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Insertion reactions of carbonylbis(η-cyclopentadienyl)-hydridoniobium with activated acetylenes

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Abstract

Carbonylbis(η-cyclopentadienyl)hydridoniobium (I) $Cp_2NbH(CO)$ reacts with $MeO_2CC{\equiv}CCO_2Me$ at −80 °C to give predominantly the (*Z*)-alkenyl complex $Cp_2Nb(CO)[\eta^1\text{-}(Z)\text{-}C(CO_2Me){=}CH(CO_2R)]$ (II), together with the *E* isomer (III) in a 3/1 ratio. Slow isomerization at ambient temperature produces a 1/5 equilibrium mixture. The structure of II was determined by X-ray diffraction methods. Activated terminal acetylenes $HC{\equiv}CR$ undergo α-insertion to yield the alkenyl complexes $Cp_2Nb(CO)[\eta^1\text{-}(CR{=}CH_2)]$ (IV, R = CO_2, Me; V, R = C(O)Me).

Introduction

The mechanism of insertion of activated acetylenes into metal–hydrogen bonds of electron-rich hydride complexes is a matter of continuing interest [1–5]. It is essential in considering the question to distinguish rigorously between the primary, kinetically controlled, products, and the secondary, often isomeric, thermodynamic products. In our recent work on insertion reactions of the metallocene hydrides Cp_2ReH [6,7], Cp_2MoH_2 [6,8], and Cp_2WH_2 [6] with activated acetylenes, several stereochemical assignments made in the literature had to be corrected. We concluded that the reactions of these metallocene hydrides with disubstituted acetylenes involve stereospecific *trans* insertion processes in all cases [6], and that the same is true for the β-insertion reactions of Cp_2ReH with activated terminal acetylenes [7].

Niobocene hydride complexes show more complex reaction patterns [9,10]. We describe here the insertion reactions of the carbonyl $Cp_2NbH(CO)$ (I) with $MeO_2CC{\equiv}CCO_2Me$ (DMAC), $HC{\equiv}CCO_2Me$ and $HC{\equiv}CC(O)Me$. Closely related reactions with acetylenes $HC{\equiv}CR$ and $RC{\equiv}CR$ bearing cyano or trifluoromethyl substituents (R = CN, CF_3) have been described previously [4].

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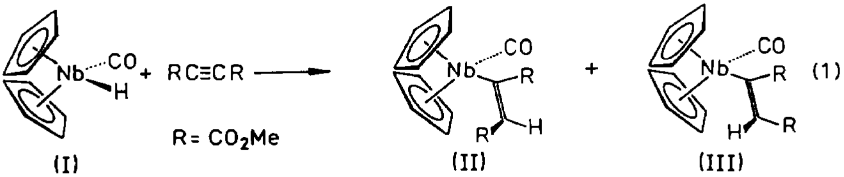
Results

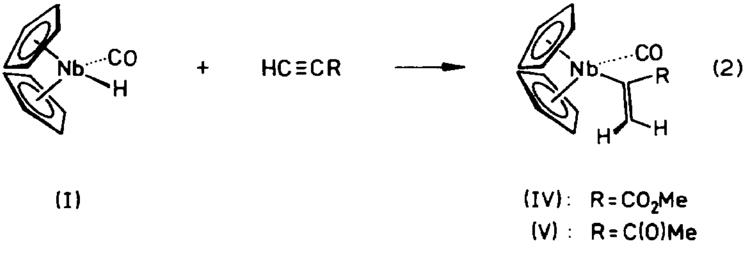
Insertion reactions

The reaction of $Cp_2NbH(CO)$ (I) with $MeO_2CC{\equiv}CCO_2Me$ is very fast even at −80 °C, and yields predominantly the (*Z*)-alkenyl complex II together with the *E* isomer III (eq. 1). The ^1H NMR spectrum of the reaction mixture shows a primary product ratio *Z*/*E* of approximately 3/1. In solution slow isomerization takes place at room temperature and after 2 days equilibrium is reached at an isomer ratio *Z*/*E* of 1/5. The *E* isomer III could not be isolated.



The structure of the *Z* isomer II was determined by an X-ray diffraction study (see below). The stereochemistry of the alkenyl group of III can be deduced from the vicinal coupling of the alkenyl proton with the α-carbonyl carbon atom [6]; the coupling constant $^3J(^{13}C{-}^1H)$ of 15 Hz for III clearly establishes the *trans* disposition of the α-ester group and the alkenyl proton. In addition, direct coupling constants $^1J(^{13}C{-}^1H)$ between the alkenyl proton and the β-carbon atom are smaller for *Z* isomers than for the corresponding *E* isomers [6]; in our complex these coupling constants are 155 Hz for II and 164 Hz for III, and thus are in agreement with the quoted generalization.

At room temperature $Cp_2NbH(CO)$ (I) reacts smoothly with activated terminal acetylenes $HC{\equiv}CR$. Regiospecific α-insertion produces alkenyl complexes $Cp_2Nb(CO)[\eta^1\text{-}(CR{=}CH_2)]$ (IV, R = CO_2Me; V, R = C(O)Me) (eq. 2).



The ^1H NMR spectra of IV and V each contain two prominent sharp singlets for the cyclopentadienyl and methyl protons, respectively. Two doublets with a small coupling constant ($^2J(^1H{-}^1H)$, IV: 4.3, V: 3.5 Hz) demonstrate the presence of a $C{=}CH_2$ group [11]. No indication of the presence of conformational isomers due to restricted rotation around the Nb–C(alkenyl) bond was found.

X-Ray diffraction results

Crystals of complex II are composed of discrete molecules at Van der Waals distances. The molecular structure of II is illustrated in Fig. 1, which also shows the atom-numbering scheme. Selected structural data are listed in Tables 1–3.

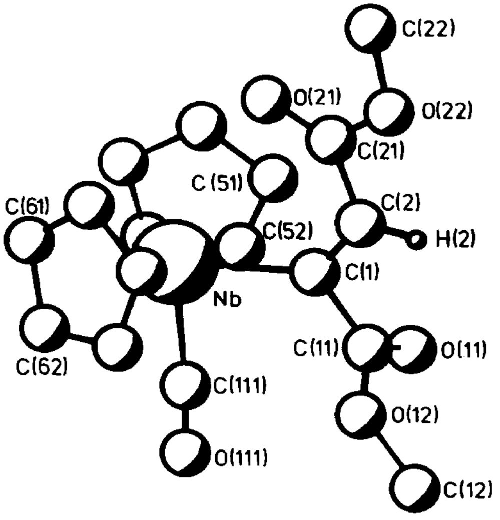


Fig. 1. The molecular structure of II.

The molecule contains a bent metallocene, a carbonyl group, and an alkenyl moiety. The cyclopentadienyl rings are nearly planar with maximum deviations from the best planes of 0.8 pm for ring A (cf. Table 3) and 1.3 pm for ring B. The

Table 1

Non-hydrogen atoms coordinates for II

Atom	x	y	z	B_{eq} [a]
Nb	0.73826(2)	0.22601(2)	0.88421(2)	2.237(7)
C(1)	0.6460(2)	0.0994(2)	0.8970(2)	2.4(1)
C(11)	0.6177(3)	0.0777(3)	0.9857(2)	2.8(1)
C(12)	0.6526(4)	−0.0084(4)	1.1062(3)	5.6(2)
O(11)	0.5482(2)	0.1084(2)	1.0211(2)	4.5(1)
O(12)	0.6782(2)	0.0199(2)	1.0220(2)	3.8(1)
C(2)	0.6098(3)	0.0409(3)	0.8408(3)	2.7(1)
C(21)	0.6160(3)	0.0491(2)	0.7485(3)	2.7(1)
C(22)	0.5780(3)	−0.0257(3)	0.6205(3)	4.5(2)
O(21)	0.6462(2)	0.1103(2)	0.7078(2)	4.2(1)
O(22)	0.5807(2)	−0.0250(2)	0.7117(2)	4.2(1)
C(51)	0.6218(3)	0.3021(3)	0.7967(4)	4.5(2)
C(52)	0.5698(3)	0.2710(3)	0.8656(4)	4.2(2)
C(53)	0.6073(3)	0.3118(3)	0.9388(4)	4.6(2)
C(54)	0.6822(3)	0.3700(3)	0.9134(3)	3.9(2)
C(55)	0.6911(3)	0.3624(3)	0.8254(3)	4.2(2)
C(61)	0.8856(3)	0.2605(3)	0.8134(3)	4.3(2)
C(62)	0.9092(3)	0.2327(3)	0.8952(3)	3.8(1)
C(63)	0.8813(3)	0.1409(3)	0.9029(3)	3.5(2)
C(64)	0.8445(3)	0.1139(3)	0.8239(3)	3.2(1)
C(65)	0.8466(3)	0.1854(3)	0.7693(3)	3.6(2)
C(111)	0.7604(4)	0.2286(3)	1.0121(3)	4.2(2)
O(111)	0.7777(3)	0.2342(3)	1.0828(2)	6.8(2)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents; in 10^4 pm^2.

Table 2

Selected bond distances (pm) and bond angles (°) for II

Nb–C(1)	229.5(3)	Nb–C(111)	203.9(3)
C(1)–C(2)	134.3(4)	C(111)–O(111)	114.2(4)
C(2)–H(2)	90.7		
C(1)–C(11)	148.7(4)	C(2)–C(21)	146.3(5)
C(11)–O(11)	119.9(4)	C(21)–O(21)	119.5(4)
C(11)–O(12)	133.1(4)	C(21)–O(22)	134.5(4)
C(12)–O(12)	143.6(4)	C(22)–O(22)	143.8(4)
Nb–C(51)	240.3(4)	Nb–C(61)	237.1(3)
Nb–C(52)	243.1(3)	Nb–C(62)	235.9(3)
Nb–C(53)	237.5(4)	Nb–C(63)	236.4(3)
Nb–C(54)	234.1(3)	Nb–C(64)	242.3(3)
Nb–C(55)	233.9(3)	Nb–C(65)	242.2(3)
C(51)–C(52)	138.2(6)	C(61)–C(62)	139.4(6)
C(52)–C(53)	140.4(6)	C(62)–C(63)	143.6(6)
C(53)–C(54)	140.8(6)	C(63)–C(64)	140.3(5)
C(54)–C(55)	139.8(5)	C(64)–C(65)	137.6(5)
C(51)–C(55)	138.9(5)	C(61)–C(65)	142.8(5)
Nb–C(111)–O(111)	175.3(4)	C(1)–Nb–C(111)	90.6(1)
Nb–C(1)–C(2)	133.5(2)	C(1)–C(2)–C(21)	125.4(3)
Nb–C(1)–C(11)	114.1(2)	C(1)–C(2)–H(2)	120.6(3)
C(11)–C(1)–C(2)	112.3(3)	C(21)–C(2)–H(2)	113.9(3)
C(1)–C(11)–O(11)	124.2(3)	C(2)–C(21)–O(21)	128.2(3)
O(11)–C(11)–O(12)	123.3(3)	O(21)–C(21)–O(22)	122.0(3)
C(11)–O(12)–C(12)	115.9(3)	C(21)–O(22)–C(22)	116.6(3)
C(51)–C(52)–C(53)	107.9(4)	C(61)–C(62)–C(63)	107.7(3)
C(52)–C(53)–C(54)	107.8(4)	C(62)–C(63)–C(64)	107.3(3)
C(53)–C(54)–C(55)	107.2(4)	C(63)–C(64)–C(65)	108.8(3)
C(51)–C(55)–C(54)	108.4(4)	C(61)–C(65)–C(64)	108.7(3)
C(52)–C(51)–C(55)	108.6(4)	C(62)–C(61)–C(65)	107.4(3)

C–C bond lengths vary from 138.2(6) to 143.6(6) pm and the Nb–C bond lengths from 233.9(3) to 243.1(3) pm. The bending angle θ, i.e. the angle between the perpendiculars of the Cp best planes A and B, is 140.2°. As expected [12], plane D formed by the atoms Nb, C(111) and C(1), almost coincides with the pseudo-equatorial plane of the bent metallocene moiety.

The Nb–CO bond is essentially linear (175.1°). The Nb–C bond length of 204.5 (3) pm lies in the range observed for other niobium carbonyl complexes [13].

Table 3

Definition of best planes and interplanar angles (°) for II

Plane A ≡ [C(51) ··· C(55)]	θ [a]	140.2
Plane B ≡ [C(61) ··· C(65)]		
Plane C ≡ [Nb(A) [b], Nb, Nb(B)]	$\angle$(C,D)	89.5
Plane D ≡ [Nb, C(1), C(111)]		
Plane E ≡ [Nb, C(1), C(2)]	$\angle$(D,E)	169.2
Plane F ≡ [O(11), C(11), O(12)]	$\angle$(E,F)	85.6
Plane G ≡ [O(21), C(21), O(22)]	$\angle$(E,G)	10.1

[a] Bending angle $\theta = 180° - \angle(A,B)$. [b] Projection of Nb atom onto plane A.

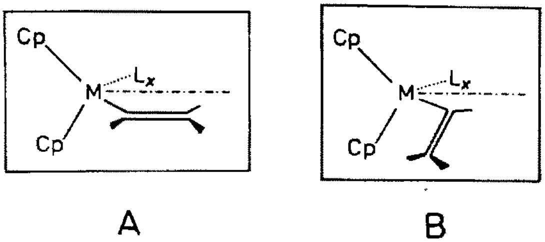


Fig. 2. The parallel (A) and perpendicular (B) conformations of η^1-alkenyl metallocene complexes.

The bond length Nb–C(1) of 229.5(3) pm is typical of a Nb–C(sp^3) single bond distance [14]. A π-interaction, which has been considered as a possible cause of restricted rotation of the alkenyl group in certain alkenyl niobocene complexes [4], must therefore be excluded. This view is reinforced by the observed C(1)–C(2) bond length of 134.3(4) pm, which does not show any lengthening.

In principle, there are two preferential conformations [2,15], a parallel conformation **A** and a perpendicular conformation **B**, as illustrated in Fig. 2. The solid state structure of II is of the perpendicular type.

The ester group in the β-position is approximately coplanar (10.1°) with the olefinic plane E, as expected, whereas the α-ester group shows nearly perpendicular (85.6°) orientation. This orientation is enforced by the proximity of the carbonyl group which shows a slight but significant bending away from the nearby α-ester group.

Discussion

The reactions of the electron-rich, coordinatively saturated, bent metallocene hydride derivatives with electron-poor acetylenes constitute a class of closely related insertion reactions. Although in many cases the stereochemical course of these reactions has not unambiguously been determined, stereospecific *trans* insertion is most usual [6,7]. While the reactions of $Cp_2NbH(CO)$ with hexafluoro-2-butyne and dicyanoacetylene are consistent with this generalization [4], the reaction of $Cp_2NbH(CO)$ with DMAC is non-stereospecific. Isomeric product mixtures have also been observed in double insertion reactions of Cp_2MoH_2 with cyanoacetylenes [5], but in this case it is not clear whether the observed mixtures were formed under kinetic control or the results of later isomerization.

Various mechanisms have been discussed for the insertion reactions considered here. A concerted mechanism for both *cis* and *trans* insertions has been proposed for the reactions of molydenocene dihydride with activated acetylenes [1,2]. The reported kinetic isotope effect, k_H/k_D of unity [1,2] does not, however, support this proposal, since partial M–H bond breaking and partial C–H bond formation is implied in the rate-determining step of the concerted mechanisms.

Nucleophilic attack of the metal lone pair on the acetylene followed by proton migration does not account for the α-regiospecificity [4] often observed with terminal acetylenes.

Recently Clark and coworkers established a mechanism for the reactions of *trans*-$PtH_2(PR_3)_2$ complexes with activated acetylenes that involves (a) a rate-determining electron transfer producing a caged radical pair, and (b) a fast proton transfer and radical combination [3]. In view of the low ionization potentials of the early *d*-metal hydride complexes [16–18] it is attractive to assume that the complexes Cp_2ReH, Cp_2MoH_2, Cp_2WH_2, and $Cp_2NbH(CO)$ react in much the same way. A mechanism with rate-determining single-electron transfer would produce a caged radical ion pair with the *trans* form dominating in the *cis/trans* equilibrium of the radical anion. Collapse of the primary radical ion pair would then give the observed products. This mechanism would not show a marked kinetic isotope effect. It would offer a straightforward explanation for the often observed *trans* stereospecificity, but not exclude occasional non-stereospecificity as in our case of the reaction of $Cp_2NbH(CO)$ with DMAC.

Since mechanistic data are scarce in this area, our discussion remains speculative. The observation of a non-stereospecific process, however, is additional fact that any mechanistic model has to account for.

Experimental

Experiments were carried out under nitrogen by Schlenk techniques. Toluene was distilled from sodium and hexane from K/Na alloy. Oxygen was removed by repeated distillation under nitrogen. $Cp_2NbH(CO)$ (I) was prepared by a published method [19].

1. Carbonylbis(η-cyclopentadienyl)[η^1-{(Z)-1,2-bis(methoxycarbocarbonyl)ethenyl}]-niobium (II)

DMAC (0.88 g, 6.19 mmol) was added dropwise to a solution of $Cp_2NbH(CO)$ (I) (1.56 g, 6.19 mmol) in toluene (15 ml) at 0 °C to give a blood-red solution. Slow addition of several 20 ml portions of hexane and cooling to −70 °C led to separation of an orange to brownish red oil which was shown (^1H NMR) to be a mixture of isomers II and III. Repeated crystallization gave pure II as large black crystals (1.66 g, 4.21 mmol; 68%), dec. (evolution of gas) 102–103 °C. Anal. Found: C, 51.79; H, 4.46. $C_{17}H_{17}NbO_5$ calc: C, 51.79; H, 4.35%.

(a) Data for II. MS (70 eV): m/e ($I_{rel.}$) 394 (4; M^+), 367 (20; ?), 366 (63; $M^+ - CO$), 363 (4; $M^+ - OMe$), 335 (8; $M^+ - CO_2Me$), 307 (7; 366 − CO_2Me), 279 (14; 307 − CO), 255 (40; $Cp_2NbH(OMe)^+$), 254 (99; $Cp_2Nb(OMe)^+$), 249 (8; ?), 248 (13; ?), 247 (13; ?), 245 (7; ?), 239 (24; Cp_2NbO^+), 225 (35; $Cp_2NbH_2{}^+$), 224 (100; Cp_2NbH^+), 223 (64; $NbCp_2{}^+$). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, C_6D_6): 6.79 s (=CH), 4.89 s (Cp), 3.72 s (OMe), 3.38 s (OMe). ^{13}C NMR ($\delta(^{13}C)$(ppm)(J (Hz)), 67.88 MHz, int. TMS, CD_3COCD_3, −10 °C, dig. resol. 2.3 Hz/pt.): 262 br (Nb-CO), 185.3 br (Nb-C=), 180.7 m (α-CO; partially obscured), 169.0 m (β-CO), 128.6 d (^1J 155) (=CH), 94.5 dquin (^1H 178, $^{2,3}J$ 6–7) (Cp), 50.9 q (^1J 145) (OMe), 50.4 g (^1J 145) (OMe). IR (KBr, vs. polystyrene): ν 1898vs (Nb-^{12}CO), 1855m (Nb-^{13}CO), 1715s (CO), 1686s (CO), 1563m (C=C) cm^{-1}.

(b) Data for III. ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, C_6D_6): 6.34 s (=CH), 4.71 s (Cp), 3.75 s (OMe), 3.44 s (OMe). ^{13}C NMR ($\delta(^{13}C)$ (ppm) (J (Hz)), 67.88 MHz, int. TMS, CD_3COCD_3, dig. resol. 1.2 Hz/pt.): 260 br (Nb-CO, observed at −10 °C), 184.5 br (Nb-C), 180.7 dq (^3J 15, ^3J 4) (α-CO), 162.4 quin ($^{2,3}J$ 4) (β-CO), 130.7 d (^1J 164) (=CH), 93.9 dquin (^1J 178, $^{2,3}J$ 7) (Cp), 50.7 q (^1J 146) (OMe), 50.3 (^1J 146) (OMe).

2. *Carbonylbis(η-cyclopentadienyl)[η^1-{1-(methoxycarbonyl)ethenyl}]niobium (IV)*

Methyl propiolate (116 mg, 1.38 mmol) was added at room temperature to a stirred solution of $Cp_2NbH(CO)$ (I) (350 mg, 1.39 mmol) in toluene (10 ml) to give an olive green solution. After 1 h stirring the solution was concentrated to 5 ml at room temperature in vacuo. Hexane (2 ml) was added dropwise, and the solution was set aside overnight at $-30\,^\circ C$ to give dark green crystals of IV. After decantation of the mother liquor, the crystals were washed with hexane and dried in vacuo, to give 318 mg (0.95 mmol; 68%), m.p. 76–78 °C, dec. (evolution of gas) $> 100\,^\circ C$, moderately air-sensitive. Anal. Found: C, 53.81; H, 4.56. $C_{15}H_{15}NbO_3$ calc: C, 53.59; H, 4.50%.

MS (70 eV): m/e ($I_{rel.}$) 308 (46; $M^+ - CO$), 254 (92; $Cp_2Nb + OCH_3{}^+$), 224 (100; Cp_2NbH^+), 223 (85; $NbCp_2{}^+$). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, C_6D_6): 6.47 d (^2J 4.3 Hz) and 5.82 d (^2J 4.3 Hz) ($=CH_2$), 4.75 s (Cp), 3.48 s (Me). ^{13}C NMR ($\delta(^{13}C)$ (ppm) (J (Hz)), 67.88 MHz, gg. int. TMS, C_6D_6): 261.3br (Nb-CO), 180.4m (CO_2Me), 160.0 m ($C{=}CH_2$), 134.5 dd (^1J 160, 147) ($=CH_2$), 92.3 dquin (^1J 180, $^{2,3}J$ 6–8) (Cp), 56.2 q (^1J 144) (OMe). IR (toluene, vs. polystyrene): ν 1911 (Nb–CO) cm^{-1}.

3. *[η^1-(3-Oxo-2-buten-2-yl)]carbonylbis(η-cyclopentadienyl)niobium (V)*

Butynone (148 mg, 2.20 mmol) was added at room temperature to a stirred solution of $Cp_2NbH(CO)$ (I) (550 mg, 2.18 mmol) in toluene (10 ml) to give a red brown solution. Volatiles were removed at room temperature in vacuo, leaving V as a spectroscopically pure, red brown powder in quantitative yield. For elemental analysis the product was sublimed at 100–135 °C (10^{-6} bar) (with considerable loss of material). M.p. 55–56 °C. Anal. Found: C, 55.99; H, 4.86. $C_{15}H_{15}NbO_2$ calc: C, 56.27; H, 4.72%.

MS (70 eV): m/e ($I_{rel.}$) 292 (100; $M^+ - CO$), 262 (10; ?), 248 (35; $Cp_2NbC_2H^+$), 239 (90; Cp_2NbO^+), 224 (58; Cp_2NbH^+), 223 (88, $NbCp_2{}^+$). ^1H NMR ($\delta(^1H)$ (ppm), 80 MHz, int. TMS, C_6D_6): 6.04 d (^2J 3.5 Hz) and 5.26 d (^2J 3.5 Hz) ($=CH_2$), 4.69 s (Cp), 2.13 s (Me). IR (KBr, vs. polystyrene): ν 1896, 1887 (Nb-CO) cm^{-1}.

4. *Determination of the structure of II*

Single crystals were grown by slow cooling to $-20\,^\circ C$ of a dilute solution of II in toluene/hexane (1/2).

$C_{17}H_{17}NbO_5$ (II); M 394.23 g mol^{-1}, orthorhombic, space group: $Pbca$ (no. 61), a 1375.4(4), b 1501.4(3), c 1575.8(4) pm, $Z = 8$, U 3.253(2) nm^3, d_0 1.608 g cm^{-3}, μ(Mo-K_α) 7.28 cm^{-1}.

The crystal selected for X-ray analysis was a parallelepiped ($0.63 \times 0.23 \times 0.33$ mm^3). The intensity data were collected on a CAD 4 automatic four-circle diffractometer (Enraf–Nonius, Delft, The Netherlands) using Mo-K_α radiation with a graphite crystal monochromator. Intensity data for reflections with $0.1° < \theta < 30°$ were collected at room temperature using the ω–2θ scan mode. Three standard reflections were measured periodically to check crystal and electronic stability. Slow decay (2.9%) was observed, and corrected by application of the program CHORT of the SDP program package [20].

The structure was solved by standard heavy atom methods using 3156 independent reflections with $I > \sigma(I)$ [20]. All but one Cp and one methyl hydrogen atom were located by difference Fourier synthesis. An absorption correction was applied using the program DIFABS [20,21] with the non symmetry-averaged data set. The least-squares full matrix refinement (219 parameters) [20] was carried out using 2260 reflections with $I > 3\sigma(I)$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for H(2) and one of each methyl group, were placed at calculated positions (d(C–H) 95.0 pm, B_{eq} 5.0×10^4 pm^2); the thermal parameters of the Cp hydrogen atoms and of H(2) were allowed to refine isotropically. Convergence resulted in an R value of 0.029 (R 0.030, unit weights, GOF 1.747) [22*].

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-52862, the names of the authors, and the journal reference.

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* Reference number with asterisk indicates a note in the list of references.