(Tetrahydrofuran)potassium *mer-trans*-tris(carbazolyl)dichloro-(tetrahydrofuran)zirconate

Cara L. Nygren,[a] M. E. T. Bragg[a] and John F. C. Turner[a,b]*

[a]406 Buehler Hall, Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA, and [b]409 Buehler Hall, Neutron Sciences Consortium, University of Tennessee, Knoxville, TN 37996, USA

Correspondence e-mail: jturner@atom.chem.utk.edu

In the title compound, $[K(C_4H_8O)][ZrCl_2(C_{12}H_8N)_3(C_4H_8O)]$, the Zr atom is pseudo-octahedral, with two Cl ligands in *trans* positions. There is extensive interaction between the potassium cation and two of the aromatic carbazolyl ligands in η^6 [C$\cdots$K = 3.167 (3)–3.331 (3) Å] and η^2 [C$\cdots$K = 3.147 (3)–3.268 (2) Å] fashions.

Comment

Trisamide complexes of transition metals show a wide range of reactivity, and the synthesis and exploration of this class of compound has been the focus of considerable research in recent years within the inorganic community (Cummins *et al.*, 1988, 1991; Schrock, 1997; Cummins, 1998a). The majority of these complexes contain hard electronic ligands (Cummins, 1998b). Recently, complexes with softer non-innocent ligands have been reported (Tanski & Parkin, 2003).


(I)
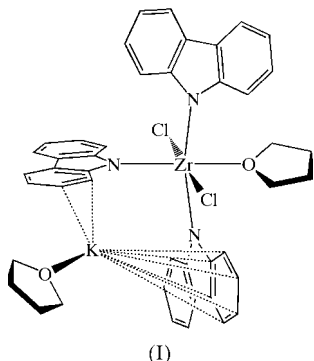
The electronic properties of the carbazolyl anion should predispose it to non-innocence when acting as a ligand at a transition metal center. Moreover, carbazolyl complexes of transition metals that are σ-bound are rare (Lopez *et al.*, 2002), and most of the known examples (Riley *et al.*, 1998, 1999, 2001) involve groups IV and V. In this paper, brief details of the synthesis and full details of the structure of the first carbazolylzirconium anion, namely *mer-trans*-tris(carbazolyl)-

dichloro(tetrahydrofuran)zirconate as the (tetrahydrofuran)-potassium adduct, (I), are reported. Examination of the Cambridge Structural Database (CSD; Allen & Motherwell, 2002; Bruno *et al.*, 2002) revealed that the first coordination sphere, consisting of three N atoms, one O atom and two Cl atoms, is unique in the structural chemistry of zirconium.

The molecular structure of (I) is shown in Fig. 1. Examination of the CSD revealed that the Zr—N bond lengths [mean Zr—N = 2.188 (17) Å; Table 1] of the carbazolyl ligands are shorter than the mean Zr—N single-bond length (2.241 Å) reported in the literature, although the Zr—N bonds in (I) are not outside the range of typical distances. The Zr—Cl bond lengths are well within the typical range of 2.379–2.776 Å (Allen & Motherwell, 2002; Bruno *et al.*, 2002), although the Zr—Cl bond in (I) is slightly shorter than the mean of these distances, *i.e.* 2.514 Å [Zr—Cl1 = 2.4276 (7) Å and Zr—Cl2 = 2.4914 (6) Å].

There are close interactions between the potassium cation and two of the carbazolyl ligands. One of the carbazolyl ligands is coordinated in a η^6 fashion, and the average distance of this interaction is 3.248 (3) Å. There is also a η^2 interaction with a carbazolyl ligand, in which the average distance is 3.208 (3) Å. This type of close interaction between a transition metal anionic complex and the counter-ion is not uncommon. However, the fact that crystallization from tetrahydrofuran (THF) results in a coordination sphere composed not solely of this ether but rather of a mixture of hard and soft bases (Pearson, 1963, 1969) was surprising, given that K$^+$ is considered a hard acid. The mixed nature of the coordination sphere prompted a further examination of the CSD. The search was based on all K$^+$–arene interactions and revealed that potassium may coordinate in a η^2, η^3 or η^6 fashion, with a range of distances, over all hapticities, of 2.856–3.927 Å.

Given the mixed hard–soft coordination sphere, we chose to compare the structure with a soft ion of similar ionic radius and equal formal charge, namely the Ag$^+$ ion, an archetypal soft acid. Surprisingly, very few Ag$^+$–arene interactions were
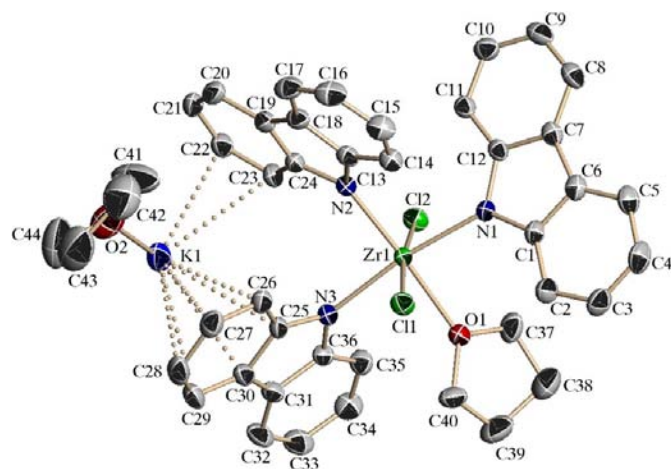
Figure 1
A view of the structure of (I), showing the atomic numbering scheme. All H atoms have been omitted for clarity, and displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

metal-organic compounds

found. In the Pearson acid–base classification (Pearson, 1963, 1969), K^+ is a hard acid, whereas Ag^+ is a soft acid; soft bases, such as arene π-electron density, would be assumed to bind more strongly to the soft acid than to the hard acid. Moreover, the Ag^+ ion is used in chromatographic separations of alkenes and other unsaturated hydrocarbons (Williams & Mander, 2001) because of this interaction of Ag^+ with the unsaturated π density, and several salts of Ag^+ are soluble in aromatic hydrocarbons, in contrast to the K^+ congeners. The dearth of structural data on arene–Ag^+ interactions and the number of arene–K^+ interactions is therefore surprising. We speculate that the formally charge-separated nature of (I), and possibly the distribution of the negative charge in the carbazolyl portion of the anion, may play a role in ensuring that the observed structure is favorable. Theoretical and experimental studies are in progress to explore this possibility.

Experimental

Treatment of a suspension of $ZrCl_4$ (2.32 g, 0.01 mol) in Et_2O, chilled to 195 K, with a freshly prepared concentrated tetrahydrofuran solution of carbazolyl potassium, formed by deprotonation of carbazole (5 g, 0.030 mol) with an excess of potassium hydride (2.4 g, 0.060 mol), resulted in a slow reaction that, on warming to room temperature, afforded a golden-yellow solution. Large leaf-like golden-yellow crystals of (I) grew spontaneously from the unstirred reaction mixture over a period of 3 d from which a block was cut for X-ray analysis. The crystal growth occurred with precipitation of a quantity of bright-yellow powder, which gave identical spectroscopic data to the crystals. The compound has been characterized by one- and two-dimensional ^1H and ^{13}C NMR spectroscopy at variable temperatures in solution and by CP–MAS ^{13}C NMR in the solid state. The spectroscopic data fully support the formulation of (I) as [K(THF)][mer-(carbazolyl)$_3$ZrCl$_2$·THF].

Crystal data

[K(C$_4$H$_8$O)][ZrCl$_2$(C$_{12}$H$_8$N)$_3$-(C$_4$H$_8$O)]
$M_r = 844.01$
Orthorhombic, $P2_12_12_1$
$a = 14.158$ (3) Å
$b = 15.486$ (3) Å
$c = 17.548$ (3) Å
$V = 3847.4$ (13) Å^3
$Z = 4$

$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7774 reflections
$\theta = 2.3$–$28.3°$
$\mu = 0.58$ mm^{-1}
$T = 173$ (2) K
Block, yellow
$0.40 \times 0.35 \times 0.25$ mm

Data collection

Bruker CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.882$, $T_{max} = 0.890$
41 736 measured reflections
9248 independent reflections

8608 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 28.3°$
$h = -18 \rightarrow 18$
$k = -19 \rightarrow 19$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.078$
$S = 1.07$
9248 reflections
479 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 1.0517P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack (1983), 5169 Friedel Pairs
Flack parameter = -0.04 (2)

Table 1
Selected geometric parameters (Å, °).

C22—K1	3.147 (3)	C30—K1	3.263 (2)
C23—K1	3.268 (2)	Cl1—Zr1	2.4276 (7)
C25—K1	3.202 (2)	Cl2—Zr1	2.4914 (6)
C26—K1	3.167 (3)	N1—Zr1	2.2056 (16)
C27—K1	3.221 (3)	N2—Zr1	2.1374 (18)
C28—K1	3.302 (3)	N3—Zr1	2.2224 (18)
C29—K1	3.331 (3)	O1—Zr1	2.2659 (16)
N2—Zr1—N1	94.61 (7)	N3—Zr1—Cl1	88.77 (5)
N2—Zr1—N3	93.23 (7)	O1—Zr1—Cl1	85.69 (5)
N1—Zr1—N3	171.90 (7)	N2—Zr1—Cl2	94.24 (5)
N2—Zr1—O1	177.06 (6)	N1—Zr1—Cl2	89.39 (5)
N1—Zr1—O1	88.34 (6)	N3—Zr1—Cl2	92.07 (5)
N3—Zr1—O1	83.83 (6)	O1—Zr1—Cl2	85.87 (5)
N2—Zr1—Cl1	94.27 (5)	Cl1—Zr1—Cl2	171.38 (2)
N1—Zr1—Cl1	88.62 (5)		

All H atoms were introduced at calculated positions and treated as riding [$U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.98 Å]. Friedel pairs were not merged.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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