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Inorganic Chemistry Communications 6 (2003) 1201-1204



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Synthesis of the sterically constrained ligand precursor cyclopentadienyl-2,6-diphenylbenzene and structure of $[(2,6-Ph_2-C_6H_3-\eta^5-C_5H_4)Zr(NEt_2)_3]$

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Received 28 April 2003; accepted 2 July 2003 Published online: 26 July 2003

Abstract

A Pd-catalysed Stille coupling of 2,6-diphenyliodobenzene with tributylcyclopentadienyltin gave the sterically constrained ligand precursor cyclopentadienyl-2,6-diphenylbenzene (1). Treatment of this precursor with tetrakis(diethylamido)zirconium(IV) gave the three-legged piano-stool complex [$(2,6-Ph_2-C_6H_3-\eta^5-C_5H_4$)Zr(NEt₂)₃] (2). Complex 2 was characterised by ¹H- and ¹³C{¹H}-NMR spectroscopy as well as by X-ray crystallography which showed significant distortions of the three-legged piano-stool geometry as a result of steric interactions with the bulky aryl substituent.

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Keywords: Crystal structures; Zirconium complexes; Cyclopentadienyl ligands; Stille couplings

1. Introduction

The synthesis of unusual cyclopentadienyl ligands is of prime importance in homogeneous catalysis since variation of electronic and steric properties can have a significant effect on a complex's structure and reactivity [1]. Catalytic cyclopentadienyl-arene coupling reactions as a route to new cyclopentadienyl ligands have only recently been investigated and those that have been described are of sterically undemanding systems: Wahren and co-workers [2] first reported stoichiometric cyclopentadienyl-arene coupling reactions using cyclopentadienylcopper and aryliodide reagents and Rosenblum and co-workers [3] reported a low-yielding reaction of NaCp with phenyliodide; in 1993, Katz, Brintzinger and co-workers [4] described a catalysed indenyltin-aryliodide Stille coupling reaction using Pd(PPh₃)₂Cl₂. There have been a number of catalysed coupling reactions described since then [5].

In this communication, we describe the Pd-catalysed Stille coupling of a cyclopentadienyltin reagent with a bulky aryliodide to give a new sterically constrained cyclopentadiene ligand precursor. We also report a tris(diethylamido)zirconium complex with this ligand that illustrates its steric effects.

2. Experimental

2.1. Synthesis of cyclopentadienyl-2,6-diphenylbenzene (1)

Iodo-2,6-diphenylbenzene [6] (4.84 g, 13.6 mmol) and tributylcyclopentadienyltin [7] (5 ml, 8.5 g, 24 mmol) were dissolved in THF (150 ml). Pd(PhCN)₂Cl₂ (47 mg, 0.123 mmol), copper(I) iodide (239 mg, 1.25 mmol) and triphenylarsine (117 mg, 0.38 mmol) were then added and the solution was heated to reflux for 72 h to give a dark-brown solution. It was poured onto water and twice extracted with petroleum ether. The orange organic layer was washed with water, dried over MgSO₄, filtered, and the solvent pumped off to give an orange residue, which was redissolved in warm petroleum ether (50 ml). A non-soluble brown precipitate could not be redissolved. Flash chromatography on a silica column with petroleum ether and crystallisation from the

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^{1387-7003/\$ -} see front matter \odot 2003 Elsevier B.V. All rights reserved. doi:10.1016/S1387-7003(03)00222-3

concentrated and cooled solution gave light-orange crystals of 1 (3.07 g, 77% yield based on the iodide). Two isomers of 1 were obtained in a 7:3 ratio for 1a and 1b, respectively. Anal. Calcd. for C23H18: C, 93.82; H, 6.18. Found: C, 92.68; H, 6.10. m.p.: 114 °C. ¹H NMR (CDCl₃): δ 7.42–7.20 (m, 13H + 13H, Ph of **1a** and **1b**), 6.23 (m, 1H, $CH_2CH = CH$ of **1a**) 6.14 (m, 1H, $CH_2CH=CH$ of 1a), 6.11 (m, 1H, $CH_2CH=CH$ of **1b**), 5.95 (m, 1H, $CH_2CH = CH$ of **1b**), 5.89 (m, 1H, $CH_2CH = CH - CH$ of 1a), 5.71 (m, 1H, $CHCH_2CH =$ CH of 1b), 2.73 (m, 2H, CH₂ of 1b), 2.50 (m, 2H, CH₂ of **1a**). ¹³C NMR (CDCl₃): for isomer **1a**: δ 134.40 (s, Cp), 132.65 (s, Cp), 132.11 (s, Cp), 129.33 (s, 2C, p-Ph), 129.30 (s, 4C, o- or m-Ph), 127.73 (s, 4C, o- or m-Ph), 126.74 (s, 1C, 4-arene), 126.38 (s, 2C, 3,5-arene), 44.78 (s, CH_2). Unassigned quaternary resonances were observed at 144.90, 142.65 and 141.96 ppm. For isomer 1b: δ 136.25 (s, Cp), 133.20 (s, Cp), 131.49 (s, Cp), 129.60 (s, 4C, o- or m-Ph), 129.30 (s, 2C, p-Ph), 127.54 (s, 4C, o- or *m*-Ph), 126.97 (s, 1C, 4-arene), 126.34 (s, 2C, 3,5-arene), 41.49 (s, CH₂). Ipso-Ph resonances were observed at 142.27 and 141.75 ppm. EI-MS: 294.1 (100%, M⁺), 293.1 (52.9%, [M-H]⁺), 279 (33.4%), 278.1 (22.62%), 265.1 (33.8%), 252.1 (20.1%), 215.1 (17.0%), 133.1 (18.6%), 51.0 (64.2%).

2.2. Synthesis of $(2,6-Ph_2-C_6H_3-\eta^5-C_5H_4)Zr(NEt_2)_3$ (2)

Cyclopentadiene 1 (625 mg, 2.13 mmol) was dissolved in toluene (20 ml) and Zr(NEt₂)₄ [8] (0.79 ml, 807 mg, 2.13 mmol) was added. The solution was then heated with stirring at 100 °C for 18 h. Solvent was then removed in vacuo and the residue dissolved in a minimum volume of diethyl ether. Cooling to -20 °C for 2 d gave colourless crystals of 2 (0.32 g, 25%). The air-sensitivity of the compound prevented attempts to obtain a good microanalytical result (the best result is most consistent with the hydrolysis product $(C_6H_3Ph_2C_5H_4)Zr(OH)_3 \cdot 0.5H_2O$: Anal. Calcd. for C₂₃H₂₁O_{3.5}Zr: C, 62.83; H, 4.76. Found: C, 62.04; H, 5.05). ¹H NMR (CDCl₃): δ 7.33–7.05 (m, 13H, Ph), 5.71 (pseudo-t, J = 3 Hz, 2H, C₅H₄), 5.44 $(pseudo-t, J = 3 Hz, 2H, C_5H_4), 2.92 (q, J = 6.8 Hz, 12H)$ CH_2), 0.74 (t, J = 6.8 Hz, 18H, CH_3). ¹³C NMR (CDCl₃): δ 144.53 (s, *ipso*-Ph), 142.36 (s, *ipso*-Ph), 131.30 (s, 2C, Ph or 3,5-arene), 129.62 (s, 4C, o- or m-Ph), 128.15 (s, 4C, oor *m*-Ph), 126.48 (s, 2C, 3,5-arene or Ph), 125.07 (s, 1C, 4arene), 114.23 (s, C₅H₄), 107.26 (s, C₅H₄), 43.95 (s, CH₂), 14.41 (s, CH₃). The ipso-Cp and 1-arene quaternary carbons were not unambiguously identified.

2.3. Crystal structure determination of complex 2

A pale yellow crystal $(0.84 \times 0.80 \times 0.20 \text{ mm}^3)$ was mounted on a glass capillary. Data collection was carried out on a Bruker P4 SMART diffractometer with a CCD detector with Mo K_{α} radiation ($\lambda = 0.71073$ Å) at

163(2) K. The θ range for data collection was from 2.19° to 26.41°. The completeness to θ was 97.5%. An absorption correction was applied with the maximum and minimum transmission factors of 1.000 and 0.824, respectively. Crystal data for $C_{35}H_{47}N_3Zr$: $M_W = 600.98$, triclinic, space group P-1, Z=2, a=9.568(2), b = 10.806(2), c = 15.754(4) Å, $\alpha = 92.707(3), \beta =$ 93.670(3), $\gamma = 103.174(3)^\circ$, V = 1579.5(6) Å³, $\mu = 0.375$ mm^{-1} , $d_{Calcd.} = 1.264 Mg m^{-3}$. The structure was solved by direct methods using SHELXS [9] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97 [10]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically. The R_{int} is 0.0189 based on 6308 independent reflections (from 19,688 collected reflections) and R_1 is 0.0232 ($wR_2 = 0.0620$) for 5991 reflections with $I > 2\sigma(I)$. Goodness-of-fit on $F^2 = 1.063$, residual electron density: 0.760 and -0.345 e Å⁻³.

3. Results and discussion

Iodo-2,6-diphenylbenzene reacts with a twofold excess of tributyl(cyclopentadienyl)tin in the presence of Pd(PhCN)₂Cl₂, Ph₃As, and CuI (in a 1:3:10 ratio with a Pd loading of 9% with respect to the iodide) in THF solvent under refluxing conditions for 3 days to give the cyclopentadienyl–aryl coupled product cyclopentadienyl-2,6-diphenylbenzene (1) in 77% yield after isolation. ¹H-NMR spectroscopy indicates the presence of ring isomers **1a** and **1b** in a 7:3 ratio. The more sterically congested allylic isomer has not been observed.



Treatment of 1 with $Zr(NEt_2)_4$ at 100 °C for 18 h in toluene gave the air-sensitive pale-yellow three-legged piano-stool complex 2. Observation of a classical AA'BB' pattern for the cyclopentadienide resonances at 5.71 and 5.44 ppm indicates the formation of a symmetric piano-stool complex. The ethyl and phenyl groups are also equivalent on the NMR timescale by both ¹H- and ¹³C-NMR spectroscopy at ambient temperature. A closely related ligand, cyclopentadienylpentaphenylbenzene, is present in the ferrocene (C₆Ph₅- η^5 -C₅H₄)(η^5 -C₅H₅)Fe, however, this ligand has not been prepared independently of the ferrocene [11].



The structure of **2** was confirmed by X-ray crystallography. Fig. 1 shows a perspective view of the complex as determined by the crystallographic analysis.

It is clear that the bulky aryl substituent has had a significant effect on the structure of **2**. One of the phenyl groups on the benzene ring is oriented towards the Zr atom with a closest Zr-C non-bonded distance of 4.0055(15) Å to C(22). This has slipped the $Zr(NEt_2)_3$ moiety away from the benzene ring as evidenced by an angle slip ψ of 5.1° between the normal of the C₅ plane and the Zr-CNT (CNT, centroid of the five-membered ring) vector: the slip distortion Δ (the distance of the centroid from the normal of the C_5 plane to the metal) is 0.202 A; and the Zr-C distances range from 2.4898(15) for C(14) to 2.6765(15) A for C(11). The angle slip and slip distortion parameters are in the ranges typical of indenyl ligands rather than cyclopentadienyl ligands [12]. The Zr-CNT distance of 2.276 Å is long for a Zr(IV)-CNT (for a Cp or Cp* ligand) distance, which are normally less than 2.24 Å [13], suggesting that the ring has also been pulled away slightly from the



Fig. 1. Perspective view of complex **2** showing the atomic-labelling scheme. The atoms are shown as 40% probability ellipsoids. Selected bond distances (Å), angles (°) and torsion angles (°): Zr(1)-N(6) 2.0689(13), Zr(1)-CNT 2.2759, Zr(1)-N(5) 2.0866(13), Zr(1)-N(4) 2.0888(13), Zr(1)-C(13) 2.5417(15), Zr(1)-C(14) 2.4898(15), Zr(1)-C(12) 2.6385(15), Zr(1)-C(15) 2.5362(14), Zr(1)-C(11) 2.6765(15), N(6)-Zr(1)-N(5) 96.70(5), CNT-Zr(1)-N(4) 112.96, N(6)-Zr(1)-N(4) 99.41(5), CNT-Zr(1)-N(5) 113.38, N(5)-Zr(1)-N(4) 117.69(5), CNT-Zr(1)-N(6) 114.77, C(43)-N(4)-C(41) 110.69(12), C(2)-C(1)-C(11)-C(12) -32.1(2), CNT-Zr(1)-N(4)-C(41) 0.1, CNT-Zr(1)-N(5)-C(53) 12.1, CNT-Zr(1)-N(6)-C(61) -89.0.

Zr atom. Another effect of the close non-bonding phenyl–Zr interaction is that two of the amido groups have been pushed away from the idealised three-legged pianostool geometry: N(5)–Zr–N(4) is 117.69(5)° compared to less than 100° for the other N–Zr–N angles.

All of the N atoms are trigonal planar with the planes of N(4) and N(5) exhibiting a perpendicular arrangement with respect to the C₅ ring. This not only minimises the steric interaction with the encroaching phenyl ring but also maximises the p_{π} -d_{\pi} bonding between these amides and an empty d orbital on the Zr atom [14,15]. The plane of the other amide is oriented parallel to the C_5 ring, which allows π donation into a different and perpendicular empty d orbital. Since N(4) and N(5) are sharing the same d orbital in their p_{π} -d_{\pi} bonding interaction, it is not surprising that the Zr-N(4) and Zr-N(5) distances (2.0888(13) and 2.0866(13) Å, respectively) are longer than the Zr-N(6) distance (2.0689(13) A). They are also at the long end for terminal amido-zirconium complexes in which the distances generally lie in the range 2.00 to 2.085 A [13,15–17]. Interestingly, the three CNT–Zr–N angles are within only a few degrees of each other: 112.96, 113.38 and 114.77° for N(4), N(5) and N(6), respectively. The angles for N(4) and N(5) are what would be expected for a compromise between maximising p_{π} -d_{\pi} bonding and minimising steric interactions with the C₅H₄ ring and compare closely with 110.3° for the perpendicular amide ligand in $[(\eta^5 - C_2 B_9 H_{11})Zr(NMe_2)_2(NHEt_2)]$ (3) [16]. The angle for N(6), however, is smaller than might be expected; for example, the parallel amide in 3 has an angle of 123.5° [16]. This smaller angle for N(6) is probably a result of steric interactions with the other diethylamido ligands that have been pushed towards it.

It is noteworthy that the Zr-phenyl interaction is non-bonding: since the three amido groups are acting as three-electron donor ligands, the Zr atom is already electronically saturated with 18 electrons and so cannot accommodate additional electrons from the phenyl group.

4. Conclusions

We have described the synthesis of a new sterically constrained cyclopentadienyl ligand by a Pd-catalysed cyclopentadienyl-aryliodide coupling reaction and a complex with Zr, which displays significant distortions as a result of the bulky aryl substituent. Further chemistry of this new ligand, especially with electron-deficient metal centres, is being explored.

Acknowledgements

The New Zealand Lotteries Science Grants Board is thanked for a grant to purchase precious metals.

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