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Key indicators

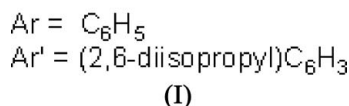
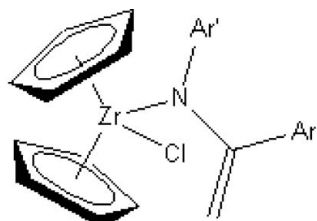
Single-crystal X-ray study
 $T = 161$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.039
 wR factor = 0.039
Data-to-parameter ratio = 10.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Chlorobis(η^5 -cyclopentadienyl)[N -(2,6-diisopropyl-phenyl)- N -(1-phenylvinyl)amide]zirconium(IV)

The title compound, $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}(\text{C}_{20}\text{H}_{24}\text{N})]$, is the second example of an enamido zirconocene to be crystallographically characterized. The geometry about nitrogen is planar, but the orientation of the aryl and vinyl substituents indicates that the nitrogen lone pair is not conjugated with their π -systems. These features are attributed to the steric bulk of the complex.

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Comment

Despite recent advances in non-metallocene polymerization chemistry, group IV metallocenes still represent the most commercially important olefin polymerization catalysts. While a large number of catalysts of this type are already known, further modification of both the cyclopentadiene rings and the sacrificial supporting ligands may lead to improved catalyst performance and polymer properties. In particular, the sacrificial ligands are important for initialization kinetics and end group functionalization. While these substituents most commonly are halides or alkyls, the use of amido ligands is also possible.



This report details the structure of a very bulky enamido complex (I), which is only the second enamido zirconocene for which the solid state structure has been reported, the first being $\text{Cp}^*\text{CpZr}(\text{NH}'\text{Bu})[\text{N}(\text{Ph})\text{C}(\text{Ph})=\text{CH}_2]$ (Zuckerman *et al.*, 2000). This compound could possibly be a pre-catalyst for olefin polymerization, or a precursor for a cationic d^0 alkene complex after abstraction of the chloride ligand.

There are a few features of the structure (Fig. 1) that are worth mentioning. While the amido N atom has a perfectly planar configuration (sum of the bond angles around N1 is equal to 360.0°), other structural features indicate that there is no delocalization of the nitrogen lone pair. The $\text{Zr1}-\text{N1}-\text{C11}-\text{C12}$ torsion angle of $38.4(6)^\circ$ precludes effective conjugation between the nitrogen lone pair and the alkene π system. The plane of the aromatic substituent on N1 is oriented nearly perpendicular to the plane of the nitrogen substituents [the $\text{Zr1}-\text{N1}-\text{C19}-\text{C20}$ torsion angle is

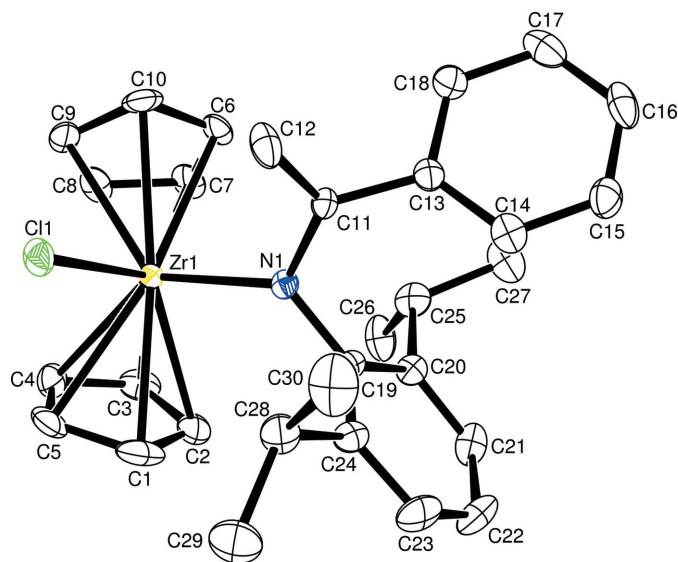


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I), drawn with 50% probability displacement ellipsoids; H atoms have been omitted for clarity.

87.5 (5)°, precluding conjugation with this aromatic system as well. Finally the Zr1–N1 bond distance is rather long at 2.141 (4) Å. More typical Zr–N bond lengths are in the range of 2.068 (3) Å found in Cp₂Zr(Cl)N(PhCH₂)₂ (Henderson *et al.*, 2002) to 2.096 (6) Å in Cp₂Zr(Cl)NHPH (Grigsby *et al.*, 1996). The conformation of the enamido fragment and the long Zr–N bond are almost certainly a consequence of the bulky nature of the ligand.

Experimental

2.8 M *n*-BuLi (3.6 mmol, 1.30 ml) in hexane was slowly added *via* a syringe to a cooled solution of diisopropylamine (0.51 ml, 3.6 mmol) in anhydrous tetrahydrofuran (THF; 20 ml). The cooling bath (213 K) was removed and the solution stirred for 1.5 h at room temperature. 2,6-Diisopropyl-*N*-(1-phenylethylidene)aniline (1.0 g, 3.6 mmol) (Kristen *et al.*, 2001) was added at 213 K to the freshly prepared lithium diisopropylamide solution and the solution was stirred for 1.5 h. The solution was then transferred to a flask charged with zirconocene dichloride (1.0 g, 3.4 mmol) in anhydrous THF, which was cooled to 203 K. After stirring for 2 h at room temperature the solvent was removed *in vacuo* and the residue taken up in 40 ml toluene. The solution was filtered into a Schlenk tube and concentrated. A yellow crystalline material (1.39 g, 72%) was obtained by cooling the solution to 278 K overnight. These crystals were used for the X-ray study without recrystallization.

Crystal data

[Zr(C₅H₅)₂Cl(C₂₀H₂₄N)]
M_r = 535.28
 Orthorhombic, *P*₂₁₂₁
a = 9.5134 (8) Å
b = 14.718 (1) Å
c = 18.591 (2) Å
V = 2603.2 (4) Å³
Z = 4
D_x = 1.366 Mg m⁻³

Mo Kα radiation
 Cell parameters from 2777 reflections
 θ = 2.4–22.6°
 μ = 0.54 mm⁻¹
T = 161.0 K
 Column, yellow
 0.20 × 0.10 × 0.08 mm

Data collection

Bruker SMART 1000
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (Blessing, 1995)
*T*_{min} = 0.870, *T*_{max} = 0.958

11464 measured reflections
 4287 independent reflections
 3249 reflections with *I* > 3σ(*I*)
*R*_{int} = 0.055
 θ _{max} = 24.7°

Refinement

Refinement on *F*
R[*F*² > 2σ(*F*²)] = 0.039
wR(*F*²) = 0.039
S = 1.09
 3249 reflections
 298 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.68 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1807 Friedel pairs
 Flack parameter: 0.06 (5)

Table 1

Selected geometric parameters (Å, °).

Zr1–C11	2.471 (1)	N1–C19	1.461 (6)
Zr1–N1	2.141 (4)	C11–C12	1.340 (7)
N1–C11	1.443 (6)		
Zr1–N1–C11–C12	38.4 (6)	Zr1–N1–C19–C20	87.5 (5)

H atoms were positioned geometrically (C–H = 0.95 Å) and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: TEXSAN (Molecular Structure Corporation & Rigaku Corporation, 1998); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: TEXSAN.

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