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Mixed sandwiches of group 3 elements: synthesis and UPS studies of pentamethylcyclopentadienylcyclooctatetraene-scandium, -yttrium and -lanthanum

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Abstract

The mixed sandwich complexes Cp*MCOT ($Cp^\star = \eta^5$-C_5Me_5; M = Sc, Y, La; COT = η^8-C_8H_8) have been prepared and characterized. IR spectra indicate that in the solid state the La compound is polymeric $(Cp^\star LaCOT)_n$, with cyclotetraene ligands. The complexes are strong Lewis acids and form bridging adducts Cp*MCOT · THF. For M = La the adduct has been isolated. The UPS spectra of Cp*MCOT are nearly identical with only minor differences in the ionizations from the highest e_2(COT) and e_1(Cp*) orbitals; this is interpreted as a strong indication that the bonding in the complexes is virtually completely ionic.

Introduction

Recent UPS studies of mixed sandwich compounds of group 4 elements Cp*MCHT and Cp*MCOT ($Cp^\star = \eta^5$-C_5Me_5; M = Ti, Zr, Hf; CHT = η^7-C_7H_7; COT = η^8-C_8H_8) showed remarkably metal-independent ionization energies of electrons from HOMO's with symmetry type e_1 and e_2. This suggests strongly dominant ionic bonding for these sandwiches with negatively charged carbocyclic rings, but consideration of intensities viz. the ratios of bands using He(I) or He(II) radiation, indicated a very substantial metal character for the C_nH_n ligand-based e_2 ionization [1]. This rather paradoxical observation led us to study analogous group 3 sandwiches Cp*MCOT, where the metals are more electropositive than their group 4 analogues [2].

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Experimental

All the compounds described in this paper are extremely air sensitive. Experiments were carried out under nitrogen by standard inert gas techniques. Solvents (pentane, ether, THF) were distilled from Na/K/benzophenone. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen under the supervision of Mr. A.F. Hamminga. IR spectra (Nujol/KBr) were recorded on a Pye-Unicam SP3-300 spectrometer, NMR spectra on a Perkin–Elmer R-24B (^{1}H, 60 MHz) and a Nicolet NT200 (^{13}C, 50.3 MHz) spectrometer. The photoelectron spectra were recorded on a Perkin–Elmer PS18 spectrometer equipped with a Helectros Development He(I)/He(II) hollow cathode light source. The spectra were obtained between 100 and 230 °C and calibrated against He, Ar and Xe as internal standards. The starting materials $ScCl_3 \cdot 3THF$, $COTYCl \cdot 2THF$ were made from the oxides or chlorides by published methods [3,4]. $Cp^{\star}Na \cdot THF$ was made from $Cp^{\star}H$ and NaH and THF as described by Den Haan et al. [5]. $Cp^{\star}Li$ was made from $Cp^{\star}H$ and BuLi in hexane. COT was purchased from Aldrich and distilled before use. K_2COT (ca. 0.3 *M* solution in THF) was prepared by treating COT with an excess of K in THF at room temperature.

$LaCl_3 \cdot xTHF$ [6]

La_2O_3 was dissolved at 0 °C in concentrated hydrochloric acid and the solution was evaporated to dryness in vacuum. The $LaCl_3 \cdot xH_2O$ obtained was finely ground and refluxed with an excess of $SOCl_2$ [7] until SO_2 and HCl evolution had stopped, then the remaining $SOCl_2$ was distilled off. The resulting $LaCl_3$ was dried in vacuum and then suspended in THF at room temperature, and the suspension was heated under reflux for 48 h. The $LaCl_3 \cdot xTHF$ was filtered off, washed with pentane, dried, and stored in ampoules under nitrogen. The products thus obtained contained variable amounts of THF; elemental analyses showed between 1.2–1.5 mol of THF per mol of La for various runs. The procedure described here was performed on ca. 10 mol scale (La_2O_3), but can be scaled up without problems. Critical steps are (i) the drying of $LaCl_3 \cdot xH_2O$, which gives a very hard solid, and (ii) the pre-complexation of anhydrous $LaCl_3$ with THF, which must carried out in an excess of THF at or below room temperature to avoid polymerization of THF. Overall yields of $LaCl_3 \cdot xTHF$ are about 90%.

$Cp^{\star}ScCOT$

To a suspension of 0.9 g (2.45 mmol) of $ScCl_3 \cdot 3THF$ in 35 ml of THF at room temperature was added 8.5 ml of a 0.29 *M* solution of $K_2C_8H_8$ in THF. The yellow solution was stirred for 0.75 h then 0.40 g (2.5 mmol) $Cp^{\star}Na$ was added. The mixture was stirred for 0.75 h and the solvent then removed in vacuum. The yellow residue was extracted with ether. Concentration and cooling to −80 °C gave off-white crystals. Sublimation of this product (160 °C/0.1 mmHg) gave 0.35 g (1.23 mmol, 50%) of a white crystalline material. Analysis, found (calcd for $C_{18}H_{23}Sc$) in %: C, 75.95 (76.04); H, 8.09 (8.15); Sc, 15.83 (15.81). MS: $m/e = 284$ (100%).

$Cp^{\star}YCOT$

$Cp^{\star}Na$ (0.65 g, 4.1 mmol) was added at room temperature to a solution of 1.13 g (3.0 mmol) of $COTYCl \cdot 2THF$ in 50 ml of ether. The mixture was stirred for 1.5 h and the solvent then removed in vacuum. The residue was suspended in pentane, the pentane evaporated off, and the residual solid powdered then vacuum sublimed (150 °C, 0.1 mmHg) to give 0.34 g (1.04 mmol, 35%) of white crystals of Cp*YCOT. Analysis, found (calcd for $C_{18}H_{23}Y$) in %: C, 66.07 (65.85); H, 7.20 (7.06); Y, 27.21 (27.08).

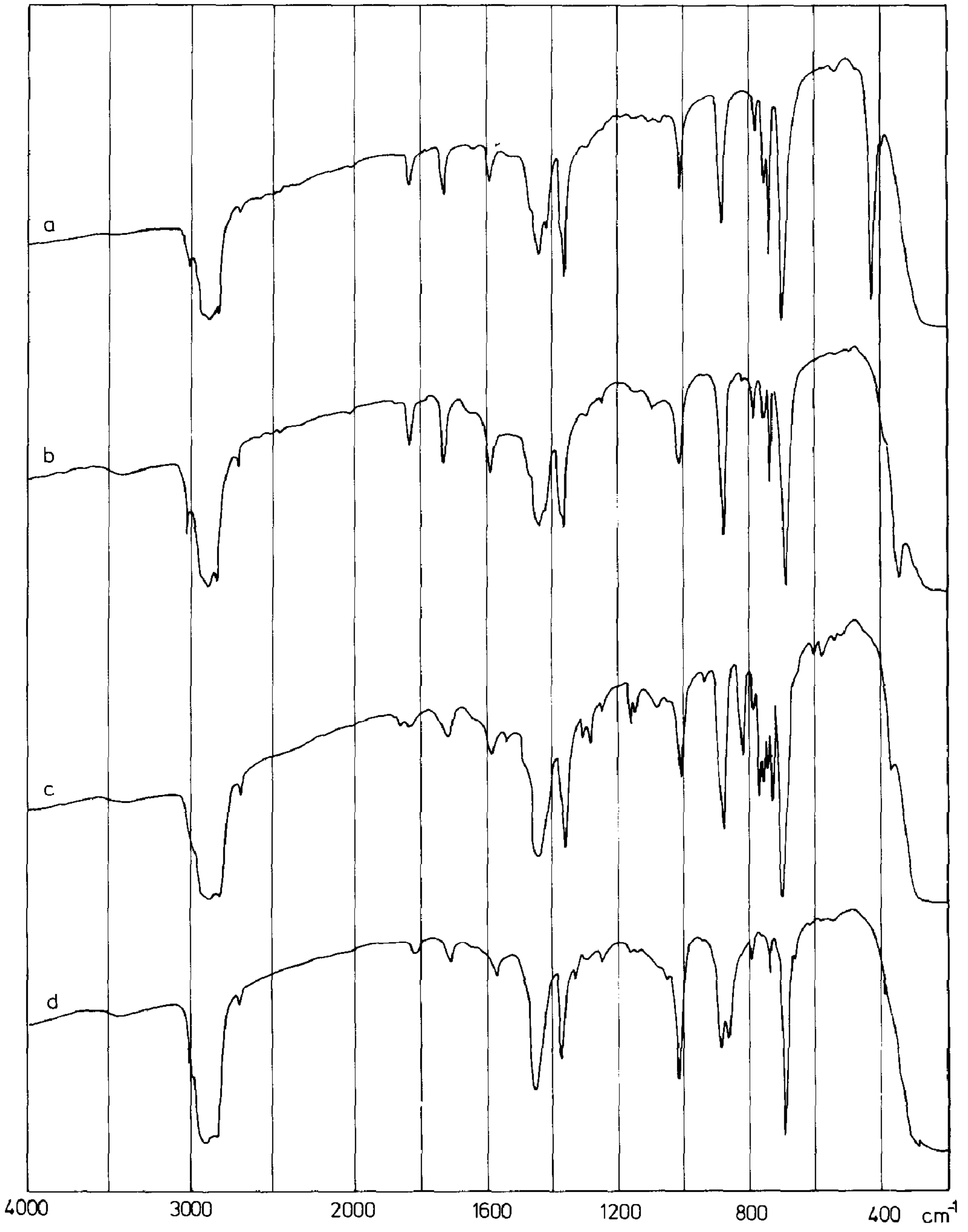

Fig. 1. IR spectra (Nujol) of (a) Cp*ScCOT, (b) Cp*YCOT, (c) $(Cp^*LaCOT)_n$ and (d) Cp*LaCOT·THF.

Table 1

^{1}H and ^{13}C NMR data for Cp*MCOT

Compound	^{1}H ^{a}		^{13}C ^{b}		
	Cp*	C_8H_8	Cp*		C_8H_8
			C-CH_3	C-CH_3	C-H
Cp*ScCOT	1.66 (15H)	6.30 (8H)	115.6 (s)	10.7 (q,125.8)	95.5 (d, 162.5)
Cp*YCOT	1.66 (15H)	6.30 (8H)	116.3 (s)	9.8 (q, 125.7)	94.8 ^{c} (d, 162.8)
Cp*LaCOT	1.59 (15H)	6.30 (8H)	^{d}	^{d}	^{d}
Cp*LaCOT·THF	1.77 (15H)	6.32 (8H)	^{d}	^{d}	^{d}

^{a} In C_6D_6, shifts in ppm relative to residual protons in solvent (δ 7.15 ppm), 30 ° C. ^{b} In C_6D_6, shifts in ppm relative to solvent signal (δ 127.96 ppm), 20 ° C, multiplicity and J(CH) (Hz) between brackets. ^{c} J(YC) 2.8 Hz. ^{d} Not recorded.

*Cp*LaCOT*

A solution of $K_2C_8H_8$ (6.0 ml, 0.6 M) in THF was added dropwise at room temperature to a suspension of 1.24 g (3.6 mmol) of $LaCl_3 \cdot 1.4$THF in 50 ml of THF followed by 0.6 g (4.2 mmol) of Cp*Li. After 2 h stirring the solvent was removed in vacuum. The residue was suspended in 50 ml of pentane and the pentane then evaporated off. The yellow powder left was dried in vacuum and sublimation (200–225 ° C/10^{-3} mmHg) then gave 0.95 g (2.5 mmol, 70%) of pale-yellow, crystalline Cp*LaCOT. Analysis, found (calcd for $C_{18}H_{23}La$): C, 57.10 (57.25); H, 6.17 (6.13); La, 36.80 (36.72)%.

*Cp*LaCOT·THF*

Freshly sublimed Cp*LaCOT (0.105 g, 0.28 mmol) was dissolved in 5 ml of THF at room temperature. The solution was cooled to − 80 ° C, and the off-white crystals that separated were isolated and identified by IR (Fig. 1) and NMR spectroscopy (Table 1).

Results and discussion

The compounds Cp*MCOT (M = Sc, Y, La) form the first complete series of neutral group 3 (mixed) sandwich compounds. As a class they are not new, since analogous cyclopentadienyl complexes CpMCOT (M = Sc, Y) have been described [3,4].

The complexes are easily accessible through metathetical reaction of the metal halide $MCl_3 \cdot n$THF and ring-introducing reagents such as Cp*Na, Cp*Li and $K_2C_8H_8$. The syntheses reported in this paper were carried out as one-pot reactions in which the reagents were mixed in the appropriate stoichiometry. The order of addition chosen was first $K_2C_8H_8$ then Cp*Na, but this is not essential; if the order is reversed the yields of Cp*MCOT are about the same. When the synthesis is carried out starting from a well-defined ring containing compound, e.g. COTYCl · 2THF, the yield is also essentially the same as in a one-pot reaction. This indicates that the reaction mixtures are good sources of Cp*M and COTM fragments, respectively, and that if the initial process is formation of other species like $Cp^{\star}_2M$ derivatives or $[(COT)_2M]^-$ anionic complexes, the kinetics of the reverse synproportionation reactions favour the synthesis of mono-ring species.

The complexes Cp*MCOT are electronically unsaturated 16e compounds and may be expected to coordinate a Lewis base to give 18e adducts Cp*MCOT · L, and is observed for all the metals. For M = La the THF adduct was isolated and characterized (IR, NMR). The THF is loosely complexed, and heating the complexes in vacuum gives the Lewis-base free sandwiches Cp*MCOT. Sublimation is an excellent method for obtaining the pure complexes Cp*MCOT. The scandium and yttrium compounds sublime under conditions (ca. 150 °C/0.1 mmHg) comparable with those reported for mixed sandwiches of group 4 [8]. Cp*LaCOT is considerably less volatile, and requires more drastic conditions for sublimation (200–225 °C/10^{-3} mmHg). This suggests that the lanthanum compound, in contrast to the scandium and yttrium analogues, is not monomeric in the solid state [9] but associated into either polymeric or oligomeric structures. Solubility differences present the same picture. Cp*ScCOT and Cp*YCOT are quite soluble in non-coordinating solvents like pentane and benzene in contrast to Cp*LaCOT. All complexes are very soluble in a basic solvent such as THF. For Y and La, the THF adducts are undoubtedly present in solution, which means that the associates present in solid Cp*LaCOT have been broken up. An interesting question is which ligands are bridging in the lanthanum sandwich. Association through bridging cyclopentadienyl ligands has been found for several complexes of the 4*f*-element e.g. $(Cp_3Pr)_n$ [10], (Cp_3La) [11], $(Cp'_2Yb \cdot THF)_n$ [12] ($Cp' = \eta^5\text{-}MeC_5H_4$). Cyclooctatetraene is also well-known to act as a bridging ligand, e.g. in $[COTNd_2THF][Nd(COT)_2]$ [13] and $(COT)_3Ti_2$ [14]. IR data indicate that association takes place through the eight-membered ring. When the spectra of the three sandwiches and the adduct Cp*LaCOT · THF are compared, the similarities between the scandium and yttrium compounds are remarkable (Fig. 1). They clearly show absorptions characteristic for η^5-Cp* (at ca. 2720m, 1480m, 1430m, 1375s, 1020m, 795w cm^{-1}) and $\eta^8\text{-}C_8H_8$ (ca. 3030m, 895s, 760m, 755s, 710s cm^{-1}. For Cp*LaCOT · THF these absorptions are readily discerned, together with characteristic peaks of coordinated THF ($\nu(COC)_{asym}$ 1020, $\nu(COC)_{sym}$ 870 cm^{-1}). The IR spectrum of $(Cp^{\star}LaCOT)_n$, however, is much more complicated, and in particular the range between 1300–500 cm^{-1} shows many absorptions. The Cp* peaks are at their normal positions, but the signals from the COT part are split or strongly shifted, indicating a radical change in coordination mode of the COT ligand.

The NMR spectra (Table 1) of Cp*ScCOT and Cp*YCOT are virtually identical, and confirm completely the proposed sandwich structure. Furthermore, Cp*LaCOT, though very sparingly soluble, seems to dissolve as a monomer in benzene. The only difference with the two other sandwiches is the Cp* resonance, which is found at slightly higher field. The resonances of Cp*LaCOT · THF are considerably shifted in d^8-THF; the Cp* protons are now at lower and the C_8H_8 protons at higher field compared with the corresponding signals from the sandwich itself and from the THF adduct in C_6D_6. The virtual invariance of the C_8H_8 and Cp* protons chemical shifts within the complete series suggests a largely ionic component in the bonding of the ligands. The available ^{13}C NMR data are consistent with this view. Unfortunately it is impossible to compare these data with those for the corresponding group 4 compounds since, owing to the paramagnetism of the latter, NMR data are

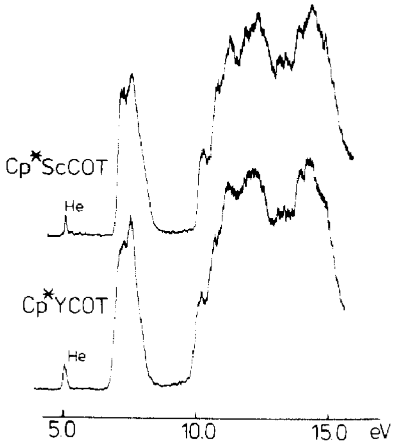

Fig. 2. He(I) spectra of Cp*ScCOT and Cp*YCOT.

not available. UPS spectroscopy proves to be a better tool in studying the bonding and charge distribution in these group 3 and group 4 compounds.

UV-photoelectron spectra

The He(I) and He(II) UP spectra of Cp*ScCOT and Cp*YCOT are presented in Fig. 2; the vertical ionization energies are summarized in Table 2. A reliable spectrum of Cp*LaCOT could not be obtained, since owing to the low volatility of the compound samples had to be heated (180–220 ° C) to give sufficiently intense spectra and at this temperature thermal decomposition occurs and the spectra of mainly decomposition products are seen. In most spectra, however, there is a broad band at about 7.5 eV, which corresponds closely with the band from the other two compounds, and from this we conclude that in the gas phase Cp*LaCOT is a sandwich with the same bonding characteristics as those of Sc and Y. The assignment of the spectra is straightforward on the basis of comparison with those of the corresponding Ti and Zr complexes and with help of the MO-diagram given by Clark and Warren [1,15].

The broad band at about 7–8 eV is a superposition of two ionization peaks which correspond to ionisation from mainly ligand e_2(COT) and e_1(Cp*) orbitals (assignment tentatively after comparison with CpTiCOT [1]). In the He(II) spectra the intensity of this band is slightly increased relative to the broad ionization band above 10 eV indicating that there is still some mixing with metal *d*-orbitals. On the

Table 2

Ionization energies

Compound	*IE* (eV) [a]			
	e_2(COT)	e_1(Cp*)	e_1(COT)	a_1(Cp*)
Cp*ScCOT	7.17	7.55	10.23	10.83
Cp*YCOT	7.04	7.44	10.19	10.69
Cp*LaCOT	7.23	7.45	[b]	[b]

[a] ±0.05 eV. [b] These ionisations could not be assigned due to presence of thermolysis products.

low energy side of the broad band above 10 eV two shoulders can be seen and are assigned to e_1(COT) and a_1(Cp★). Upon comparing the ionisations in compounds Cp★MCOT for M = Ti, Zr with those for M = Sc, Y and La, we see that for the latter metals the energies decrease, reflecting the lower electronegativities of the group 3 elements and higher ionicity of the metal-to-ring bonding.

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References

1 R.R. Andrea, A. Terpstra, A. Oskam, P. Bruin and J.H. Teuben, J. Organomet. Chem., 307 (1986) 307.
2 N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press Ltd., Oxford, 1984.
3 A. Westerhof and H.J. de Liefde Meijer, J. Organomet. Chem., 116 (1976) 319.
4 J.D. Amerson, A.P. Masino and J. Takats, J. Organomet. Chem., 65 (1974) C33.
5 K.H. den Haan, J.L. de Boer, J.H. Teuben, A.L. Spek, B. Kojic-Prodic, G.R. Hays and R. Huis, Organometallics, 5 (1986) 1726.
6 K. Rossmanith and C. Auer-Welsbach, Monatsh. Chem., 96 (1965) 602.
7 J.H. Freeman and M.L. Smith, J. Inorg. Nucl. Chem., 7 (1958) 224.
8 J. Blenkers, P. Bruin and J.H. Teuben, J. Organomet. Chem., 297 (1985) 61.
9 X-Ray structure analysis has shown that the Ti and Zr analogues, Cp★MCOT, are monomeric: (a) L.B. Kool, M.D. Rausch and R.D. Rogers, J. Organomet. Chem., 297 (1985) 289; (b) R.D. Rogers and J.H. Teuben, J. Organomet. Chem., submitted.
10 W. Hinrichs, D. Melzner, M. Rekwoldt, W. Jahn and R.D. Fischer, J. Organomet. Chem., 251 (1983) 299.
11 S.H. Eggers, J. Kopf, and R.D. Fischer, Organometallics, 5 (1986) 383.
12 H.A. Zinnen, J.J. Pluth and W.J. Evans, J. Chem. Soc., Chem. Commun., (1980) 810.
13 C.W. DeKock, S.R. Ely, T.E. Hopkins and M.A. Brault, Inorg. Chem., 17 (1978) 625.
14 H. Breil and G. Wilke, Angew. Chem., 78 (1966) 942; H. Dierks and H. Dietrich, Acta Crystallogr. Sect. B, 24 (1968) 50.
15 D.W. Clark and K.D. Warren, Inorg. Chim. Acta, 24 (1977) 35.