Journal of Organometallic Chemistry, 297 (1985) 61–67
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

GROUP IV MIXED SANDWICH COMPOUNDS: SYNTHESIS OF PENTAMETHYLCYCLOPENTADIENYL-TITANIUM, -ZIRCONIUM AND -HAFNIUM CYCLOHEPTATRIENYL AND CYCLOOCTATETRAENE COMPLEXES

J. BLENKERS, P. BRUIN and J.H. TEUBEN*

Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

(Received June 27th, 1985)

Summary

The first complete series of Group IV sandwich complexes Cp*MCHT (M = Ti, Zr, Hf) ($\text{Cp}^\star = \eta^5\text{-C}_5\text{Me}_5$, $\text{CHT} = \eta^7\text{-C}_7\text{H}_7$) has been made and characterized. Cp*HfCHT is the first reported sandwich compound of hafnium. The d^1, η^8-C_8H_8(COT) complex Cp*MCOT were also synthesised similarly for M = Ti, Zr, but the complexes with M = Hf was not obtained; the failure to obtain Cp*HfCOT is ascribed to kinetic factors. Cp*ZrCOT is the first thermally-stable paramagnetic organozirconium(III) compound isolated in the solid state. The IR, ^{1}H, ^{13}C NMR, ESR and electronic absorption spectra are discussed.

Introduction

Mixed sandwich complexes $\text{CpM}(\eta^n\text{-C}_n\text{H}_n)$ (M = early transition metal, $n = 7, 8$) have attracted much interest for over a decade. Spectroscopic, chemical reactivity and theoretical studies have been performed to gain insight into the factors governing the electronic structures of these systems [1–9]. Comparative studies have been made on isotopic and isoelectronic complexes with emphasis on variation of the metal within a $3d$ or $4d$ transition metal series. Variations of properties within a group have rarely been investigated, and the series of mixed sandwich complexes are incomplete for Groups III, IV and V.

With the objective of studying the effects of variation of the metal on the electronic structure within a series of early transition metal mixed sandwich compounds we began an investigation of complexes of the type Cp*MCHT (M = Group IV metal) and Cp*MCOT (M = Group III and Group IV metal) and we present below the results for the Group IV metals Ti, Zr and Hf.

Experimental

All experiments were carried out under nitrogen using standard inert gas techniques. Solvents (pentane, ether, THF and toluene) were distilled from Na/benzophenone or a Na/K melt. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen, under the supervision of Mr. A.F. Hamminga. The IR spectra (nujol/KBr) were recorded on a Pye-Unicam SP3-300 spectrometer, UV-VIS spectra on a Perkin–Elmer-EPS-3T spectrometer, NMR spectra on a Hitachi Perkin–Elmer R-24B (^1H, 60 MHz) and a Nicolet NT200 spectrometer (^{13}C, 50.3 MHz), and the ESR spectra on a Varian E-4 EPR spectrometer. The starting materials $Cp^{\star}MCl_3$ were made by published procedures [10]. Cycloheptatriene (Aldrich), cyclooctatetraene (Aldrich) and Mg (Fluka) were obtained commercially and used without purification. The method described by Demerseman [11] was used for the synthesis of the mixed sandwich compounds $Cp^{\star}MCHT$ and $Cp^{\star}MCOT$. Detailed procedures for $Cp^{\star}TiCHT$ and $Cp^{\star}ZrCOT$ are given below. Analytical results and other relevant data are shown in Table 1.

Synthesis of Cp**TiCHT*

A solution of 2.01 g (6.9 mmol) $Cp^{\star}TiCl_3$ in 30 ml of THF was added dropwise with stirring to a mixture of 0.6 g (25 mmol) Mg turnings, 1.2 ml of cycloheptatriene, and 10 ml of THF. After 15 h stirring at room temperature the solvent was removed in vacuum and the tarry residue was suspended in pentane. The pentane was pumped off and the dry powdered product was sublimed (100–150°C, 0.1 mmHg) to give 0.71 g (2.6 mmol, 37%) of deep blue crystals.

Synthesis of Cp**ZrCHT and Cp***HfCHT*

The procedures were analogous to that used for synthesis of $Cp^{\star}TiCHT$. $Cp^{\star}HfCHT$ always contained some (up to ca. 10%) $Cp^{\star}ZrCHT$. (The latter comes from the Zr contaminants in commercial $HfCl_4$, leading to enrichment of the Zr component in the reaction).

Synthesis of Cp**ZrCOT*

A mixture of 1.73 g (5.2 mmol) of $Cp^{\star}ZrCl_3$, 0.58 ml (5.2 mmol) of cyclooctatetraene and 0.15 g (6.3 mmol) of Mg in 30 ml of THF was stirred at room temperature for 24 h. Then the solvent was stripped in vacuum and the residue extracted with pentane. The dark-brown product crystallized out from the concentrated pentane extracts. Recrystallisation from pentane gave 1.29 g (3.9 mmol, 75%) of black $Cp^{\star}ZrCOT$. The compound can also be purified by sublimation (100–150°C, 0.1 mmHg).

Synthesis of Cp**TiCOT*

This compound was prepared in the same way as $Cp^{\star}ZrCOT$. Analytically pure material was obtained by sublimation (100–150°C, 0.1 mmHg).

Attempted synthesis of Cp**HfCOT*

Reduction of $Cp^{\star}HfCl_3$ with Mg or Na/Hg in THF or toluene in the presence of cyclooctatetraene, followed by work-up as above gave no $Cp^{\star}HfCOT$. Instead a low yield of a brown diamagnetic compound identified as $Cp^{\star}Hf(H)COT$ (analysis, IR, ^1H NMR) was obtained after sublimation of the crude reaction mixture.

Results

The novel compounds Cp*MCHT (M = Ti, Zr, Hf) have been made by reduction of Cp*MCl$_3$ with Mg in THF in the presence of C$_7$H$_8$. For the cyclooctatetraene analogues Cp*MCOT this method gave acceptable yields for M = Ti, Zr. For Hf only low yields of a hydride identified as Cp*Hf(H)COT were isolated. The new complexes are air-sensitive, crystalline compounds giving excellent elemental analyses (Table 1). They were characterized by IR and UV-vis spectroscopy (Table 1) and the IR spectra are a very useful diagnostic aid. The spectra show characteristic absorptions of Cp* ligands (2720(m), 1480(m), 1425(s), 1375(s), 1025(m), 795(w) cm^{-1}) and of the carbocyclic rings η^7-C$_7$H$_7$ (ca. 3040(w), 930(s), 830(s), 740(vs), 720(vs) cm^{-1}) and η^8-C$_8$H$_8$ (ca. 3000(w), 910(m), 900(m), 760(m), 740(vs) cm^{-1}) [2,3]. Within a series the IR spectra are virtually identical.

TABLE 1

YIELDS, SPECTROSCOPIC DATA AND ELEMENTAL ANALYSES FOR Cp*MCHT AND Cp*MCOT

Compound	Yield (%)	Colour	Electronic [a] absorption spectrum	Analysis (Found (calcd.) (%)) C	H	M
Cp*TiCHT	37	blue	675(32)	74.45 (74.45)	8.15 (8.08)	17.24 (17.46)
Cp*ZrCHT	26	purple	535(160)	64.22 (64.29)	7.02 (6.98)	28.35 (28.72)
Cp*HfCHT	10	orange	476(145)	51.86 (50.43)	5.63 (5.48)	44.55 (44.09)
Cp*TiCOT	81	green	454(145), 710(120) 925(50)	75.19 (75.26)	8.07 (8.07)	16.74 (16.67)
Cp*ZrCOT	75	black	425(920), 496(sh, 685) 611(425)	65.38 (65.40)	7.03 (7.01)	27.57 (27.59)

[a] In toluene, λ_{max} nm, (ϵ) in l mol^{-1} cm^{-1}, range 340–1200 nm.

TABLE 2

^{1}H AND ^{13}C NMR DATA FOR Cp*MCHT; ESR DATA FOR Cp*MCOT

Compound	^{1}H [a]		^{13}C [b]			ESR [c]		
	Cp*	C$_7$H$_7$	Cp* *C*-CH$_3$	C-*C*H$_3$	C$_7$H$_7$ *C*-H	g_{av}	a_H	a_M
Cp*TiCHT	1.79(s,15H)	5.25(s,7H)	111.7(s)	11.6(q,126.4)	89.2(d,166.6)	–	–	
Cp*ZrCHT	1.77(s,15H)	5.08(s,7H)	113.8(s)	10.4(q,126.4)	82.8(d,165.7)	–	–	
Cp*HfCHT	1.80(s,15H)	4.95(s,7H)	112.2(s)	10.4(q,126.6)	79.4(d,161.7)	–	–	
Cp*TiCOT	–	–	–	–	–	1.9846	3.3	11.4
Cp*ZrCOT	–	–	–	–	–	1.9758	3.8	– [d]

[a] Shifts are in ppm, referenced to TMS (δ 0.00) at 60 MHz and 30°C in C$_6$D$_6$. [b] Shifts are in ppm, referenced to TMS (δ 0.00) at 50.3 MHz and 19°C in C$_6$D$_6$. Multiplicity and coupling constants ^1J(CH) in Hz between brackets. [c] Solution ($c \sim 10^{-3}$–10^{-4} M) spectra (M = Ti, pentane, −120°C; M = Zr, pentane/toluene (5/1), −140°C). g-Values calculated with DPPH (g = 2.0036) as reference. Hyperfine splitting constants, a_H and a_M, given in gauss. [d] Not observed.

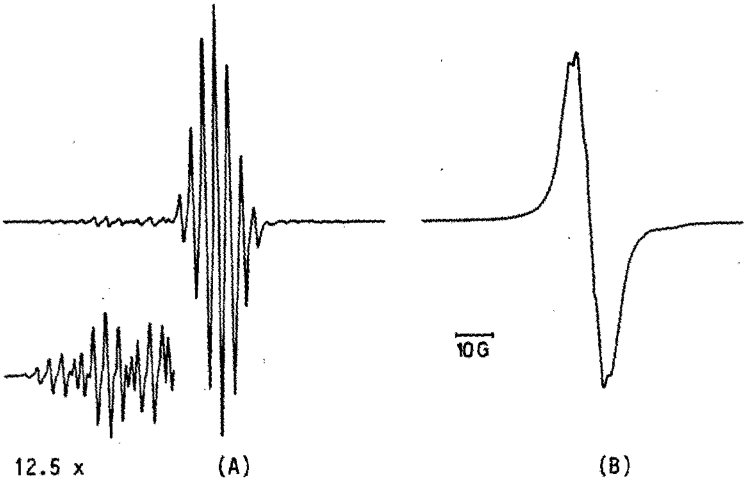

Fig. 1. ESR spectra of (A) Cp*TiCOT in pentane (−120°C) and (B) Cp*ZrCOT in pentane/toluene (−140°C).

The CHT compounds are diamagnetic and ^{1}H and ^{13}C NMR data for them are given in Table 2.

The ESR data for the paramagnetic compounds Cp*MCOT are listed in Table 2. Cp*TiCOT (−120°C) gives a well resolved signal (Fig. 1) with satellites due to interaction of the unpaired electron with ^{47}Ti ($I = 5/2$, abundance 7.75%) and ^{49}Ti ($I = 7/2$, abundance 5.51%). The spectrum of Cp*ZrCOT (−140°C) is less well resolved, but the hyperfine interaction constant, a_H, can be determined; no zirconium isotope ^{91}Zr ($I = 5/2$, abundance 11.2%) satellites are observed.

Discussion

The synthesis of the Cp*MCHT (M = Ti, Zr, Hf) complexes provides the first complete series of Group IV sandwich complexes. Moreover Cp*HfCHT is the first hafnium sandwich reported. Both NMR and IR data are completely compatible with structures with parallel planar rings, like those found for CpTiCHT [12]. The sandwich structure of Cp*TiCHT has recently been established [13].

The ^{1}H and ^{13}C NMR data (Table 2) can be compared with those of related compounds. The resonances of the pentamethylcyclopentadienyl ligand are independent of the metal. The ^{13}C shifts of both ring and methyl carbon atoms are surprisingly constant, falling within a range of 3 ppm. Such invariance of the Cp* ^{13}C resonances (ring C at 112–114 ppm, methyl-C at 10.4–11.6 ppm) with the metal has also been observed for other series of Group IV derivatives such as Cp*M(C_4H_7)(C_4H_6) [14], Cp*M(C_6H_{10})Cl [15] and Cp$_2^*$MR$_2$ [16] and suggests that on varying the metal the electronic situation in the Cp* ligand hardly changes. This could be the case if the Cp*–M bonding is essentially ionic, an assumption which is very likely on theoretical grounds [9]. The resonances due to the cycloheptatrienyl ligand have a larger spread. The proton resonances of the Ti (5.25 ppm) and Zr (5.08 ppm) compounds are at higher field than those of their unsubstituted analogues CpMCHT (Ti 5.47, Zr, 5.23 ppm) [4]. This can be explained by assuming that there is a higher negative charge on the seven-membered ring in the case of Cp*MCHT. It follows that the (negative) charge on this ligand would vary Ti < Zr < Hf, in accord with the electronegativity order of the metal atoms. The ^{13}C chemical shift order observed for Cp*MCHT (M = Ti, 89.2; M = Zr, 82.8; M = Hf, 79.4 ppm) is also consistent with the proposed charge variation on the cycloheptatrienyl ring and in this respect it parallels the observations for CpMCHT (M = Ti, Zr) [4]; however, it is not possible to draw conclusions about the charge distribution between the cyclopentadienyl and pentamethylcyclopentadienyl systems.

All three compounds show only one band in the electronic absorption spectra (visible and near IR range).The simplest interpretation is to assign this band to excitation of an electron from the HOMO to the LUMO. In terms of the qualitative MO-scheme frequently used for this type of compounds [1] it is the $1e_2$ to $3a_1$ transition. The position of the $3a_1$ orbital (metal d_{z^2}) can then be estimated relative to the $1e_2$ level; the values (in eV) are: 1.84 (M = Ti), 2.32 (M = Zr) and 2.60 (M = Hf). According to Zeinstra et al. [9] the $1e_2$ level for CpTiCHT has mainly ligand (CHT) character. With Cp* in place of Cp inductive effects will raise the metal orbital energy leading to an increase of ligand character of the $1e_2$ orbitals. The observed electronic absorption spectra reflect the decrease in electronegativity of the metal going from Ti to Zr to Hf.

Previously Group IV cyclopentadienylcyclooctatetraene complexes were limited to titanium [5,6]. Cp*ZrCOT, formally a Zr^{III}, d^1, complex is one of the few known well characterized thermally stable paramagnetic organozirconium(III) compounds. There is considerable interest in paramagnetic Zr^{III} compounds, but most information has been obtained from solution ESR studies on complexes prepared in situ, the identities of which are hard to establish unequivocally (cf. ref. 17–19).

The complexes Cp*MCOT (M = Ti, Zr) have virtually identical IR spectra, showing the characteristic Cp* and COT (see Results) absorptions which indicate a structure with parallel planar ligands sandwiching the metal atom. The sandwich structure for Cp*TiCOT was established recently [13]. The ESR spectra in toluene/pentane (Fig. 1, Table 2) of the compounds at room temperature are rather wide singlets (Ti, 9 G; Zr, 27 G) with g-values close to that calculated for a free electron; only in the case of Ti is there detectable hyperfine splitting. For Cp*TiCOT cooling to −120°C produces a well resolved signal displaying 9 lines due to superhyperfine splitting with eight equivalent protons of the cyclooctatetraene ligand, and also satellites due to interaction of the unpaired electron with ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$). The isotropic hyperfine constant, a_{Ti} 11.4 G, is slightly smaller than for CpTiCOT [5]. On the other hand the proton superhyperfine interaction, a_H, is 3.3 G, the value reported for CpTiCOT. In our complexes the a_H value can be attributed unequivocally to interaction with the eight protons of the cyclooctatetraene ligand, since the methyl protons of the cyclopentadienyl group show no observable interaction; the results of calculations by Samuel et al. [5] are thus confirmed.

The ESR spectrum of Cp*ZrCOT also shows proton superhyperfine splitting on cooling, but even at −140°C the signal is not completely resolved. The a_H value is 3.8 G, somewhat larger than that for the titanium compound. Since zirconium hyperfine splitting is not observed, comparison with other zirconium ESR data is not possible.

The electronic absorption spectra ($\lambda > 400$ nm, Table 1) of the COT compounds are more complicated than those of the CHT complexes due to low energy excitations from the $1a_1$ (metal d_{z^2}) level to nearby antibonding orbitals. The spectra show three separate absorptions, which are at higher energy for the Zr than for the Ti complex. Samuel et al. have assigned the spectrum of CpTiCOT [5] and on the basis of their interpretation we assign the bands at 925 nm (611 for Zr) and 710 nm (496 for Zr) to transitions from $1a_1$ to $3e_1$ for the first band, and from the bonding, cyclooctatetraene based, $1e_2$ to $3a_1$, the essentially pure metal d_{z^2} orbital for the latter. The band at 454 nm (425 for Zr) is not present for CpTiCOT, and the nature of this excitation is unclear. It could be related primarily to the Cp* ligand, and possibly due to transition from the Cp* $2e_1$ orbital to $3a_1$. This orbital will be raised [1,10] in energy with respect to the Cp $2e_1$ in CpTiCOT, and the transition normally seen in the UV may be shifted into the visible region. A better interpretation of the electronic absorption spectrum may be possible after UPS studies have given a better guide to the actual order of the molecular ortibals.

The fact that Cp*HfCOT could not be made by the method which works excellently for Ti and Zr does not imply that the compound cannot exist and it is possible that it could be made by other routes. Reaction of Cp*$HfCl_3$ with strong reducing agents such as Na/Hg or Mg in the presence of cyclooctatetraene does take place easily; ESR monitoring gave no evidence for the presence of even small amounts of Cp*HfCOT at any stage of the reaction. One of the products present at an early stage is the diamagnetic Cp*Hf(COT)Cl (identified by comparison of NMR with an authentic sample [20]) and this shows that transfer of a COT ligand to Hf and removal of the chlorine atoms is not the problem. The reaction is almost intractable from this stage on. Since reaction of Cp*Hf(COT)Cl with Mg or Na/Hg also takes place readily, transfer of an electron also seems to present no problem. In our opinion, after the initial reduction step of Cp*Hf(COT)Cl i.e. after formation of $[\text{Cp*Hf(COT)Cl}]^-$ the system enters a stage of high kinetic lability leading to a variety of products including the hydride Cp*Hf(COT)H; such spectacular and apparently kinetic differences between Zr and Hf chemistry are well known to workers in early transition metal chemistry. Reverse behaviour has been observed for the synthesis of Cp*M(diene)Cl from Cp*MCl_3, diene and Mg [21]; in this case the Hf system is much cleaner, and only very low yields are obtained for Zr.

Acknowledgements

We thank Drs. G. Bekendam and M. Kroes for helpful discussions and able experimental assistance.

References

1 J.C. Green, Structure and Bonding, 43 (1981) 37.
2 C.J. Groenenboom, H.J. de Liefde Meijer, F. Jellinek and A. Oskam, J. Organomet. Chem., 97 (1975) 73.
3 C.J. Groenenboom, G. Sawatzky, H.J. de Liefde Meijer and F. Jellinek, J. Organometal. Chem., 76 (1974) C4.
4 C.J. Groenenboom and F. Jellinek, J. Organometal. Chem., 80 (1974) 229.
5 E. Samuel, G. Labauze and D. Vivien, J. Chem. Soc. Dalton, (1979) 956.
6 M. Vliek, C.J. Groenenboom, H.J. de Liefde Meijer and F. Jellinek, J. Organomet. Chem., 97 (1975) 67.

7 D.W. Clack, and K. Warren, Theoret. Chim. Acta, 46 (1977) 313.
8 D.W. Clack, and K. Warren, Inorg. Chim. Acta, 24 (1977) 35.
9 J.D. Zeinstra, and W.C. Nieuwpoort, Inorg. Chim. Acta, 30 (1978) 103.
10 A. Terpstra, J.N. Louwen, A. Oskam and J.H. Teuben, J. Organomet. Chem., 260 (1984) 207.
11 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 101 (1975) C24.
12 J.D. Zeinstra and J.L. de Boer, J. Organomet. Chem., 54 (1973) 207.
13 L.B. Kool, M.D. Rausch and R.B. Rogers, in press.
14 J. Blenkers, H.J. de Liefde Meijer and J.H. Teuben, J. Organomet. Chem., 218 (1981) 383.
15 B. Hessen, J. Blenkers and J.H. Teuben, to be published.
16 (a) J.E. Bercaw, E. Rosenberg and J.D. Roberts, J. Am. Chem. Soc., 96 (1974) 612; (b) D.M. Duggan, Inorg. Chem., 20 (1981) 1164.
17 A. Hudson, M.F. Lappert and R. Pickon, J. Chem. Soc. Chem. Commun., (1983) 374.
18 E. Samuel, Inorg. Chem., 22 (1983) 2967.
19 J.M. Atkinson, P.B. Brindley, A.G. Davies, J.A.A. Hawari, J. Organomet. Chem., 264 (1984) 253.
20 J.L. Spencer, personal communication.
21 J. Blenkers, Thesis, Groningen University, 1982.