)–C(15)	1.423(7)
Ti(1)–Z(4)	2.021(4) ^a	Ti(1)–C(15)	2.425(4)	C(15)–C(11)	1.397(7)
Ti(2)–P(2)	2.565(1)	Ti(1)–C(26)	2.282(4)	C(16)–C(17)	1.438(6)
Ti(2)–C(26)	2.201(4)	Ti(1)–C(27)	2.348(4)	C(17)–C(18)	1.420(7)
Ti(2)–Z(2)	2.023(4) ^a	Ti(1)–C(28)	2.447(4)	C(18)–C(19)	1.392(6)
Ti(2)–Z(3)	2.091(5) ^a	Ti(1)–C(29)	2.401(4)	C(19)–C(20)	1.419(6)
		Ti(1)–C(30)	2.296(4)	C(20)–C(16)	1.427(6)
P(1)–C(111)	1.836(5)				
P(1)–C(112)	1.830(6)	Ti(2)–C(16)	2.279(4)	C(21)–C(22)	1.404(7)
P(1)–C(113)	1.830(5)	Ti(2)–C(17)	2.335(4)	C(22)–C(23)	1.399(7)
		Ti(2)–C(18)	2.443(5)	C(23)–C(24)	1.414(8)
P(2)–C(211)	1.828(5)	Ti(2)–C(19)	2.411(5)	C(24)–C(25)	1.399(7)
P(2)–C(212)	1.831(6)	Ti(2)–C(20)	2.306(4)	C(25)–C(21)	1.403(7)
P(2)–C(213)	1.827(5)				
		Ti(2)–C(21)	2.388(5)	C(26)–C(27)	1.450(6)
		Ti(2)–C(22)	2.430(5)	C(27)–C(28)	1.403(6)
		Ti(2)–C(23)	2.439(4)	C(28)–C(29)	1.393(7)
		Ti(2)–C(24)	2.407(5)	C(29)–C(30)	1.429(7)
		Ti(2)–C(25)	2.378(5)	C(30)–C(26)	1.439(6)
P(1)–Ti(1)–C(16)	81.2(1)	Ti(1)–P(1)–C(111)	118.9(2)		
P(1)–Ti(1)–Z(1)	103.0(1)	Ti(1)–P(1)–C(112)	118.5(2)		
P(1)–Ti(1)–Z(4)	106.2(1)	Ti(1)–P(1)–C(113)	114.2(2)		
C(16)–Ti(1)–Z(1)	110.7(2)	C(111)–P(1)–C(112)	100.0(3)		
C(16)–Ti(1)–Z(4)	108.2(2)	C(111)–P(1)–C(113)	101.9(2)		
Z(1)–Ti(1)–Z(4)	134.0(2)	C(112)–P(1)–C(113)	100.4(3)		
P(2)–Ti(2)–C(26)	81.7(1)	Ti(2)–P(2)–C(211)	118.4(2)		
P(2)–Ti(2)–Z(2)	106.0(1)	Ti(2)–P(2)–C(212)	117.8(2)		
P(2)–Ti(2)–Z(3)	102.6(1)	Ti(2)–P(2)–C(213)	116.3(2)		
C(26)–Ti(2)–Z(2)	108.2(2)	C(211)–P(2)–C(212)	100.5(3)		
C(26)–Ti(2)–Z(3)	111.4(2)	C(211)–P(2)–C(213)	99.1(3)		
Z(2)–Ti(2)–Z(3)	113.7(2)	C(212)–P(2)–C(213)	101.5(3)		

^a Z(1) Centre of the ring containing C(11)–C(15), Z(2) (C(16)–C(20)), Z(3) (C(21)–C(25)), Z(4) (C(26)–C(30)).

A comparison of the ¹H and ¹³C NMR data of the cyclopentadienyl rings in 7–9 indicates that the electron density in the rings depends only slightly on the metal. The phosphorus nuclei in 7–9, on the other hand, experience enhanced shielding on proceeding down the group. The same trend is observed in the series Cp₂M(PMe₃)(CO) (M = Ti, Zr and Hf) [6].

X-Ray structure

The molecule of $\{\text{Cp}(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}[\text{PMe}_3]\}_2$ (7) is shown in Fig. 1. Bond distances and angles of 7 are given in Table 2. The molecule consists of an assembly of two planar η^5 -bound Cp rings and two planar bridging ($\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$) rings. The two PMe₃ ligands are *cis* to one another, as are the two C₅H₅ rings. Their characteristic metal bond distances and bond angles are compared with those of similar titanocene derivatives in Table 3. The most interesting feature of the molecule is the Ti(1)–(C₅H₄)₂–Ti(2) core shown in Fig. 2.

TABLE 3

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) IN 7 AND RELATED COMPOUNDS

	Ti-Z	Ti-P	Z-Ti-Z	Ref.
[Cp(μ -[η^1 : η^5 -C ₅ H ₄])Ti[PMe ₃]] ₂ (7)	2.099(5) ^a	2.589(1)	134.0(2)	this work
	2.091(5) ^a	2.565(1)	133.7(2)	
	2.021(4) ^b			
	2.023(4) ^b			
Cp ₂ Ti(PMe ₃)(CO)	2.036(6)	2.544(1)	136.9(3)	[6]
	2.044(6)			
Cp ₂ Ti(PMe ₃) ₂	2.057(12)	2.524(4)	133.2(5)	[1]
	2.062(14)	2.527(3)	134.3(6)	
	2.049(12)	2.527(2)		
Cp ₂ TiCl(PMe ₃)	2.071(7)	2.599(1)	132.3(3)	[6]
	2.064(7)			
Cp ₂ Ti(CO) ₂	2.032	–	138.6	[8]
	2.018			

^a Cp ring. ^b C₅H₄ ring.

The lengths of the Ti(1)–C(16) and Ti(2)–C(16) bonds as well as those of the Ti(1)–C(26) and Ti(2)–C(26) bonds are very similar, and indicate that the two bridgehead carbon atoms C(16) and C(26) are involved in a three center bond. As a consequence the aromatic character of the two C₅H₄ ligands is considerably disrupted. Each C₅H₄ ring is bent towards one metal atom in a way that its π -electrons can overlap with the hybrid orbitals of the metal (Z–Ti: 2.021(4) and 2.023(4) Å).

A similar type of bridgehead carbon atom (C(16) and C(26) of the two C₅H₄-bridges equidistant from Ti(1) and Ti(2)) was also found in the Ti₂(C₅H₄) core of

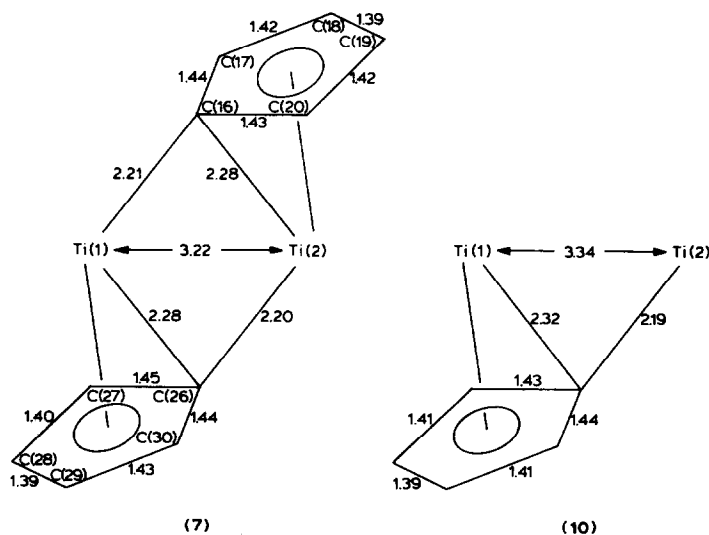


Fig. 2. Selected bond distances of the Ti₂(C₅H₄)₂ core of 7 and the Ti₂C₅H₄ core of Cp₃(C₅H₄)Ti₂·(C₄H₈O)·C₄H₈O (10) [7].

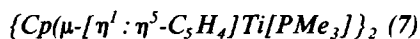
$\text{Cp}_3(\text{C}_5\text{H}_4)\text{Ti}_2(\text{C}_4\text{H}_8\text{O}) \cdot (\text{C}_4\text{H}_8\text{O})$ (**10**) [7]. Two bridging ($\eta^1 : \eta^5$) C_5H_4 ligands are also present in $\text{Cp}_2\text{Th}(\text{C}_5\text{H}_4)_2$ [9] and $\text{Cp}_2\text{Nb}_2(\text{H})_2(\text{C}_5\text{H}_4)_2$ [10].

Electron counting suggests that **7** is a 17-electron complex and should be paramagnetic. The diamagnetism of **7**, however, might be explained by a direct Ti(1)–Ti(2) bond or by spin pairing through the bridges, as is the case for dimeric $(\text{Cp}_2\text{TiSR})_2$ complexes [11]. Though Pez suggested a Ti–Ti bond for **10** (Ti–Ti: 3.34 Å [7]) we prefer the latter explanation for the diamagnetism of **7** even though the Ti(1)–Ti(2) distance (3.22 Å) is somewhat shorter than that in **10**.

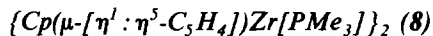
Experimental

Preparations

All operations were performed under prepurified argon. THF and toluene were dried over Na/K alloy and freshly distilled. $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$ (**5**) was prepared by the literature procedure [2]. Mass spectral data are based on ^{48}Ti , ^{90}Zr and ^{180}Hf isotopes.



A mixture of Cp_2TiCl_2 (1.00 g, 4.02 mmol), magnesium turnings (0.5 g, 20.6 mmol), and PMe_3 (0.38 ml, 4.0 mmol) in ca. 75 ml THF was stirred at room temperature. The mixture turned successively green, blue, olive-green, and finally burgundy. After 24 h the solvent was removed in vacuo and the residue was extracted with toluene. The toluene solution was filtered, then concentrated, and kept at -20°C , to give complex **7** as air-sensitive black-violet crystals (880 mg, 86%); m/e 506 (M^+).



By the procedure described for **7** [Cp_2ZrCl_2 (500 mg, 1.72 mmol), magnesium turnings (200 mg, 8.2 mmol) and PMe_3 (0.16 ml, 1.7 mmol) in 30 ml THF] complex **8** was obtained as air-sensitive dark-red needles (460 mg, 91%).



The procedure described above for **7** [Cp_2HfCl_2 (500 mg, 1.32 mmol), magnesium turnings (160 mg, 6.6 mmol) and PMe_3 (0.125 ml, 1.32 mmol) in 20 ml THF] afforded complex **9** as very air-sensitive red crystals (470 mg, 92%); m/e 770 (M^+).

Spectroscopic measurements

The following instruments were used: NMR: JEOL FX 90Q; Mass: Varian CH7 (electron impact, 70 eV).

X-Ray structure of $\{\text{Cp}(\mu\text{-}[\eta^1 : \eta^5\text{-C}_5\text{H}_4])\text{Ti}[\text{PMe}_3]\}_2$ (**7**)

A crystal (approx. $0.3 \times 0.3 \times 0.4$ mm) was sealed under argon in a Lindeman glass capillary. All data were collected at 20°C using a Philips PW1100 diffractometer and graphite-monochromated Mo- K_α radiation (λ 0.71069 Å). Crystal data for $\text{C}_{26}\text{H}_{36}\text{P}_2\text{Ti}_2$: monoclinic, space group $P2_1/c$, a 13.056(2), b 11.406(3), c 17.408(3) Å, β 99.51(2)°, V 2557(1) Å³, Z 4, D_c 1.315 g cm⁻³, μ 7.0 cm⁻¹. A total of 4498 unique reflections was measured by using θ – 2θ scans for values of 2θ reflections ranging from 4 to 50°. The reflection intensities were corrected for Lorentz and

TABLE 4
ATOMIC COORDINATES FOR 7

Atom	x	y	z	U_{eq}
Ti(1)	0.6924(1)	0.1112(1)	0.3820(0)	0.028(1)
P(1)	0.7088(1)	0.3301(1)	0.3465(1)	0.038(1)
C(111)	0.6074(4)	0.4328(4)	0.3651(3)	0.054(6)
C(112)	0.7165(5)	0.3680(4)	0.2455(3)	0.060(6)
C(113)	0.8266(4)	0.4014(4)	0.3969(3)	0.053(5)
Ti(2)	0.8253(1)	-0.0857(1)	0.3093(0)	0.026(1)
P(2)	0.7900(1)	-0.1328(1)	0.1632(1)	0.034(1)
C(211)	0.7571(5)	-0.0121(5)	0.0944(3)	0.071(7)
C(212)	0.8934(4)	-0.2042(5)	0.1211(3)	0.065(7)
C(213)	0.6798(4)	-0.2292(5)	0.1300(3)	0.059(6)
C(11)	0.7009(4)	0.2191(4)	0.5036(3)	0.046(5)
C(12)	0.6168(4)	0.1428(5)	0.4985(3)	0.049(5)
C(13)	0.6554(4)	0.0278(5)	0.5003(3)	0.048(6)
C(14)	0.7640(4)	0.0326(4)	0.5075(3)	0.043(5)
C(15)	0.7921(4)	0.1533(5)	0.5093(3)	0.045(5)
C(16)	0.8473(3)	0.1054(3)	0.3467(2)	0.029(4)
C(17)	0.9342(3)	0.0428(4)	0.3893(3)	0.036(4)
C(18)	0.9996(3)	-0.0019(4)	0.3387(3)	0.040(5)
C(19)	0.9566(4)	0.0316(4)	0.2634(3)	0.039(5)
C(20)	0.8661(3)	0.0982(3)	0.2683(2)	0.031(4)
C(21)	0.8868(4)	-0.2125(4)	0.4161(3)	0.043(5)
C(22)	0.9219(4)	-0.2628(4)	0.3515(3)	0.044(5)
C(23)	0.8347(4)	-0.2985(4)	0.2989(3)	0.044(5)
C(24)	0.7450(4)	-0.2701(4)	0.3308(3)	0.043(5)
C(25)	0.7780(4)	-0.2175(4)	0.4032(3)	0.041(5)
C(26)	0.6640(3)	-0.0223(4)	0.2832(2)	0.028(4)
C(27)	0.5861(3)	-0.0461(4)	0.3317(3)	0.035(4)
C(28)	0.5156(3)	0.0471(4)	0.3303(3)	0.040(5)
C(29)	0.5442(3)	0.1332(4)	0.2812(3)	0.040(5)
C(30)	0.6326(3)	0.0908(4)	0.2511(2)	0.033(4)

polarization effects. The set of 3820 reflections with $I > 1.5\sigma(I)$ was used in the subsequent calculations. The structure was solved by direct methods (MULTAN [12]) and refined by Fourier and least-squares techniques. (Hydrogen atoms were ignored). In the final cycle of refinement the maximum shift-error was 0.09. $R = 0.066$; $R_w(F) = 0.054$. The final difference map had a maximum value of 0.47 $e\text{\AA}^{-3}$. Atom scattering factors for neutral atoms [13], corrected for anomalous dispersion [14] were used. The computer programs used were those of the SHELX-76 System [15]. Atomic parameters are listed in Table 4. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD 51770, the names of the authors, and the full journal citation.

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References

- 1 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Wolf, *Angew. Chem.*, 97 (1985) 425; *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 394.
- 2 L.B. Kool, M.D. Rausch, H.G. Alt and M. Herberhold, Twelfth International Conference on Organometallic Chemistry, Austria, September 8–13, 1985; Abstract 185.
- 3 K.I. Gell, T.V. Harris and J. Schwartz, *Inorg. Chem.*, 20 (1981) 481.
- 4 K.I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 103 (1981) 2687.
- 5 H.H. Brintzinger and J.L. Bercaw, *J. Am. Chem. Soc.*, 92 (1970) 6182.
- 6 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Wolf and U. Thewalt, *J. Organomet. Chem.*, 297 (1985) 159.
- 7 G.P. Pez, *J. Am. Chem. Soc.*, 98 (1977) 8072.
- 8 J.L. Atwood, K.E. Stone, H.G. Alt, D.C. Hrcir and M.D. Rausch, *J. Organomet. Chem.*, 132 (1977) 367.
- 9 E.C. Baker, K.N. Raymond, T.J. Marks and W.A. Wachter, *J. Am. Chem. Soc.*, 96 (1974) 7586.
- 10 L.J. Guggenberger, *Inorg. Chem.*, 12 (1973) 294.
- 11 G. Fachinetti and C. Floriani, *J. Chem. Soc., Dalton Trans.*, (1974) 2433.
- 12 MULTAN-84, P. Main, University of York, England.
- 13 D.T. Cromer and J.B. Mann, *Acta Cryst.*, A24 (1968) 321.
- 14 SHELX-76 Program System, G.M. Sheldrick, University of Göttingen, unpublished.