Nitrile and Isocyanide Adducts of Oxygen-bridged Cationic Biscyclopentadienyl Titanium(IV) and Zirconium(IV) Fragments

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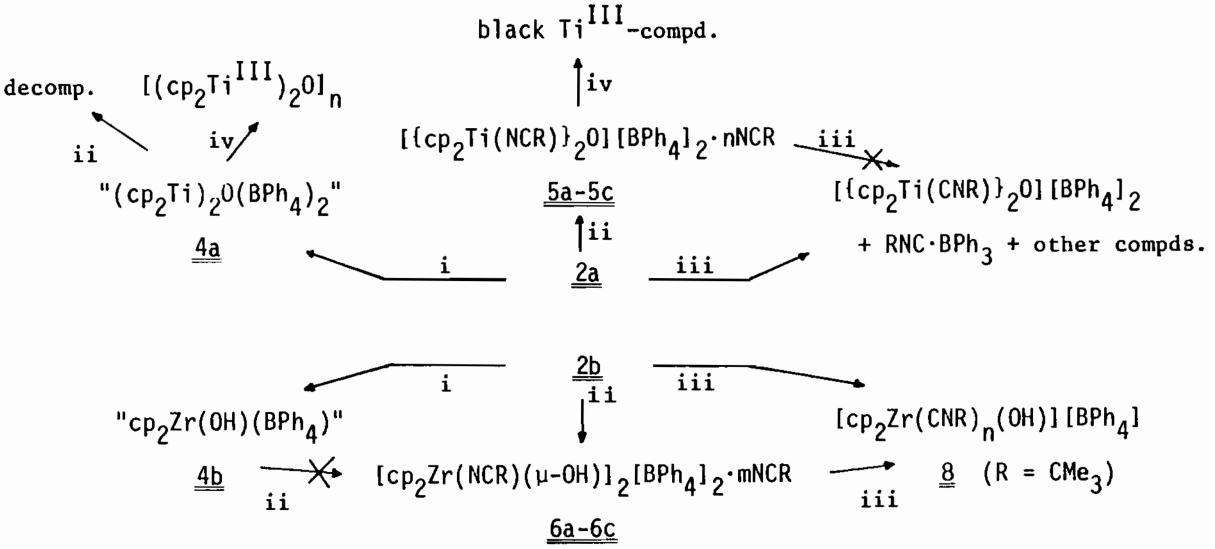
Abstract

The well-accessible new aqua complex salts $[\{cp_2M(H_2O)\}_2O][BPh_4]_2\cdot pH_2O$ (**A**) and $[cp_2M(OH)(H_2O)_n][BPh_4]\cdot mH_2O$ (**B**) (M = Ti or Zr) can easily be dehydrated or converted into anhydrous nitrile and isocyanide derivatives. While, according to crystallographic X-ray studies, the nitrile complexes with M = Ti are of the expected type **A**, the binuclear **cation** of the salt $[cp_2Zr(NC\text{-}n\text{-}Pr)(\mu\text{-}OH)]_2[BPh_4]_2\cdot 4NC\text{-}n\text{-}Pr$ turns out to be a novel 18 electron system of Zr(IV).

The still continuing investigation of mechanistic details of Ziegler–Natta polymerisations [1] has focused considerable interest on cationic complexes of the type $[cp'_2M^{IV}R'L]^+$ (**1**) ($cp' = \eta^5\text{-}C_5R_5$ with R = H or Me; M = Ti [1], Zr [2] and even Th [3]; R′ = alkyl or aryl; L = uncharged Lewis base and a ligand vacancy, respectively). In view of the well-confirmed utility of non-negligible amounts of water in the presence of the usual co-catalyst $AlR''Cl_{3-n}$ [4], we describe here some hydrated homologues of **1** with M = Ti and Zr, L = H_2O and R′ = $\frac{1}{2}$ O and OH, respectively, along with some derivatives with L = NCR″ and CNR″.

The yellow (M = Ti) and white (M = Zr) precipitates **2** [5]** resulting in excellent yields according to eqn. (1) are probably free of the cations $[cp_2M(H_2O)_n]^{2+}$ (n = 2 or 3; **3**), as the intensity ratio of

$$cp_2MCl_2 \xrightarrow[H_2O]{Na[BPh_4],\ exc.} [\{cp_2M(H_2O)\}_2O][BPh_4]_2\cdot pH_2O \text{ and/or } [cp_2M(OH)(H_2O)_n][BPh_4]\cdot mH_2O\ (\mathbf{2}) \quad M = Ti\ (\mathbf{2a}),\ Zr\ (\mathbf{2b}) \tag{1}$$



Scheme 1. Reagents and conditions: i, high vacuum, 30 °C; ii, pure NCR (R = Me, Et, Pr^n), room temperature; iii, CNR (exc., R = c-C_6H_{11}, Bu^n) in n-hexane, room temperature; iv, high vacuum, 70–120 °C.

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**See 'Supplementary Material'.

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their cp and Ph proton resonances** lies constantly around 1/2. Moreover, notable amounts of pure BPh_3 can be isolated from the n-hexane applied to wash the precipitates suggesting that in the strongly acidic solutions of **3** (pH ≤ 1) facile proton attack of one BPh_4^- counter-anion takes place.

At high vacuum and 30 °C, both **2a** and **2b** can be transferred (Scheme 1) into their completely anhydrous derivatives **4a**** and **4b**** which turn out, possibly due to partial η^n-$PhBPh_3$ coordination [3], unable to form any isolable adducts with H_2O, NCR and CNR. Between 55 and 100 °C at a high vacuum, **4a** undergoes reductive elimination to the dark blue and reportedly [6] polymeric, $[(cp_2Ti^{III})_2O]_n$, well-subliming BPh_3 and probably Ph–Ph.

Aliphatic nitriles RCN (R = Me, Et, n-Pr) readily withdraw all H_2O from **2a** and **2b** affording in almost quantitative yields the corresponding nitrile–solvated nitrile adducts $[\{cp_2Ti(NCR)\}_2O][BPh_4]_2 \cdot nNCR$, **5a–5c****, and $[\{cp_2Zr(NCR)\}_2(\mu\text{-}OH)_2][BPh_4]_2 \cdot mNCR$, **6a–6c****, respectively. Owing to difficulties in arriving at throughout stoichiometrically well-defined dry solvates, the elemental analyses and ^1H NMR spectroscopic results** (at least in view of the intensity ratios I(cp)/I(CNR) and I(Ph)/I(NCR)) did not match in all cases with the results of the crystallographic X-ray studies of modestly dried single crystals† of **5a** (n = 1) and **6c** (m = 4).

The cation of **5a** (Fig. 1) resembles that of the salt $[\{cp_2Ti(NCC_2H_4Ph)\}_2O][FeCl_4]_2 \cdot PhC_2H_4CN \cdot C_6H_6$ (**7**) [7] the rather short distance $(Ti–O)_{ave}$ of 1.83 Å, the large Ti–O–Ti′ angle of 176.1° and the acute angle spanned by the two Ti–N vectors of 79.5(2)° being as usual indicative of ambilateral O → Ti π-donor bonding. **5** loses BPh_3 like **2a**, at a high vacuum and *ca.* 70 °C, the concomitant colour change (to almost black) taking place, however, not below *ca.* 120 °C. (Attempts to characterize a still orange–red 'intermediate' of possible composition $(cp_2TiPh)_2O$ are presently in progress.)

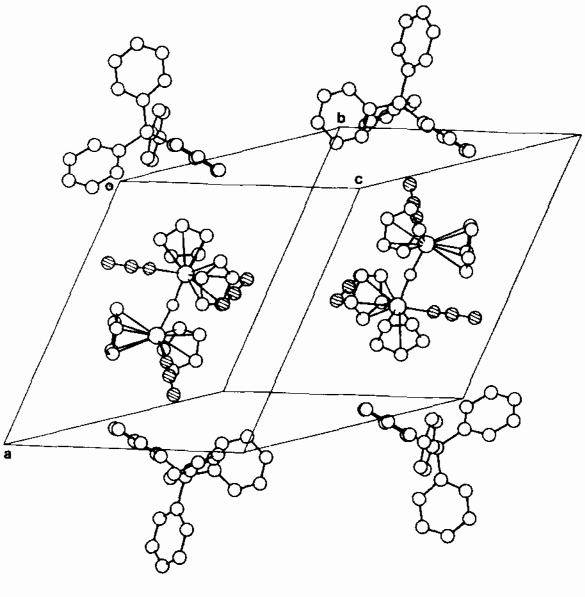

Fig. 1. Unit cell of **5a** (Schakal plot; dashed circles of nitrile atoms). Selected distances and angles: $[Ti1–C(cp1)]_{ave}$ 2.363(06); $[Ti1–C(cp2)]_{ave}$ 2.375(06); Ti1–N1 2.141(05); Ti2–N2 2.148(05) Å; cent1–Ti1–cent2 131.3(3); cent3–Ti2–cent4 132.7(3); O–Ti1–N1 94.0(2); O–Ti2–N2 93.8-(2)°.

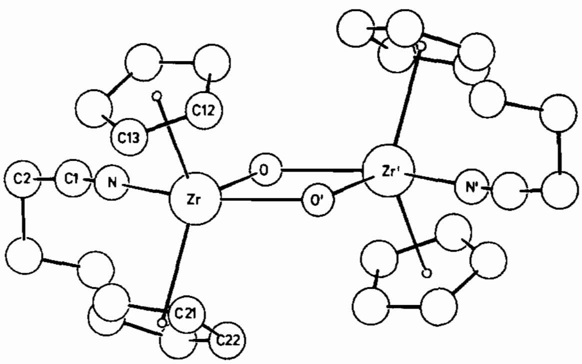

Fig. 2. Schakal plot of the cation of **6c**. Selected distances and angles: O...O′ 2.369(05); $[Zr–C(cp1)]_{ave}$ 2.512(06); $[Zr–C(cp2)]_{ave}$ 2.536(06) Å; O–Zr–O′ 66.4(01); Zr–O–Zr′ 113.6(02); Zr–N–C1 175.9(05); N–Zr–cent1 97.8(02)°.

The $(ZrNOO')_2$ fragment of the centrosymmetric cation of **6c** (Fig. 2) (Zr–O, 2.154(03); Zr–O′, 2.174(03); Zr–N, 2.327(05) Å; angle N–Zr–O′, 139.5(02)°) is coplanar as expected by theory [8]*.

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†To avoid rapid weathering, all crystals had to be coated, under an atmosphere of the respective nitrile, with a thin film of oxygen-free paraffin oil. Crystal data of **5a**: $C_{74}H_{69}N_3OB_2Ti_2$; M_r = 1130.80; triclinic, space group $P\bar{1}$ (No. 2, Int. Tab.); a = 13.869(5), b = 14.125(5), c = 18.583(5) Å, α = 91.94(2), β = 103.71(3), γ = 117.64(2)°; V = 3089.0(19) Å^3; Z = 2, D_{calc} = 1.22 g cm^{-3}. Structure refinement to $R(F)$ and $R_w(F)$ of 0.059 and 0.058, respectively, by using 5618 symmetry-independent reflections with $|F_o| > 3\sigma(F_o)$. Crystal data of **6c**: $C_{92}H_{104}N_6O_2B_2Zr_2$; M_r = 1529.93; triclinic, space group $P\bar{1}$ (No. 2, Int. Tab.); a = 11.202(2), b = 13.543-(5), c = 13.553(3) Å; α = 76.67(3), β = 84.61(3), γ = 82.17-(2)°; V = 1977.9(10) Å^3; Z = 1 (asymmetric unit: half a molecule), D_{calc} = 1.28 g cm^{-3}. Data were collected on a Syntex P2$_1$ diffractometer at 22 °C (Mo Kα radiation, λ = 0.709261 Å, $2\theta_{max}$ = 45.0°). Structure refinement to $R(F)$ and $R_w(F)$ = 0.065 by using 5347 symmetry-independent reflections with $|F_o| > 3\sigma(F_o)$. The structures of **5a** and **6c** were solved by direct methods (SHELXS-84), Fourier- and least-squares techniques. See also 'Supplementary Material'.

*Some apparently mononuclear $(C_5Me_5)_2Zr(OH)X$-systems (X = Cl, OH, H) have already been described [9]. See also 'Note Added in Proof'.

Both the angle cent–Zr–cent′ of 124.8(03)° and the Zr••Zr′ distance of 3.623(02) Å exceed only weakly the corresponding data of the recently described complex $(cp_2Zr)_2(\mu\text{-}S)_2$ (122.7° and 3.529(2) Å, respectively) [10]†. The presence of coordinated and uncoordinated (the latter in two non-equivalent lattice sites) NC-n-Pr is also reflected by the appearance of three different ν-CN bands in the IR spectrum of **6c****. The formation of the heretofore unreported cations $[(cp_2ZrL)_2(\mu\text{-}OH)_2]^{2+}$ may be favoured in the presence of BPh_4^- anions that are likely to hamper the otherwise facile protolytic rupture of cp–Zr bonds [11]. Our present findings not only describe the structures of **5** and **6** in general, but probably also the main structural features of their precursors **2a** and **2b**.

With isocyanides **2a** and **2b** afford strictly anhydrous products, too, the derivatives of **2a** displaying usually ν-CN absorptions (IR) in three different ranges: (i) close to the absorption of free RNC ($R = c\text{-}C_6H_{11}$, 2150 cm^{-1}); (ii) at wave numbers most likely for RNC coordinated to cationic d^0-systems†† ($R = c\text{-}C_6H_{11}$, 2220 cm^{-1}); and, occasionally, (iii) notably close to the absorptions of adducts $RNC\cdot BPh_3$ [12] ($R = c\text{-}C_6H_{11}$, 2270 cm^{-1}). Unlike **2a**, **2b** reacts with $n\text{-}C_4H_9NC$ to one singular, light brown isocyanide complex **8**** (ν-CN, 2230 cm^{-1}, broad), which product is likewise accessible from **6b**. Reaction of **2b** and **6a** with $c\text{-}C_6H_{11}NC$ leads presumably to mixtures of products (from **2b**: light brown, ν-CN, 2170 and 2275 cm^{-1}; from **6a**: 2165, 2210, 2265 and 2310 cm^{-1}), the latter light yellow material being not free of CH_3CN. The nitrile complexes **5** do not react with RNC at all.

Supplementary Material

Additional information (marked** in the text) is available from the authors on request. See also ref. 13.

Acknowledgements

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Note Added in Proof

Very similar data have also been reported for the non-ionic complex $[cp_2Zr(OCOCF_3)(\mu\text{-}OH)]_2$: S. Klima and U. Thewalt, *J. Organomet. Chem., 354* (1988) 77.

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† These authors have alluded on the significance of exceptionally acute cent–M–cent′ angles in view of theoretical predictions [8]. See also 'Note added in Proof'.

** See 'Supplementary Material'.

†† One recent example of this still very rare type is the salt $[cp_2Ti(CNBu^t)(\eta^2\text{-}CMe{=}NBu^t)][BPh_4]\cdot MeCN$ (ν-CN: 2190 cm^{-1}); see ref. 1.