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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF BIS-ISONITRILE COMPLEXES $Cp_2M(CNR)_2$ (M = Ti, Zr; R = 2,6-dimethylphenyl)

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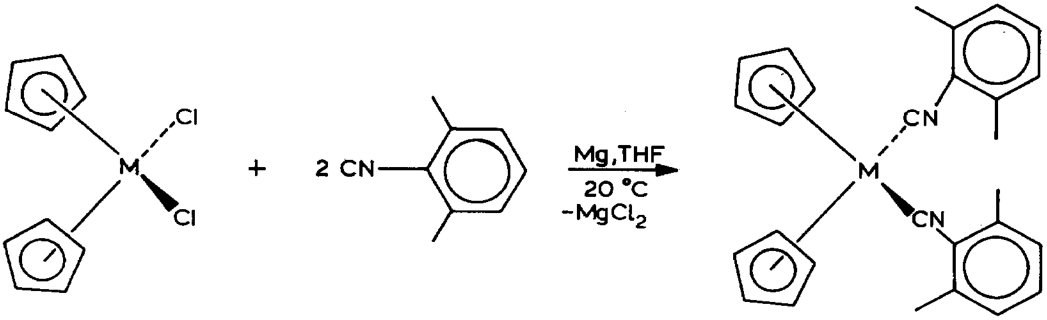
Summary

Bis-isonitrile complexes $Cp_2M(CNR)_2$ (M = Ti, Zr), where RNC is the sterically hindered 2,6-dimethylphenyl isonitrile, can be prepared in high yield by reduction of Cp_2MCl_2 with magnesium in THF solution in the presence of the isonitrile. ^1H NMR spectroscopy reveals that with the titanium complex dissociation of the isonitrile ligands takes place in solution.

Isonitrile complexes of the Group 4 metals are rare [1]. The first diamagnetic mono-isonitrile complexes of Ti, Zr and Hf were prepared only recently [2].

We previously reported that the reduction of Cp_2MCl_2 (M = Ti, Zr, Hf) with magnesium in THF solution in the presence of either CO or PMe_3 leads to the low-valent complexes $Cp_2M(CO)_2$ (M = Ti, Zr, Hf) or $Cp_2M(PMe_3)_2$ (M = Ti, Zr), respectively [3,4]. We now find that 2,6-dimethylphenyl isonitrile is also able to stabilize the $[Cp_2M]$ fragment. Thus, reductions of Cp_2MCl_2 (M = Ti, Zr) with Mg in THF in the presence of two equivalents of 2,6-dimethylphenyl isonitrile afford the diamagnetic bis(isonitrile) complexes $Cp_2M(CNC_6H_3Me_2)_2$ (**1**, **2**) in high yield.

The IR spectra of **1** and **2** contain two $\nu(C{\equiv}N)$ bands at 2038/1937 and 2027/1912 cm^{-1}, respectively, indicating that the isonitrile function still has triple bond character (Table 1). The comparative weakness of the metal-to-isonitrile backbonding also becomes apparent in the temperature dependent ^1H NMR spectra of **1**; only at −60°C are sharp signals observed (Table 1), and as the solution is allowed to warm to room temperature all the signals broaden. We attribute this to a facile dissociation of the isonitrile ligands of **1** in solution. Complex **2** behaves differently, the ^1H and ^{13}C NMR spectra giving sharp signals even at room



(1 : M = Ti ;
2 : M = Zr)

temperature (see Table 1). A pseudo tetrahedral structure of **2** has been revealed by a preliminary X-ray diffraction study [5].

Experimental

General data. All operations were performed under argon. Pentane and THF were dried over Na/K alloy and freshly distilled. 2,6-Dimethylphenyl isonitrile was used as obtained from Fluka Chemical Co. Mass spectral values are based on ^{48}Ti and ^{90}Zr, and were obtained on a Varian CH7 mass spectrometer at 70 eV. ^{1}H and ^{13}C NMR spectra were recorded in toluene-d_8 at 90 MHz and 22.5 MHz, respectively, on a FT JEOL FX 90Q NMR spectrometer, and chemical shifts are in δ values downfield from SiMe$_4$; the residual methyl proton resonance at δ 2.09 ppm in the ^{1}H NMR and the corresponding signals at δ 20.4 ppm in the ^{13}C NMR spectrum of the solvent toluene-d_8 were used as internal references. IR spectra were recorded with a Perkin–Elmer 297 spectrometer. Elemental analyses were performed by Pascher Laboratories, Bonn, West Germany.

Reduction of dicyclopentadienyltitanium dichloride in the presence of 2,6-dimethylphenyl isonitrile: synthesis of $Cp_2Ti(CNC_6H_3Me_2)_2$ (1). A mixture of Cp_2TiCl_2 (1.0 g, 4.02 mmol), magnesium turnings (0.5 g, 20.6 mmol) and 2,6-dimethylphenyl isonitrile (1.11 g, 8.46 mmol), and 50 ml of THF was stirred at room temperature. The mixture gradually darkened. After 24 h the solvent was removed in vacuo from

TABLE 1

IR, ^{1}H AND ^{13}C NMR DATA FOR $Cp_2M(CNC_6H_3Me_2)_2$ COMPLEXES (M = Ti, Zr)

	IR^a (cm^{-1}) ν(CN)	^{1}H NMR^b (ppm)		^{13}C NMR^b (ppm)			
		δ(Cp)	$\delta(CNC_6H_3Me_2)$	δ(Cp)	δ(CN)	δ(Me)	$\delta(C_6H_3)$
$CNC_6H_3Me_2$	2115	–	Me 2.06(s) C_6H_3 6.62(m)	–	170.4	18.6	134.6/128.8/ 128.3/127.8
$Cp_2Ti(CNC_6H_3Me_2)_2$ (1)	2038/1937	5.10 (s,10H)	Me 2.15(s,12H) C_6H_3 6.68(m, 6H)	94.7	^{c}	18.6	134.7/128.8/ 128.3
$Cp_2Zr(CNC_6H_3Me_2)_2$ (2)	2027/1912	5.39 (s,10H)	Me 2.16(s,12H) C_6H_3 6.69(m,6H)	96.7	170.0	19.0	134.7/130.2/ 127.2/126.4

^{a} In pentane solution. ^{b} In toluene-d_8, −60 °C. ^{c} Not observed.

the deep violet solution. The residue was extracted with pentane, and the extract filtered through a frit. The solvent was removed in vacuo without heating to leave **1** as lustrous black-violet needles. Yield: 1.66 g (93%). Found: C, 75.99; H, 6.72; N, 6.02. $C_{28}H_{28}N_2Ti$ calcd.: C, 76.35; H, 6.42; N, 6.36%. Mass spectrum: *m/e* 440 (M^+), 375 (M^+–Cp), 309 (M^+–Cp_2H), 178 (Cp_2Ti^+), 130 ($CNC_6H_3Me_2$).

Reduction of di(cyclopentadienyl)zirconium dichloride in the presence of 2,6-dimethylphenyl isonitrile: synthesis of $Cp_2Zr(CNC_6H_3Me_2)_2$ *(2).* A mixture of Cp_2ZrCl_2 (5 g, 17.2 mmol), magnesium turnings (2 g, 82.3 mmol), 2,6-dimehylphenyl isonitrile (4.51 g, 34.4 mmol) and 200 ml THF was stirred at room temperature. After 20 h the solution was dark-violet. The solvent was removed in vacuo, and the residue extracted with ca. 500 ml pentane and the extract filtered. The filtrate was concentrated in vacuo to ca. 200 ml and cooled to −20°C, to give complex **2** as black-violet needles. Yield: 6.7 g (81%). Found: c, 68.84; H, 6.28; N, 5.38. $C_{28}N_{28}N_2Zr$ calcd.: C, 69.52; H, 5.83; N, 5.79%. Mass spectrum: *m/e* 482 (M^+), 417 ($M^+ -$ Cp), 351 ($M^+ - CNC_6H_3Me_2$), 220 (Cp_2Zr^+), 130 (CNC_6H_3-$Me_2{}^+$).

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5 Preliminary X-ray data for **2**: monoclinic, space group $C2/c$, a 37.508(7), b 13.441(4), c 17.443(3) Å, β 114.19(2)°, $Z = 12$.