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Note

Reactivity of cationic decamethylmetallocene complexes towards ketones

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Reaction of decamethylmetallocene cations $[Cp^*_2M]^+$ (M = Sc, Ti, V) with acetone and benzophenone resulted in the formation of the corresponding acetone adducts $[Cp^*_2M(OCMe_2)_n]^+$ (M = Sc, $n = 2$; M = Ti, $n = 1$; M = V, $n = 1$) and benzophenone adducts $[Cp^*_2M(OCPh)]^+$. The stoichiometry of these adducts is determined by both the electronic configuration of the metal center as well as steric pressure imparted by the large Cp*-ligands. In addition, the M–O–C angle is controlled by the number of free valence orbitals of the Cp^*_2M unit.

1. Introduction

Early transition metal complexes play an important role in the (selective) transformation of ketones [1], such as the reduction [2], hydrosilylation [3], olefination [4], the addition of metal-alkyl fragments [5], the Aldol condensation [6] and the reductive coupling to form diols (pinacol coupling) [7]. It is expected that the initial step in these transformations is the coordination of the substrate via oxygen. It is known, that ketones can bind to early transition metals in different ways, depending on the metal center, ranging from κO-bound adducts [8], to side-on bound η^2-ketone complexes [7b,9] and dimeric structures [10].

We have been interested in the coordination chemistry of cationic decamethylmetallocene cations of trivalent metal centers [11]. Here we describe the reactivity of $[Cp^*_2M][BPh_4]$ (M = Sc, Ti, V) with acetone and benzophenone to probe the influence of the electronic structure of the metallocene fragment on the coordination mode of the ketone ligand.

2. Experimental section

2.1. Materials and methods

All reactions and manipulations of air and moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques. Reagents were purchased from commercial suppliers and used as received, unless stated otherwise. THF-d_8 and cyclohexane were dried over Na/K alloy prior to use and THF was dried by percolation over columns of aluminum oxide, BASF R3-11 supported Cu oxygen scavenger, and mol. sieves (4 Å). $[Cp^*_2M][BPh_4]$ (M = Sc, Ti, V) were prepared according to literature procedures [11]. ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances. IR spectra of KBr pellets of the samples were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. Despite many attempts we were not able to obtain satisfactory elemental analysis data because of low, but reproducible, carbon values. This is a common observation for organometallic complexes with a high carbon content and is associated with the formation of inert carbide species [11]. In all cases, V_2O_5 was added to the samples to reduce the formation of such species.

2.2. *Preparation of* $[Cp^*_2M(OCMe_2)_n][BPh_4]$ *(M = Sc, n = 2; M = Ti, n = 1; M = V, n = 1)*

Metallocene cations $[Cp^*_2M][BPh_4]$ were dissolved in 1,2-difluorobenzene. To the resulting solutions a small excess of acetone was added. Recrystallization from 1,2-difluorobenzene/cyclohexane resulted in small amounts of single crystals of the corresponding acetone adducts. No attempts were made to optimize the yields. $[Cp^*_2Sc(OCMe_2)_2][BPh_4]$: ^1H NMR (THF-d_8, RT, 200 MHz) δ 7.31 (br, $\Delta\nu_{1/2}$ 15 Hz, BPh_4), 6.87 (t, 7.2 Hz, BPh_4), 6.72 (t, 7.2 Hz, BPh_4), 2.38 (br, $\Delta\nu_{1/2}$ 15 Hz, $OCMe_2$), 1.79 (s, Cp*) ppm. $[Cp^*_2Ti(OCMe_2)][BPh_4]$: IR (KBr pellet) 3051(s), 3031(s), 2996(s),

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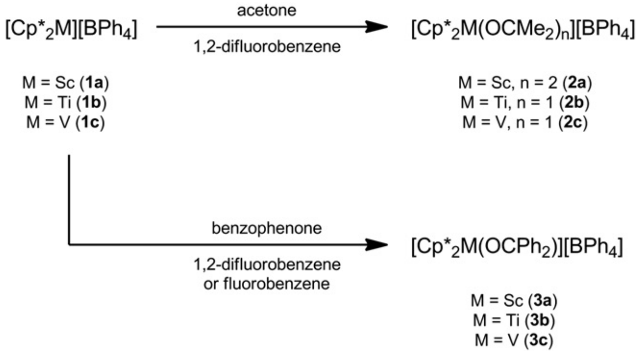

Scheme 1. Synthesis of acetone adducts **2a**–**c** and benzophenone adducts **3a**–**c**.

2980(s), 2963(s), 2902(s), 2859(m), 1665(s), 1579(m), 1478(s), 1426(s), 1378(s), 1355(m), 1264(*w*), 1254(m), 1181(*w*), 1143(m), 1065(m), 1029(m), 1019(m), 909(*w*), 859(*w*), 844(m), 802(*w*), 734(s), 705(s), 624(*w*), 606(s), 533(*w*), 482(*w*), 461(m), 414(*w*) cm^{-1}. $[Cp^*_2V(OCMe_2)][BPh_4]$: IR (KBr pellet) 3025(s), 3031(m), 2997(m), 2982(m), 2963(m), 2920(s), 2851(w), 1744(w), 1672(s), 1582(m), 1479(s), 1448(w), 1426(s), 1381(m), 1356(w), 1321(m), 1281(m), 1262(s), 1183(w), 1151(w), 1128(w), 1068(s), 1019(s), 887(w), 844(w), 801(m), 733(s), 706(s), 663(w), 639(w), 606(m), 527(w), 466(w), 414(w) cm^{-1}.

2.3. *Preparation of $[Cp^*_2M(OCPh_2)][BPh_4]$ (M = Sc, Ti, V)*

Metallocene cations $[Cp^*_2M][BPh_4]$ were dissolved in fluorobenzene (M = Sc) or 1,2-difluorobenzene (M = Ti, V). To the resulting solutions a small excess of benzophenone was added. Recrystallization by slow diffusion of cyclohexane into these solutions resulted in small amounts of single crystals of the corresponding benzophenone adducts. No attempts were made to optimize the yields. $[Cp^*_2Sc(OCPh_2)][BPh_4]$: ^1H NMR (THF-d_8, RT, 200 MHz) δ 7.76 (d, 6.8 Hz, OCPh$_2$), 7.63 (d, 7.4 Hz, OCPh$_2$), 7.51 (t, 7.4 Hz, OCPh$_2$), 7.3 (br, BPh$_4$), 6.84 (t, 7.6 Hz, BPh$_4$), 6.69 (t, 6.9 Hz, BPh$_4$), 1.91 (s, Cp*) ppm. IR (KBr pellet) 3054(s), 3032(s), 3000(s), 2998(s), 2947(s), 2908(s), 2898(s), 2872(s), 2859(s), 1656(w), 1605(s), 1585(s), 1554(s), 1480(w), 1447(m), 1425(w), 1381(w), 1324(s), 1292(s), 1280(m), 1182(w), 1159(w), 1064(w), 1029(w), 999(w), 940(w), 921(w), 842(w), 808(w), 770(w), 734(m), 703(w), 635(m), 614(w), 471(w) cm^{-1}. $[Cp^*_2Ti(OCPh_2)][BPh_4]$: IR (KBr pellet) 3054(s), 3000(s), 2982(s), 2920(s), 2908(s), 2850(s), 1657(w), 1618(w), 1581(m), 1544(m), 1505(m), 1482(w), 1446(m), 1526(m), 1380(w), 1327(m), 1289(w), 1266(m), 1203(w), 1182(w), 1152(w), 1100(w), 1065(m), 1023(m), 999(w), 942(w), 925(w), 842(w), 807(w), 748(m), 733(m), 703(s), 636(w), 612(w), 566(w), 546(w), 450(w), 413(w) cm^{-1}.

2.4. *Crystal data*

Crystals with suitable dimensions were mounted on top of a glass fiber, by using glovebox techniques and aligned on a Bruker [12] SMART APEX CCD diffractometer. The final unit cell was identified, the structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF [13]. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis of **2a**–**c** resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined.

In the case of the benzophenone adducts, refinement was complicated by disorder problems. In the case of compound **3a** one of the co-crystallized mono-fluorobenzene solvent molecules was disordered over a rotation of 120°. The electron density of the F-atom appeared to be spread out, indicating rotational disorder. A disorder model (50:50 for F:H on both positions: bonded to C41 and C43) was used in the final refinement. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp^2 or sp^3 hybridization at the C-atom as appropriate with $U_{\mathrm{iso}} = c \times U_{\mathrm{equiv}}$ of their parent atom, where $c = 1.2$ for the aromatic/non-methyl hydrogen atoms and $c = 1.5$ for the methyl hydrogen atoms and where values U_{equiv} are related to the atoms to which the hydrogen atoms are bonded. The methyl groups were refined as rigid groups, which were allowed to rotate free. In **3b** both difluorobenzene solvent molecules were rotational disordered by 60° and 120°. The atoms connected to C31 and C33 of one fluorobenzene molecule and to C41, C42, C43 and C44 of the other have a site occupancy factor of 0.5 (meaning in the average disorder 0.5 F and 0.5 H is bonded to each involved carbon). The hydrogen atoms were included in the final refinement riding on their carrier atoms similar to **3a**. In compound **3c** unrealistic displacement parameters were observed suggesting some degree of dynamic disorder, which is in line with the weak scattering power of the crystals investigated (dynamic means that the smeared electron density is due to fluctuations of the atomic positions within each unit cell). This dynamic behavior is especially seen in the positions concerning the cyclohexane molecule, which is located over an inversion center. The hydrogen atoms were included similar to compounds **3a**.

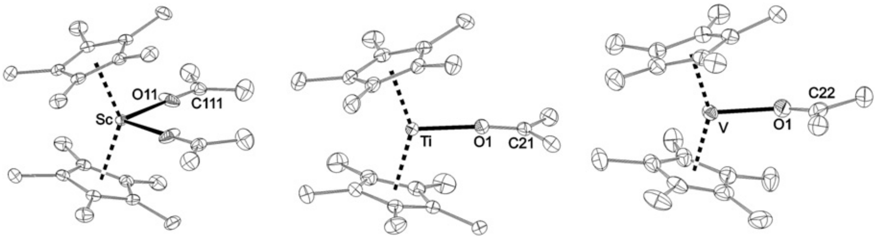

Fig. 1. ORTEP representation of the cation of **2a**–**c** showing 50% probability ellipsoids. The anions are omitted for clarity.