ELSEVIER

Journal of Organometallic Chemistry 492 (1995) 53–57

Journal of Organometallic Chemistry

Insertion of phenyl azide and diphenyldiazomethane into bis(cyclopentadienyl)zirconacyclopentanes. Crystal structure of an 18-electron alkyl zirconocene triazenido complex

Tim Luker, Richard J. Whitby *, Michael Webster

Department of Chemistry, University of Southampton, Southampton S017 1BJ, UK

Received 25 August 1994

Abstract

The terminal nitrogen atoms of phenyl azide and diphenyldiazomethane insert into one of the carbon–zirconium bonds of zirconacyclopentanes to give novel 18 electron azazirconacycles that are very stable towards hydrolysis. An X-ray diffraction study has been carried out on the triazenido alkyl zirconocene complex **5**. Hydrogenolysis of the diphenyldiazomethane inserted zirconacycle gives a primary amine, the first example of the direct formation of amines from organozirconium compounds.

Keywords: Amine; Early transition metals; Group 4; Metallacycle; Zirconium; Crystal structure

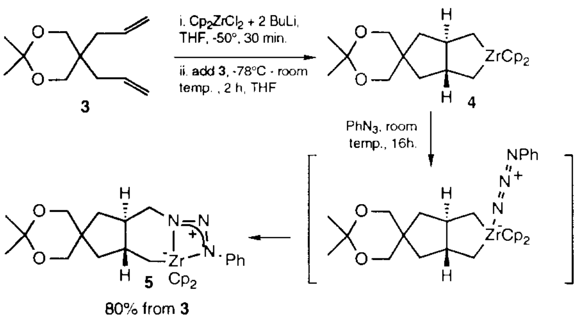
1. Introduction

Zirconacyclopentanes are readily formed by the reductive coupling of 1,*n*-dienes [1,2] using the 'Cp_2Zr' equivalent zirconocene(1-butene), generated in situ [3] from dibutylzirconocene, and are useful intermediates for organic synthesis. Further elaboration by the insertion of carbon monoxide [2], isocyanides [4], lithium chloroallylide [5], aldehydes [6], halogens [1,2b] and oxygen [1] have been reported, as well as metathesis reactions with Ph_2SnCl_2, Se_2Cl_2, and S_2Cl_2 [1,7]. As part of a study aimed at forming nitrogen heterocycles from these zirconacycles we set out to insert nitrogen into the carbon–zirconium bonds. Although metathesis with phosphines such as Ph_2PCl and $PhPCl_2$ occurs readily, attempts to carry out such reactions with analogous nitrogen-containing reagents such as RNHCl and $RNCl_2$ have not been successful [8]. Previous workers have shown that the insertion of phenyl azide [9] and diphenyldiazomethane [10] into dialkylziconocenes results in the formation of carbon–nitrogen bonds (Eq. 1). The insertions of phenyl azide into $(C_5Me_5)_2HfH_2$ [11] and of diphenyldiazomethane into the zirconium–phosphorus bond of $Cp_2Zr(Cl)P(SiMe_3)_2$ [12] have also been reported. These precedents encouraged us to examine the insertion of phenyl azide and diphenyldiazomethane into the bicyclic zirconacycle **4**.

$$\underset{\mathbf{1}\ R = Me,\ CH_2Ph}{Cp_2Zr(NRNCPh_2)(R)} \xleftarrow{Ph_2C=N_2} Cp_2ZrR_2 \xrightarrow{PhN_3} \underset{\mathbf{2}\ R = Me,\ Ph}{Cp_2Zr(NRNNPh)(R)} \tag{1}$$

2. Results and discussion

Reaction of zirconocene dichloride in tetrahydrofuran with 2 equivalents of butyllithium at −78°C to



Scheme 1.

---

[*] Corresponding author.

SSDI 0022-328X(94)05220-4

form dibutyl zirconocene, followed by addition of the diene **3** and warming to room temperature, gave the zirconacyclopentane **4**. Removal of the solvent in vacuo, addition of benzene and filtration under argon gave a lithium-chloride-free solution of **4**. Addition of 1 equivalent of phenyl azide (room temperature, 16 h) resulted in clean conversion to a new complex that had NMR data in accord with the hoped for triazenido compound **5** (Scheme 1). Removal of most of the benzene in vacuo and addition of hexane gave **5** as a yellow crystalline solid in 80% yield based on the diene **3**. Remarkably **5** proved stable to air and water, surviving an aqueous work-up intact and no change being observed after exposure of the crystals to light and air for 2 weeks. This allowed a more convenient preparation involving addition of phenyl azide to the THF solution of **2** (16 h, room temperature), followed by addition of water, extraction of the product into ether, drying ($MgSO_4$), and removal of solvent, which gave **5** in similar yield and purity.

The air- and water-stability of **5** is in marked contrast to the behaviour of the acyclic analogues **2**, which are reported [9] to be 'very air sensitive'. Indeed we know of no other zirconium species containing a carbon–zirconium σ-bond that are so inert. An explanation for this unreactivity is that a bidentate coordination mode of the triazenido moiety gives an electronically saturated (18 electron) zirconium centre. A likely mechanism of the protonolysis of carbon–zirconium bonds (Eq. 2) requires initial donation of an oxygen lone pair to the metal centre, which is disfavoured for **5**. An X-ray structure determination of **5** was carried out (Fig. 1, Table 1), and confirmed the bidentate nature of the triazo-ligand–metal interaction. The terminal nitrogen–zirconium bond lengths differ by only 0.1 Å and the N–N bonds by only 0.014 Å. There is no interaction between N(2) and the metal (the ZrN_3 ring is flat) and thus the coordination is not of an η^3-allyl type. An interesting comparison is with the analogous all-carbon system [13] **6**, in which the allyl moiety is coordinated 'side on' to the metal. The Zr–N bond lengths in **5** are 0.2–0.3 Å longer than those in related '16-electron' 2-aza-1-zirconacyclo-butanes and -butenes [14]. There is no sign of slippage to give η^3-coordination of the cyclopentadienyl rings; all the cyclopentadienyl Zr–C bond lengths are in the range 2.50–2.55 Å.

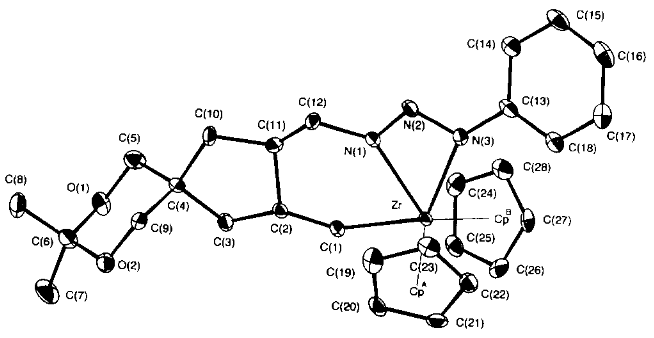
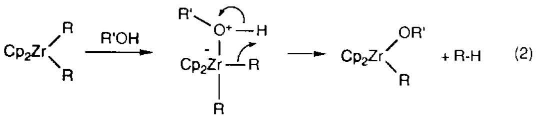
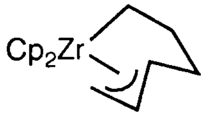


Fig. 1. Molecular structure of **5** $(Cp)_2Zr(C_{14}H_{25}N_3O_2)$ showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity Selected bond distances (Å) and angles (°): Zr–N(1) 2.277(4), Zr–N(3) 2.368(4), Zr–C(1) 2.344(5), N(1)–N(2) 1.306(6), N(2)–N(3) 1.320(6), Zr–Cp^A 2.218, Zr–Cp^B 2.238, N(1)–N(2)–N(3) 106.1(4), N(2)–N(3)–C(13) 114.6(4), N(2)–N(1)–C(12) 113.8(4), C(1)–Zr–N(1) 75.1(2), N(1)–Zr–N(3) 53.7(1), Cp^A–Zr–Cp^B 130.0, Zr–N(1)–N(2)–N(3) 3.6, N(3)–Zr–N(1)–N(2) 2.4. Cp^A and Cp^B are the centroids of the cyclopentadienyl rings C(19)–C(23) and C(24)–C(28) respectively.





6

Analogously, the insertion of diphenyldiazomethane into **4** gave the azazirconacycle **7**. Although this is not air stable, protonation with methanol was shown by NMR spectroscopic monitoring to take 8 days to reach completion. This considered together with the nature of the acyclic precedent **1** [10], suggests that the imine nitrogen of **7** is also strongly coordinated to the metal. The analogous zirconacycle **9** was prepared from the diene **8** in order to avoid problems caused by the presence of the acid-sensitive acetonide group in **7**. Cleavage from the metal and reduction of the N–N bond was accomplished by hydrogenation in the presence of hydrochloric acid [15] and gave the amine **10** in 50% overall yield. This transformation represents the first synthesis of amines by insertion of nitrogen into a Zr–C bond, and should find use in the selective monofunctionalisation [16] of zirconacyclopentanes.

In summary we have characterised an unambiguously 18-electron alkyl triazenido zirconium complex and noted the remarkable unreactivity of its zirconium–carbon bond. We have also developed a method for converting carbon–zirconium bonds into primary amines by utilising the insertion of diphenyldiazomethane.

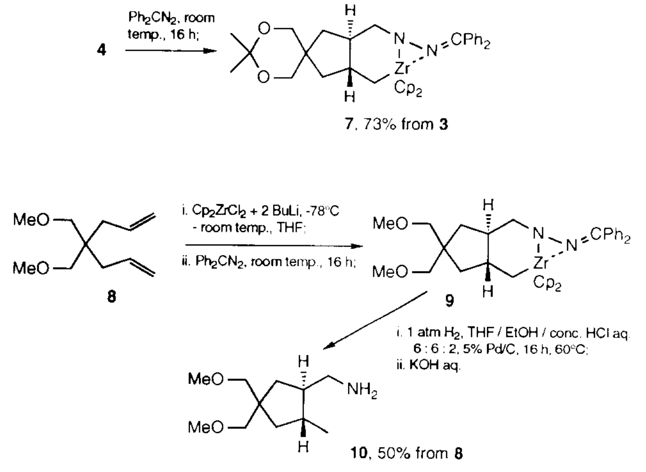
3. Experimental details

The NMR spectra were recorded on Bruker AM360, AC300, and JEOL GX270 spectrometers with tetramethylsilane (proton) or the solvent peak (carbon-13) as reference. Carbon-13 signals are shown as s, d, t, q depending on the number of attached protons (0–3)

Table 1
Fractional atomic coordinates and equivalent isotropic temperature factors ($\times 10^3$ Å^2) of **5**

	x	*y*	*z*	*U*
Zr	0.43434(5)	0.95253(3)	0.78143(2)	11.9(2)
O(1)	−0.1854(5)	1.0026(2)	1.0660(2)	21.9(20)
O(2)	−0.3371(4)	0.9549(4)	0.9782(1)	20.9(18)
N(1)	0.4238(5)	0.8463(2)	0.8531(2)	17.8(21)
N(2)	0.5359(5)	0.7937(2)	0.8316(2)	17.1(23)
N(3)	0.6043(5)	0.8305(2)	0.7822(2)	17.5(21)
C(1)	0.2595(6)	1.0025(3)	0.8619(2)	16.8(27)
C(2)	0.1392(5)	0.9447(3)	0.8957(2)	14.2(24)
C(3)	0.0263(6)	0.9882(3)	0.9464(2)	17.8(27)
C(4)	−0.0431(6)	0.9168(3)	0.9870(2)	15.7(25)
C(5)	−0.0605(7)	0.9401(3)	1.0562(2)	22.7(27)
C(6)	−0.3481(6)	0.9792(3)	1.0428(3)	21.2(29)
C(7)	−0.4510(8)	1.0592(4)	1.0430(3)	34.6(34)
C(8)	−0.4273(8)	0.9111(4)	1.0830(2)	28.6(30)
C(9)	−0.2192(6)	0.8912(3)	0.9653(2)	17.8(27)
C(10)	0.0838(7)	0.8436(3)	0.9785(2)	20.9(27)
C(11)	0.2238(6)	0.8773(3)	0.9363(2)	19.2(27)
C(12)	0.3120(7)	0.8099(3)	0.8996(2)	21.7(29)
C(13)	0.7357(6)	0.7848(3)	0.7541(3)	17.7(27)
C(14)	0.8343(6)	0.7267(3)	0.7871(3)	20.2(27)
C(15)	0.9594(6)	0.6822(3)	0.7571(3)	24.2(30)
C(16)	0.9905(7)	0.6945(3)	0.6932(3)	26.3(31)
C(17)	0.8954(7)	0.7533(3)	0.6600(3)	27.0(31)
C(18)	0.7686(6)	0.7989(3)	0.6905(2)	21.0(28)
C(19)	0.1782(7)	0.8756(3)	0.7406(3)	24.9(31)
C(20)	0.1484(6)	0.9622(4)	0.7319(3)	20.9(27)
C(21)	0.2645(7)	0.9920(3)	0.6870(2)	21.2(29)
C(22)	0.3649(6)	0.9225(3)	0.6688(2)	21.0(28)
C(23)	0.3101(6)	0.8512(3)	0.7008(2)	20.5(28)
C(24)	0.6379(6)	1.0466(4)	0.8404(2)	23.6(27)
C(25)	0.5367(6)	1.1006(3)	0.8035(3)	20.9(29)
C(26)	0.5719(7)	1.0864(3)	0.7408(2)	22.0(26)
C(27)	0.6921(6)	1.0221(3)	0.7373(2)	21.0(28)
C(28)	0.7357(6)	0.9991(3)	0.7986(3)	24.0(30)
Cl(1) [a]	0.322(1)	1.2628(6)	1.0206(5)	30.0
Cl(2) [a]	0.020(2)	1.229(1)	1.038(1)	30.0
Cl(3) [a]	0.139(3)	1.212(1)	1.026(1)	30.0

[a] Atoms of a disordered and partially occupied CH_2Cl_2 solvate molecule.



Scheme 2.

which was determined by DEPT experiments. For ease of comparison the labelling of proton and carbon spectra for **5** and **10** uses the non-systematic numbering of the Fig. 1. Protons are given the numbers of the carbons to which they are attached.

3.1. 6,6-Bis(cyclopentadienyl)-5-phenyl-10-spiro(4,4-dimethyl-3,5-dioxacyclohexane)-3,4,5-triaza-tricyclo-[6.3.0.0^{3,6}]dodec-3-ene **5**

To a stirred solution of zirconocene dichloride (0.438 g, 1.5 mmol) in THF (5 ml) under argon at −78°C was added ^{n}BuLi (1.20 ml of a 2.5 M solution in hexanes, 3 mmol). The mixture was stirred at this temperature for 1 h then a solution of the acetonide **3** (0.353 g, 1.5 mmol) in THF (2 ml) was added and the mixture allowed to warm to room temperature during 2 h to yield a solution of zirconacyclopentane **4** [17]. The tetrahydrofuran was removed in vacuo, the residue extracted into benzene (10 ml) and the extract filtered to give a lithium chloride-free solution of **4** (quantitative by NMR). ^{1}H NMR (270 MHz, C_6D_6) δ/ppm 5.82 (10 H, s), 3.83 and 3.76 (2H, d, *J* 11 Hz, AB system), 2.06 (2H, br, d, *J* 7 Hz), 1.47 (6H, s), 1.35–0.87 (8H, m); ^{13}C NMR (67.5 MHz, C_6D_6) δ/ppm 110.6 (s), 71.4 (t), 51.5 (t), 43.4 (t), 36.4 (d), 35.9 (s), 25.0 (q).

To the stirred solution of zirconacyclopentane **4** (1.5 mmol) in benzene (10 ml) at 5°C under argon was added a solution of phenyl azide [18] (0.179 g, 1.5 mmol) in benzene (2 ml). The mixture was then stirred at room temperature for 15 h then concentrated in vacuo (total volume ca. 5 ml) and hexane (20 ml) was added. The solution was cooled to 5°C and the yellow crystals formed filtered off, washed with hexane (2 × 10 ml), and dried under vacuum to yield the title zirconacycle **5** (0.643 g, 80%) (m.p. 166–169°C (decomp.) from dichloromethane–hexane). ^{1}H NMR (360 MHz, C_6D_6): δ/ppm 7.280–7.343 (4H, m), 7.010 (1H, tt, *J* 2.1, 6.5 Hz), 5.642 (5H, s), 5.597 (5H, s), 3.973 (1H, dd, *J* 5.0, 14.1 Hz, H-12), 3.684 (1H, d, *J* 11.0 Hz, H-5*), 3.609 (2H, s, 2H-9*), 3.580 (1H, d, *J* 11.0 Hz, H-5*), 2.946 (1H, dd, *J* 11.9, 14.1 Hz, H-12), 2.019 (1H, dd, *J* 7.2, 13.2 Hz, H-3), 1.934 (1H, dd, *J* 17.3, 13.2 Hz, H-10), 1.649 (1H, m, H-2), 1.510 (3H, s), 1.486 (3H, s), 1.303 (1H, m, H-11), 1.126 (1H, dd, *J* 8.7, 10.4 Hz, H-1), 1.092 (1H, dd, *J* 10.0, 14.2 Hz, H-10), 1.022 (1H, dd, *J* 10.6, 13.2 Hz, H-3), 0.007 (1H, dd, *J* 1.8, 10.3 Hz, H-1). ^{13}C NMR (90.56 MHz, C_6H_6): δ/ppm 150.65 (s), 130.05 (d), 123.66 (d), 117.03 (d), 110.72 (d, Cp), 109.18 (d, Cp), 98.36 (s, C-6), 71.46 (t, C-5*), 71.31 (t, C-9*), 61.08 (t, C-12), 48.89 (t, C-3), 47.36 (d, C-11), 47.01 (d, C-2), 46.70 (t, C-1), 40.45 (t, C-4), 25.66 (q), 24.30 (q). IR (CCl_4) ν_{max}/cm^{-1} 1594 m, 1484 m, 1449 w, 1380 m, 1367 m, 1283 s, 1251 m, 1231 m, 1198 m. Anal.: Found C, 62.1; H, 6.7; N, 7.7%. $C_{28}H_{35}N_3O_2Zr$ Calc. C, 62.6; H, 6.6; N, 7.8%. * The relative assignments of C/H-5 and C/H-9 are arbitrary, but the C/H pairing is correct.

3.2. 4,4-Bis(cyclopentadienyl)-3-(1-aza-2,2-diphenylethenyl)-8-spiro(4,4-dimethyl-3,5-dioxacyclohexane)-3-aza-bicyclo[4.3.0]nonane 7

Metallacycle **4** (1.5 mmol) was prepared as a solution in benzene as described above. The solution was cooled to 5°C, diphenyl diazomethane [18] (0.219 g, 1.5 mmol) in benzene (2 ml) added, and the mixture warmed to room temperature. After 15 h at room temperature hexane was added (20 ml) and the mixture cooled to 5°C. The white crystals which formed were filtered off under argon and washed with hexane (2 × 10 ml). Solvent was removed in vacuo to yield the title metallacycle **7** as an off white solid (0.668 g, 73%). ^{1}H NMR (360 MHz, C_6D_6): δ/ppm 7.663 (2H, m), 7.249 (2H, m), 7.14–7.16 (6H, m), 5.869 (5H, s), 5.665 (5H, s), 3.652 (1H, d, J 11.2 Hz, H-5*), 3.561 (1H, d, J 11.2 Hz, H-9*), 3.482 (2H, d, J 11.1 Hz, H-5 + H-9*), 2.897 (1H, dd, J 5.0, 13.0 Hz, H-12), 2.017 (1H, dd, J 7.1, 13.2 Hz, H-3), 1.893 (1H, dd, J 11.2, 13.0 Hz, H-12), 1.720 (1H, dd, J 7.3, 13.0 Hz, H-10), 1.602 (1H, m, H-2), 1.441 (3H, s), 1.438 (3H, s), 1.377 (1H, m, H-11), 1.118 (1H, t, J 11.7 Hz, H-1), 1.064 (1H, dd, J 10.7, 13.2 Hz, H-3), 0.880 (2H, m, H-1 and H-10). ^{13}C NMR (90.56 MHz, C_6H_6): δ/ppm 139.78 (s), 137.86 (s), 135.77 (s), 131.84 (d), 128.95 (d), 128.82 (d), 128.11 (d), 126.89 (d), 125.25 (d), 110.09 (d, Cp), 108.82 (d, Cp), 97.96 (s, C-6), 71.31 (t, C-9*), 70.86 (t, C-5*), 58.83 (t, C-12), 48.60 (t, C-3), 47.88 (d, C-11), 46.55 (d, C-2), 40.35 (t, C-1), 38.84 (s, C-4), 37.50 (t, C-10), 25.88 (q), 23.34 (q). IR (CCl_4) ν_{max}/cm^{-1} 1548.9 br s, 1493.8 m, 1443.3 m, 1249.9 s, 1200.1 s. M/Z (EI): 610.2146 (M^+, $C_{35}H_{40}N_2O_2Zr$ requires 610.2137, 18%), 595 (6), 580 (4), 545 (12), 400 (54), 297 (100), 220 (77), 180 (58), 84 (58). * The relative assignments of C/H-5 and C/H-9 are arbitrary, but the C/H pairing is correct.

3.3. 3R*,4R*-3-Aminomethyl-1,1-di(methoxymethyl)-4-methyl-cyclopentane 10

To a stirred solution of zirconocene dichloride (0.293 g, 1 mmol) in THF (5 ml) under argon at −78°C was added dropwise *n*-butyllithium (0.8 ml of a 2.5 M solution, in hexanes, 2 mmol). After 20 min a solution of 4,4-di(methoxymethyl)-1,6-heptadiene (0.193 g, 1 mmol) in THF (3 ml) was added and the mixture allowed to warm to room temperature during 2 h. It was then cooled to 0°C and diphenyldiazomethane (0.214 g, 1.1 mmol) in THF (4 ml) was added. The solution was stirred at room temperature for 15 h then concentrated in vacuo and added by syringe to a suspension of 10% palladium on charcoal in ethanol (8 ml) and concentrated by hydrochloric acid (2 ml) under hydrogen (1.1 atm.). The reducing mixture warmed to 60°C and stirred at this temperature for 15 h then allowed to cool to room temperature. The black suspension was filtered through Celite® then brought to pH14 by the addition of solid potassium hydroxide pellets. The aqueous phase was extracted with diethyl ether (3 × 50 ml) and the combined organic layers washed with water (2 × 30 ml) and brine (30 ml) and dried over anhydrous sodium sulphate, and the solvent removed to give the crude product as a yellow oil. Column chromatography on silica (33% NH_3 in H_2O:MeOH:CH_2Cl_2::1:19:30 as eluent) gave the title amine **10** as a colourless oil (0.100 g, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.287 (6H, s), 3.156 (4H, m), 2.816 (1H, dd, J 3.7, 12.5 Hz), 2.425 (1H, dd, J 8.3, 12.3 Hz), 1.767 (1H, dd, J 7.0, 12.9 Hz), 1.713 (1H, dd, J 7.0, 12.9 Hz), 1.571 (2H, br s), 1.482 (2H, m), 1.056 (1H, dd, J 10.3, 13.0 Hz), 1.002 (1H, dd, J 10.7, 11.9 Hz), 0.913 (3H, d, J 6.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 77.96 (t), 77.81 (t), 59.29 (2q), 49.83 (d), 45.71 (t), 45.38 (s), 41.93 (t), 37.61 (t), 37.27 (d), 18.49 (q); IR ν_{max}/cm^{-1} 3371.9 (w, br), 3288.7 (w, br), 2948.8 (s), 2923.4 (s), 2869.3 (s), 2824.0 (s), 1597.2 (m), 1459.0 (m), 1387.8 (m), 1198.4 (m), 1109.0 (s), 936.6 (m), 919.1 (w), 732.5 (m). HRMS (EI) 201.1713 (M^+, $C_{11}H_{23}NO_2$ requires 201.1729).

3.4. X-Ray structure determination of 5

$C_{28}H_{35}N_3O_2Zr$, $M_r = 536.8$, orthorhombic, $P2_12_12_1$, $a = 7.970(3)$, $b = 15.914(3)$, $c = 21.242(1)$ Å, $V = 2694.2$ Å^3, $Z = 4$, $D_c = 1.323$ g cm^{-1}, $F(000) = 1120$, $\mu = 4.3$ cm^{-1}, $T = 150$ K, λ(Mo Kα) = 0.71069 Å.

Suitable bright yellow crystals were grown by diffusion of pentane into a dichloromethane solution of **5** at −20°C.

Data were collected from a crystal of 0.30 × 0.20 × 0.12 mm^3 on an Enraf-Nonius FAST area detector diffractometer fitted with a graphite monochromated Mo rotating anode radiation source. Data were collected over ca. a hemisphere (14878 reflections, 2θ(max) = 60.1°), and after averaging there remained 6989 unique reflections (R_{int} 0.085). No absorption corrected was applied. The structure was solved by direct methods using SHELXS-86 [20] and refined by full-matrix least-squares using SHELX-76 [21] to R (R_w) = 0.039 (0.056) for 324 parameters (4194 observed reflections ($F > 4\sigma(F)$), anisotropic non-H atoms, 2θ(max) = 50°, $w^{-1} = [\sigma^2(F) + 0.0008F^2]$, max. shift/error 0.04). The methyl H atoms were introduced in calculated positions (d(C–H) = 1.08 Å) and the remainder were located from a difference electron density map but not refined. Some small peaks in the map well removed from the molecule were associated with the Cl atoms of a disordered and partial CH_2Cl_2 solvate molecule. These Cl atoms were given a fixed isotropic temperature factor and the atom population refined to 0.14 of a CH_2Cl_2 molecule. The coordinates reported correspond to the enantiomorph with the lower R factor (R_w 0.056 compared with 0.059). Residual electron density was in the range 1.32 to −1.88 $eÅ^{-3}$. Neutral atom complex scattering factors were taken from SHELX-76 and Ref. [22] (Zr only) and final atomic coordinates are given in Table 1. Complete lists of bond lengths and angles and tables of thermal parameters and hydrogen atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank SERC for a studentship and Prof. M.B. Hursthouse of the SERC X-Ray crystallography service at Cardiff for collecting the X-ray data. RJW thanks Pfizer Central Research UK for financial support.

References and notes

[1] W.A. Nugent and D.F. Taber, *J. Am. Chem. Soc., 111* (1989) 6435.

[2] (a) D.R. Swanson, C.J. Rousset, E. Negishi, T. Takahashi, T. Seki, M. Saburi and Y. Uchida, *J. Org. Chem. 54* (1989) 3521; (b) C.J. Rousset, D.R. Swanson, F. Lamaty and E. Negishi, *Tetrahedron Lett., 30* (1989) 5105.

[3] E. Negishi, F.E. Cederbaum and T. Takahashi, *Tetrahedron Lett., 27* (1986) 2829.

[4] J.M. Davis, R.J. Whitby and A. Jaxa-Chamiec, *Tetrahedron Lett. 33* (1992) 5655; J.M. Davis, R.J. Whitby and A. Jaxa-Chamiec, *Tetrahedron Lett., 35* (1994) 1445; J.M. Davis, R.J. Whitby and A. Jaxa-Chamiec, *Synlett*, (1994) 111.

[5] T. Luker and R.J. Whitby, *Tetrahedron Lett. 35* (1994) 785.

[6] C. Copéret, E. Negishi, Z. Xi, and T. Takahashi, *Tetrahedron Lett., 35* (1994) 695.

[7] P.J. Fagan, W.A. Nugent, and J.C. Calabrese, *J. Am. Chem. Soc., 116* (1994) 1880.

[8] R.J. Whitby, D.F. Hewlett, and M.I. Kemp, unpublished work.

[9] K.W. Chiu, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *Polyhedron, 3* (1984) 79.

[10] S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem., 22* (1983) 2029.

[11] G.L. Hillhouse and J.E. Bercaw, *Organometallics, 1* (1982) 1025.

[12] E. Hey, M.F. Lappert, J.L. Atwood and S.G. Bott, *Polyhedron, 7* (1988) 2083.

[13] G. Erker, K. Engel, U. Dorf, J.L. Atwood and W.E. Hunter, *Angew. Chem. Suppl.*, (1982) 1974.

[14] P.J. Walsh, F.J. Hollander and R.G. Bergman, *Organometallics, 12* (1993) 3705; P.J. Walsh, A.M. Baranger and R.G. Bergman, *J. Am. Chem. Soc., 114* (1992) 1708.

[15] J.E. Baldwin, R.M. Adlington and I.M. Newington, *J. Chem. Soc., Chem. Commun.*, (1986) 176.

[16] T. Takahashi, K. Aoyagi, R. Hara and N. Suzuki, *Chem. Lett.*, (1992) 1693.

[17] Complex **4** was observed as an intermediate in a study reported in Ref. [1], and isolated in studies reported in Refs. [4] and [5], but the spectroscopic data were not previously reported.

[18] R.O. Lindsay and C.F.H. Allen in L.I. Smith (Ed.) '*Organic synthesis*', vol. 22, 1942, p. 96.

[19] J.B. Miller, *J. Org. Chem., 24* (1959) 560.

[20] G.M. Sheldrick, SHELXS-86, *Program for crystal structure solution*, University of Göttingen, Germany, 1986.

[21] G.M. Sheldrick, SHELX-76, *Program for crystal structure determination*, University of Cambridge, 1976.

[22] *International tables for X-ray crystallography*, Vol. 4, Kynoch, Birmingham, 1974.