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Molecular and Crystal Structures of Adducts $(Cp_2YCl)_2L$ (L = 2THF, DME, 1,4-Dioxane)

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Abstract—The adducts $[Cp_2Y(\mu\text{-}Cl)]_2 \cdot 2THF$ (**5**), $\{[Cp_2Y(\mu\text{-}Cl)]_2 \cdot 1,4\text{-dioxane}\}_n$ (**6**), and $Cp_2Y(DME)(\mu\text{-}Cl)(Cl)YCp_2$ (**7**) have been synthesized and studied by X-ray crystallography. In **5**, the $(Cp_2YCl)_2$ moiety is coordinated to two THF molecules ($d_{(Y-O)}$ = 2.478 Å); in **6** the $(Cp_2YCl)_2$ dimers are linked by 1,4-dioxane to form a polymer chain ($d_{(Y-O)}$ = 2.601 Å). In asymmetric adduct **7**, the DME molecule is bound through both O atoms to the same Y atom (d(Y–O) = 2.382 and 2.448 Å), and one of the chlorine atoms is bridging and the other chlorine atom is terminal.

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Metallocene derivatives of rare-earth elements and yttrium are Lewis acids and readily form adducts with donor ligands. The structure of these adducts is determined to a great extent by the steric properties of the metallocene moiety and also depends on the type of O-ligand [1]. For example, dimeric yttrium chloride with bulky C_5Me_5 groups $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$ (**1**) reacts with L to form mononuclear adducts $(C_5Me_5)_2YCl \cdot L_n$, where n varies as a function of the structure of L [1]. As distinct from **1**, complexes with unsubstituted C_5H_5 groups do not dissociate under the action of L, such as THF; rather they form dimeric adducts, for example, $[(Cp_2Ln(\mu\text{-}Cl)]_2 \cdot L_2$ ($Cp = C_5H_5$, Ln = Nd (**2**) [2] and Er (**3**) [3]).

Assuming that a change in the type of L can considerably influence the bonding in the complexes with unsubstituted Cp groups, we synthesized and studied adducts of the dimer $[(Cp_2Y(\mu\text{-}Cl)]_2$ (**4**) with different L's. Here, we report the data on three adducts: $(Cp_2YCl)_2 \cdot (C_4H_8O)_2$ (**5**), $[(Cp_2YCl)_2 \cdot C_4H_8O_2]_n$ (**6**), and $Cp_2Y(C_4H_{10}O_2)(\mu\text{-}Cl)(Cl)YCp_2$ (**7**), obtained by the reaction of **4** with THF, 1,4-dioxane, and 1,2-dimethoxyethane (DME), respectively.

RESULTS AND DISCUSSION

It is known that, in dimer **4** [4], each yttrium atom (d^0 state) has a vacant orbital and is able to coordinate an extra ligand [5]. Therefore, the reaction of **4** with THF yields adduct **5** (Fig. 1), in which the $Y(\mu\text{-}Cl)_2Y$ bond persists and the yttrium atoms each coordinate a THF molecule, thus becoming coordinatively saturated (CN = 9). The structure of adduct **5** resembles the structures of adducts **2** and **3**, and many structural parameters of these complexes (for example, ClErCl, 72.2°; Er–Cl, 2.666, 2.797 Å; Er–O, 2.590 Å; Er···Er, 4.42 Å [3]) are rather close to those of **5**.

In adduct **6**, obtained by the reaction of **4** with 1,4-dioxane, the same type of bonding as in **5** is observed. Each Y atom in **6**, in addition to the Cp ligands, is coordinated to two Cl atoms and the O atom lying in the bisector plane of the Cp_2Y moiety (Fig. 2). The $(Cp_2YCl)_2$ dimers in **6** are linked in a chain by 1,4-dioxane molecules. The latter adopt a chair conformation and act as bidentate nonchelating ligand. Comparison of structures **5** and **6** shows that the distance d(Y···Y) in **5** (4.418 Å) is 0.04 Å longer than in **6** (4.376 Å) (in **4**, d(Y···Y) = 4.069 Å [4]). Conversely, d(Y–O) in **5** (2.478 Å) is 0.12 Å shorter than in **6** (2.601 Å). This points to a greater strength of the Y–THF bond and is consistent with the higher donor properties of THF as compared to those of 1,4-dioxane [1].

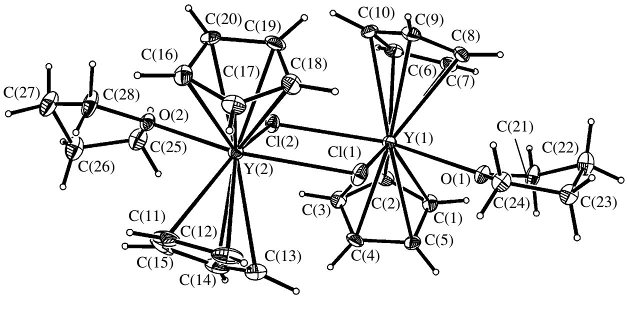


Fig. 1. Structure of adduct **5**. Selected bond angles (Å) and bond angles (deg): Y(1)–Cl(1), 2.661(1); Y(1)–Cl(2), 2.810(1); Y(1)–O(1), 2.478(2); Y(1)–Cp(1), 2.382(2); Y(1)–Cp(2), 2.389(2); Y(2)–Cl(1), 2.793(1); Y(2)–O(2), 2.452(2); Y(1)···Y(2), 4.418(1); Cl(1)Y(1)Cl(2), 72.71(2); Cl(1)Y(1)O(1), 75.97(6); Cp(1)Y(1)Cp(2), 127.5; Y(1)Cl(1)Y(2), 108.19(3).

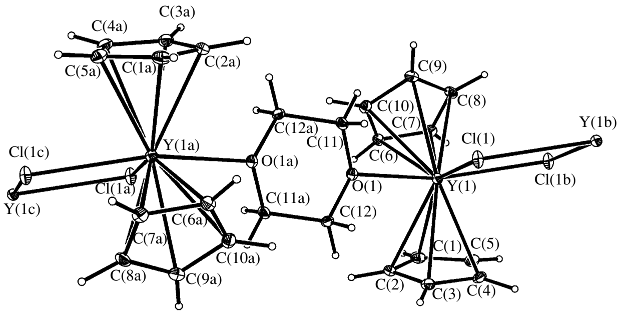
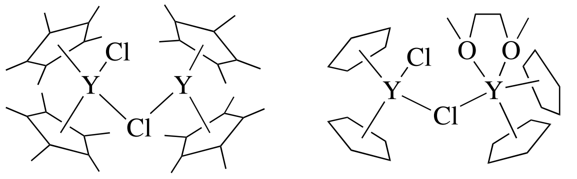


Fig. 2. Structure of a fragment of the polymer chain of adduct **6**. Selected bond lengths (Å) and bond angles (deg): Y(1)–Cl(1), 2.693(1); Y(1)–Cl(1b), 2.789(1); Y(1)–O(1), 2.601(2); Y(1)–Cp(1), 2.368(2); Y(1)–Cp(2), 2.402(2); Y(1)···Y(1b), 4.376(1); Cl(1)Y(1)Cl(1b), 74.08(2); Cl(1)Y(1)O(1), 71.72(4); Cl(1b)Y(1)O(1), 145.21(4); Cp(1)Y(1)Cp(2), 126.6; Y(1)Cl(1)Y(1b), 106.00(2).

The product of the reaction of **4** with DME (adduct **7**), unlike compounds **5** and **6**, has an unusual asymmetric structure (Fig. 3). Here, the DME molecule is coordinated to the Y(1) atom through both O atoms (d(Y–O) = 2.382, 2.448 Å), which leads to the cleavage of one of the bridging bonds Y(μ-Cl)$_2$Y so that the chlorine atom becomes a terminal atom bonded to the Y(2) atom. It is evident that this bond rearrangement **7** is associated with the strong chelation between DME and yttrium, which takes place readily [6], in contrast to the chelation between 1,4-dioxane and yttrium.

It is worth noting that nonequivalent metal atoms are rarely encountered in dimeric metallocenes and, in this respect, adduct **7** resembles complex **1** [1, 7] (Scheme 1).



1 **7**

Scheme 1.

However, whereas both Y atoms in **1** are coordinatively unsaturated (CNs are 7 and 8) (C_5Me_5, like C_5H_5, occupies three coordination sites [1]), one of the metal atoms in **7** is coordinatively saturated (CNs are 8 and 9). This fact, along with the higher steric hindrance in **1** (d(Y ··Y) is 5.354 Å in **1** and 5.038 Å in **7**), can account for the difference in activity between **1** and **7** with respect to O-ligands. In particular, complex **1**, as mentioned above, readily dissociates upon its reaction with O-ligands [1]. Adduct **7**, which forms in a DME excess, does not undergo further transformation into two mononuclear molecules $Cp_2Y(DME)Cl$, as might be expected taking into account strong metal–DME chelate bonds.

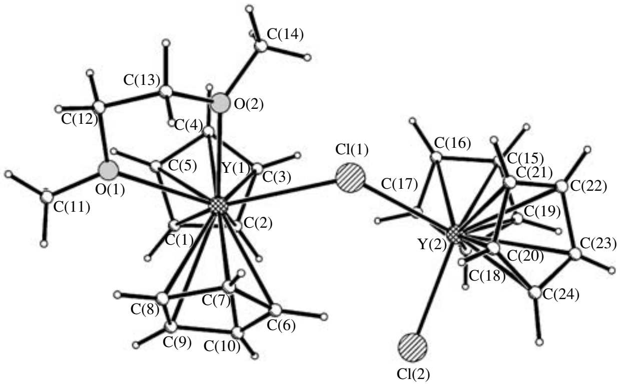


Fig. 3. Structure of Adduct **7**. Selected bond lengths (Å) and bond angles (deg): Y(1)–O(2), 2.382(3); Y(1)–O(1), 2.448(3); Y(1)–Cl(1), 2.785(1); Y(2)–Cl(1), 2.657(1); Y(2)–Cl(2), 2.575(1); Y(1)–Cp(1), 2.37; Y(1)–Cp(2), 2.38; Y(2)–Cp(1), 2.36; Y(2)–Cp(2), 2.36; Y(1)···Y(2), 5.038(1); O(2)Y(1)O(1), 65.77(1); Cl(2)Y(2)Cl(1), 98.10(3); Y(2)Cl(1)Y(1), 135.50(5); Cp(1)Y(1)Cp(2), 129.3; Cp(3)Y(2)Cp(4), 129.0.

EXPERIMENTAL

All operations were carried out in an argon atmosphere or vacuum. Solvents were purified by distillation with sodium benzophenone ketyl. $(Cp_2YCl)_2$ was synthesized by a known procedure [8]. ^{1}H NMR spectra were recorded on a Bruker DPX300 spectrometer.

Adduct 5. $(Cp_2YCl)_2$ (0.2 g) was dissolved in a mixture of toluene (22 mL) and THF (3 mL) at 20°C, and the solution was evaporated to ~1/3 of the initial volume and left overnight at 18°C. The resulting colorless crystals (0.07 g) were separated, washed with toluene (1 mL), and dried in vacuum.

For $C_{28}H_{36}Cl_2O_2Y_2$

Anal. calcd. (%): Cl, 10.85; Y, 27.22.

Found (%): Cl, 10.30; Y, 26.85.

^{1}H NMR (300 MHz, C_6D_6, 20°C, δ, ppm): 6.19 (s, 10H, Cp), 3.45 (br s, 4H, CH_2O), 1.27 (br s, 4H, C_2H_4). One crystal was selected for X-ray crystallography.

Adduct 6. $(Cp_2YCl)_2$ (0.27 g) was dissolved in a warm (45°C) mixture of toluene (35 mL) and 1,4-dioxane (6 mL), and the solution was allowed to slowly cool (24 h) in a water bath to room temperature. The resulting colorless crystals (0.11 g) were separated, washed with toluene (1 mL), and dried in vacuum.

For $C_{24}H_{28}Cl_2O_2Y_2$

Anal. calcd. (%): Cl, 11.89; Y, 29.81.

Found (%): Cl, 11.31; Y, 29.44.

^{1}H NMR (300 MHz, C_6D_6, 20°C, δ, ppm): 6.19 (s, 20H, Cp), 3.36 (s, 8H, dioxane). One crystal was selected for X-ray crystallography.

Adduct 7 was obtained analogously to adduct **5**. For $(Cp_2YCl)_2$ (0.2 g) in a mixture of toluene (25 mL) and DME (2.5 mL), 0.06 g of colorless crystals of **7** were obtained.

Experimental details and crystal data of adducts **5**, **6**, and **7**

Adduct	**5**	**6**	**7**
Empirical formula	$C_{28}H_{36}Cl_2O_2Y_2$	$C_{24}H_{28}Cl_2O_2Y_2$	$C_{24}H_{30}Cl_2O_2Y_2$
FW	653.28	597.18	599.20
Crystal size, mm	0.30 × 0.40 × 0.55	0.20 × 0.30 × 0.40	0.25 × 0.30 × 0.35
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*P*2(1)/*c*	*P*–1	*P*2(1)2(1)2(1)
a, Å	15.549(2)	8.175(1)	11.6501(15)
b, Å	21.263(2)	8.201(1)	13.6572(16)
c, Å	8.4090(9)	10.346(1)	15.455(2)
α, deg	90	89.003(2)	90
β, deg	102.651(2)	73.059(2)	90
γ, deg	90	60.284(2)	90
V, Å^3	2712.7(5)	569.49(10)	2459.0(5)
Z	4	1	4
D, g cm^{-3}	1.600	1.741	1.619
Θ range, deg	1.65–27.00	3.82–29.00	1.99–29.00
Number of unique reflections	5879 (2758)	20218 (5783)	21811 (6525)
Absorption μ, mm^{-1}	5.323	4.478	4.931
R_1	0.0720	0.0300	0.0827
wR_2 $[I > 2s(I)]$	0.0654	0.0540	0.0721

For $C_{24}H_{30}Cl_2O_2Y_2$

Anal. calcd. (%): Cl, 11,83; Y, 29.67.

Found (%): Cl, 11.54; Y, 29.50.

^{1}H NMR (300 MHz, $C_6D_5CD_3$, 20°C, δ, ppm): 6.11 (s, 20H, Cp), 3.24 (s, 4H, CH_2), 3.06 (s, 6H, CH_3). One crystal was selected for X-ray crystallography.

Details of the X-ray diffraction studies of single crystals of **5**, **6**, and **7** sealed in capillaries and their crystallographic data are listed in the table. The sets of reflection intensities were collected on a Bruker SMART diffractometer with MoK_α radiation at 120 K. Corrections for absorption were applied with the SADABS program [9]. The structures were solved by direct methods. The non-hydrogen atoms were located from difference syntheses and refined on F^2_{hkl} in the anisotropic approximation. The hydrogen atoms were placed in the geometrically calculated positions and refined as riding on their bonded carbon atoms with $U(H) = nU(C)$, where $U(C)$ is the equivalent temperature factor of the corresponding carbon atom and n = 1.2 and 1.5 for sp^2 and sp^3 carbon atoms, respectively. All calculations were performed with the SHELXTL PLUS 5 program package [10].

Atomic coordinates and complete structural data are deposited with the Cambridge Crystallographic Data Center: CCDC no. 293793 for **5**, no. 244037 for **6**, and no. 293792 for **7**.

REFERENCES

1. Evans, W.J., Fujimoto, C.H., Johnston, M.A., and Ziller, J.W., *Organometallics*, 2002, vol. 21, p. 1825.
2. Zhongsheng, J., Yongsheng, L., and Wen-Oi, C., *Sci. Sin., Ser. B (Engl. Ed.)*, 1987, vol. 30, p. 1136.
3. Ji-Zhu, J., Zhong-Sheng, J., and Wen-Oi, C., *Jiegou Huaxue (J. Struct. Chem.)*, 1992, vol. 11, p. 204.
4. Lobkovskii, E.B., Soloveichik, G.L., Bulychev, B.M., and Erofeev, A.B., *Zh. Strukt. Khim*, 1984, vol. 25, p. 170.
5. Lauher, J.M. and Hoffman, R., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 1729.
6. Baischl, U., Dell Amico, D.B., Calderazzo, E., et al., *Inorg. Chim. Acta,* 2004, vol. 357, p. 1538.
7. Evans, W.J., Rausch, M.D., Hunter, W.E., et al., *Organometallics*, 1985, vol. 4, p. 553.
8. Holton, J., Lappert, M.F., Ballard, D.G.H., et al., *J. Chem. Soc., Dalton Trans.*, 1979, no. 1, p. 45.
9. Sheldrick, G.M., *SADABS*, v. 2.01, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, USA, 1998.
10. Sheldrick, G.M., *SHELXTL, v. 5.10, Structure Determination Software Suite*, Bruker AXS, Madison, 1998.