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HALO(ALKOXO) AND MONOCYCLOPENTADIENYL(HALO)ALKOXO DERIVATIVES OF TITANIUM, ZIRCONIUM AND HAFNIUM *

A. GÓMEZ-CARRERA, M. MENA, P. ROYO and R. SERRANO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Alcalá de Henares, Madrid (Spain)

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Summary

The chlorides MCl_4 (M = Ti, Zr, Hf) react with the diols 4,4′-$Me_2C(C_6H_4OH)_2$ and 1,2-$(OH)_2Ar$, Ar = C_6H_4, 4-MeC_6H_3, or 4-$Bu^tC_6H_3$ to give the halogenoalkoxo derivatives $MCl_2(O_2Ar)$. For M = Ti these react with bases L (L = 2,2′-bipy, THF, Et_2O) to give the corresponding adducts $TiCl_2(O_2Ar)L$, and with TlCp to give the monocyclopentadienyl complexes $CpTiCl(O_2Ar)$. The best way of preparing the analogous zirconium derivatives is through the reaction of $CpZrCl_3 \cdot DME$ with $(HO)_2Ar$.

Introduction

Halogeno-, alkoxo- and organo-titanium compounds are known as catalysts for the polymerization of olefins [1], and organozirconium derivatives have recently been shown to have a high activity in this reaction [2]. We describe the preparation of several halogeno(alkoxo) and cyclopentadienyl halogeno(alkoxo) derivatives of the Group 4 elements with 4,4′-isopropylidenediphenol and *o*-catechols.

Results and discussion

The reaction of metal halides with alcohols is one of the most useful methods of obtaining metal halo-alkoxides [3,4]. We have used the chelating diols mentioned below in reactions with MCl_4 (M = Ti, Zr, Hf) to prepare the dichlorodialkoxides

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* This paper is dedicated to Prof. R. Usón on the occasion of his 60th birthday

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I–III according to eq. 1:

$$\mathrm{MCl_4 + (HO)_2Ar \xrightarrow{toluene} MCl_2(O_2Ar) + 2HCl} \qquad (1)$$

$\mathrm{(HO)_2Ar} =$ $\mathrm{4,4'\text{-}Me_2C(C_6H_4OH)_2}$ (a) Ia: M = Ti;
$\mathrm{1,2\text{-}(HO)_2C_6H_4}$ (b) Ib: M = Ti;
IIb: M = Zr;
IIIb: M = Hf
$\mathrm{1,2\text{-}(HO)_2\text{-}4\text{-}Me\text{-}C_6H_3}$ (c) Ic: M = Ti;
$\mathrm{1,2\text{-}(HO)_2\text{-}4\text{-}Bu^t\text{-}C_6H_3}$ (d) Id: M = Ti;

The products are only soluble in donor solvents with the exception of Id, whose solubility in benzene allows cryoscopic measurement of its molecular weight; the value is 853 (calcd. 283) indicating that it exists as a trimer. Donor solvents such as methanol, cleave the bridges in the oligomeric structure as is the case for other halogeno(alkoxo)derivatives [3,4]. In donor solvents, solvated monomeric species are present.

Complexes Ia–d react rapidly with ethers or 2,2′-bipyridine to give the corresponding adducts IV, according to eq. 2:

$$\mathrm{TiCl_2(O_2Ar)} + n\mathrm{L} \longrightarrow \mathrm{TiCl_2(O_2Ar)L}_n \qquad (2)$$

IVa, L = bipy; $n = 1$ IVc, L = bipy; $n = 1$
IVa′, L = THF; $n = 2$ IVc′, L = $\mathrm{Et_2O}$; $n = 1$
IVb, L = bipy; $n = 1$ IVd, L = bipy; $n = 1$

The adducts IV are also soluble in donor solvents, but are only slightly soluble in other solvents, the solubility increasing in the order $\mathrm{(C_6H_4)_2CMe_2 < C_6H_4 < C_6H_3Me < C_6H_3Bu^t}$. A molecular weight determination in dichloromethane for IVc′ gave a value (700) close to that for a dimer (the monomer requires 315).

Complexes Ia–d react readily with $\mathrm{Tl(C_5H_5)}$ to give monocyclopentadienyl derivatives V, according to eq. 3:

$$\mathrm{TiCl_2(O_2Ar) + Tl(C_5H_5) \xrightarrow{DME} \underset{(Va\text{–}d)}{(\eta^5\text{-}C_5H_5)TiCl(O_2Ar)} + TlCl} \qquad (3)$$

The presence of the cyclopentadienyl ring increases the solubility probably because these compounds are monomeric in benzene, as has been shown to be the case for Vb, prepared by another route [5]. An exception to this behaviour is the much less soluble complex Va derived 4,4′-isopropylidenediphenol, which cannot act as a chelate to give polymeric species containing bridging dialkoxo groups between different titanium atoms.

This method is not satisfactory for reaction of the zirconium complex IIb, with the very poorly soluble $\mathrm{Tl(C_5H_5)}$. In this case the reaction shown by eq. 4 provides a more convenient route to the cyclopentadienyl-alkoxo complexes VI

$$\mathrm{(\eta^5\text{-}C_5H_5)ZrCl_3 \cdot DME + (HO)_2Ar \xrightarrow{toluene} \underset{(VIb\text{–}d)}{(\eta^5\text{-}C_5H_5)ZrCl(O_2Ar)}} + \mathrm{2HCl + DME} \qquad (4)$$

In this reaction DME is displaced to give white solids which are completely insoluble in all solvents, indicating that they are probably polymeric as a consequence of the higher acid character of the metal centre.

IR spectra

Complicated spectra of limited utility for structural assignment are given by all the alkoxo complexes. The most important absorptions which can be reasonably assigned are shown in Table 1. The stretching ν(Ti–Cl) vibrations appear between 400 and 450 cm^{-1} [4,6], and those for ν(Zr–Cl) are at lower wavenumbers. The ν(M–O) absorption bands appear in the region 600–650 cm^{-1} [3].

The ν(CO) and ν(C=C) vibrations of the alcohols are shifted on coordination providing good evidence for the formation of the alkoxo derivative [4,7]. The formation of the adducts IV results in additional absorption bands, some of which can be used to confirm the coordination of the ligand, as shown in Table 1. Although we cannot make a definite assignment of all the bands, the IR behaviour observed suggests that the oligomeric structures are formed through bridging alkoxo groups, since the ν(M–Cl) vibrations appear in the region associated with terminal metal–chlorine bonds.

NMR spectra

The low solubilities of all the reported complexes prevents their study in non-polar solvents. The data in MeOH-d_4 only gives information about the monomeric solvated species formed by cleavage of the possible alkoxo-bridges, and confirms the presence of the various components.

All the ^{1}H NMR spectra show a complex signal between δ 7.13 and 6.52 ppm due to the phenyl protons of the alkoxo ligand, a singlet between δ 1.52–1.55 ppm for methyl groups of b, and one at δ 1.02–1.23 ppm for t-butyl groups of d. The cyclopentadienyl protons give a singlet at δ 6.20–6.55 ppm for complexes V–VI. Complex multiplets are observed at δ 7.7–9.0 ppm for 2,2′-bipyridine, and characteristic resonances due to Et_2O and THF are observed for IVc and IVa′, respectively.

Experimental

All experiments were performed under N_2 using Schlenk-type glassware. Solvents were dried by standard methods and distilled under N_2. Commercial $TiCl_4$ was freshly distilled over Cu and the diols were purified by sublimation. $CpZrCl_3 \cdot$ DME was prepared by a published procedure [8].

C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyzer, and the results are listed in Table 2. IR spectra between 4000 and 200 cm^{-1} were recorded as Nujol mulls on a 505 Perkin–Elmer spectrophotometer. ^{1}H NMR were recorded on a Varian FT-80A instrument. Molecular weights were determined with a Knauer pressure osmometer.

$TiCl_2(O_2Ar)$ (Ia–d)

A solution of 45.5 mmol of the corresponding diol (a–d) in 70 ml of toluene or carbon tetrachloride was added dropwise to a stirred solution of 2.18 g (45.5 mmol) of $TiCl_4$ in 20 ml of the same solvent at −10°C; HCl was evolved. The resulting

TABLE 1

SELECTED IR ABSORPTIONS FOR ALKOXO COMPLEXES (cm^{-1})

Complex	ν(M–Cl)	ν(M–O)	ν(C–O)	ν(C=C)	Internal ligand
Ia	410s, 450m	620m, 640m	1235s	1585m,br	
Ib	420s, 450m, 465s	630s, 655s	1235m	1565w, 1590m	
Ic	460s, 440m, 430s	615m	1250m	1595m	
Id	490m, 470m, 460s, 435m		1240m, 1220m	1590m, 1585sh	
IIb	370s,br, 300m,sh	615s	1250vs,br	1595m	
IIIb	360s,br, 340s,br	615s, 630sh	1255vs,br	1595m	
IVa	355s,br		1250s,br		1030s (ν(CN))
IVa′	370s, 345m		1250vs,br	1600m, 1610w	8755 (ν_s(COC)) 1050m (ν_{as}(CO))
IVb	430s, 455m	660vs	1230s		1030s (ν(CN))
IVc	430m, 455w	660s			1030s (ν(CN))
IVc′	430s, 465w	680s	1260s, 1275sh	1595m	
IVd	430m, 450w		1210vs		1030m (ν(CN))
Va		620w, 645w	1245s,br	1595w, 1610w	
Vb	405sh, 420m, 440m	630s, 650s	1250s	1570m	
Vc	400m, 420m, 440m	655s	1260s, 1275sh	1580w, 1595m	
Vd	405w, 430m,br	660s	1260vs	1575w, 1595m	
VIb	370w,br	620s	1255s	1590m	
VIc	350sv,br	640m	1255s, 1275sh	1600w, 1580w	
VId	350w, br	650sh, 640m	1275sh, 1260s, 1250sh	1585m, 1600sh	

TABLE 2

ANALYTICAL DATA FOR ALKOXO COMPLEXES

Complex	Analysis (Found (calcd.) (%))		
	C	H	N
$TiCl_2(OC_6H_4)_2CMe_2$ (Ia)	52.22	4.71	
	(52.21)	(4.09)	
$TiCl_2(O_2C_6H_3Me)$ (Ic)	34.68	2.69	
	(34.88)	(2.51)	
$TiCl_2(O_2C_6H_3Bu^t)$ (Id)	42.21	4.74	
	(42.42)	(4.27)	
$ZrCl_2(O_2C_6H_4)$ (IIb)	25.47	2.22	
	(26.64)	(1.49)	
$HfCl_2(O_2C_6H_4)$ (IIIb)	20.03	2.24	
	(20.16)	(1.13)	
$TiCl_2(OC_6H_4)_2CMe_2$(bipy) (IVa)	58.71	5.10	5.27
	(59.90)	(4.40)	(5.59)
$TiCl_2(OC_6H_4)_2CMe_2$ (THF)$_2$ (IVa′)	56.47	7.08	
	(56.46)	(6.18)	
$TiCl_2(O_2C_6H_4)$(bipy) (IVb)	50.81	3.67	6.75
	(50.1)	(3.16)	(7.31)
$TiCl_2(O_2C_6H_3Me)$(bipy) (IVc)	52.01	3.95	7.15
	(51.41)	(3.55)	(7.06)
$TiCl_2(O_2C_6H_3Me)(OEt_2)$ (IVc′)	40.69	5.45	
	(41.93)	(5.12)	
$TiCl_2(O_2C_6H_3Bu^t)$(bipy) (IVd)	53.86	5.12	5.65
	(54.70)	(4.59)	(6.38)
$(\eta^5\text{-}C_5H_5)TiCl(OC_6H_4)_2CMe_2$ (Va)	63.09	5.27	
	(64.11)	(5.11)	
$(\eta^5\text{-}C_5H_5)TiCl(O_2C_6H_3Me)$ (Vc)	52.33	4.00	
	(53.27)	(4.10)	
$(\eta^5\text{-}C_5H_5)TiCl(O_2C_6H_3Bu^t)$ (Vd)	56.80	5.01	
	(57.62)	(5.48)	
$(\eta^5\text{-}C_5H_5)ZrCl(O_2C_6H_4)$ (VIb)	43.04	3.96	
	(44.06)	(3.0)	
$(\eta^5\text{-}C_5H_5)ZrCl(O_2C_6H_3Me)$ (VIc)	46.43	4.56	
	(45.92)	(3.53)	
$(\eta^5\text{-}C_5H_5)ZrCl(O_2C_6H_3Bu^t)$ (VId)	50.60	5.07	
	(50.61)	(4.81)	

solution was warmed to room temperature then refluxed for a further 4 h. The solution was cooled to room temperature at which crystals of Ia, (dark-red) Ib (black) and (Ic) and Id (brown) separated. The products were filtered off, washed with toluene and hexane, and vacuum-dried for several hours.

The t-butyl derivative Id is more soluble, but a dark-brown microcrystalline powder was obtained, after concentration of the original solution and addition of hexane.

All the yields were in the range 90–95%.

^1H NMR data: Ia (CD_3OD); δ 7.02 (d, J 9Hz, 4H, C_6H_4), 6.65 (d, J 9 Hz, 4H, C_6H_4) and 1.55 (s, 6H, CH_3); Ib (CD_3OD), δ 6.7 (s, br); Ic (CD_3OD) δ 6.52 (m, 3H, C_6H_3) and 2.1 (s, 3H, CH_3); Id (CD_3OD) δ 6.78, 6.68 (m, 3H, C_6H_3) and 1.23 (s, 9H, $C(CH_3)_3$).

$MCl_2(O_2Ar)$ ($M = Zr$, Hf (IIb, IIIb))

A solution of equimolar amounts (around 10 mmol) of the Zr or Hf tetrachlorides and pyrocatechol in 50 ml of toluene was refluxed. After 4 h HCl evolution ceased, the suspension was cooled to room temperature and filtered. The cream-coloured solid obtained was washed with toluene and dried in vacuum for several hours. Yield ca. 70%.

^1H NMR data: IIb (CD_3OD) δ 6.85 (m); IIIb (CD_3OD) δ 6.89 (m)

$TiCl_2(O_2Ar)L_n$ (IVa′, IVc′)

About 1 g of the corresponding dihalogenotitanium catecholate (Ia or Ic) was dissolved in 100 ml of warm THF (for Ia) or diethyl ether (for Ic), and the solution was concentrated, then cooled. Red-orange IVa′ or black IVc′ crystallized out, and was filtered off and vacuum dried. Yield 97–98%.

^1H NMR data: IVa′ (CD_3OD) δ 7.02 (d, J 9Hz, 4H, C_6H_4), 6.65 (d, J 9 Hz, 4H, C_6H_4), 3.68 (t, J 6 Hz, 8H, $O(C\mathit{H}_2)_2(CH_2)_2$), 1.8 (q, J 3 Hz, 8H, $O(CH_2)_2(C\mathit{H}_2)_2$) and 1.52 (s, 6H, CH_3). Ivc′ (CD_3OD) δ 6.52 (m, 3H, C_6H_3), 3.45 (q, J 6.7 Hz, 4H, $O(C\mathit{H}_2)_2(CH_3)_2$), 2.17 (s, 3H, CH_3) and 1.13 (t, J 7.5 Hz, 6H, $O(CH_2)_2(C\mathit{H}_3)_2$).

$TiCl_2(O_2Ar)$bipy (IVa, IVb, IVc, IVd)

5 mmol of 2,2′-bipyridine was added to a solution of Ia, Ib, Ic or Id (5 mmol) in 60–80 ml of methanol (Ia), THF (Ib, c), or toluene (Id). The solutions were stirred for 30–60 min then concentrated and hexane was added. The solutions were cooled, the red-brown adducts crystallized out in nearly quantitative yields.

^1H NMR data: IVa (DMSO-d_6) δ 8.8–7.8 (m, 8H, $N_2C_{10}H_8$) 6.98 (d, J 9 Hz, 4H, C_6H_4), 6.67 (d, J 9 Hz, 4H, C_6H_4) and 1.50 (s, 6H, CH_3); IVb (CD_3OD) δ 9.0–7.7 (m, 8H, $N_2C_{10}H_8$) and 6.66 (s, br, 4H, C_6H_4) and 2.12 (s, 3H, CH_3); IVc (CD_3OD) 9.0–7.7 (m, 8H, $N_2C_{10}H_8$), 6.52 (m, 3H, C_6H_3) and 2.12 (s, 3H, CH_3) IVd (CD_3OD) 8.9–7.7 (m, 8H, $N_2C_{10}H_8$) 6.78–6.65 (m, 3H, C_6H_3) and 1.20 (s, 9H, $C(CH_3)_3$).

$CpTiCl(O_2Ar)$ (Va–d)

TlCp (0.58 g (2.15 mmol)) was added to a solution of 2.15 mmol of Ia–d in 50 ml DME. The mixture was stirred overnight, then TlCl precipitate was filtered off, and the solution evaporated to dryness. The residue was recrystallized from THF/hexane to give Va–d. The yields were in the range 70–80%.

^1H NMR data: Va (CD_3OD) δ 7.00 (d, J 9 Hz, 4H, C_6H_4), 6.66 (d, J 9 Hz, 4H, C_6H_4), 6.55 (s, 5H, Cp); Vb (CD_2Cl_2) δ 7.02 (m, 4H, C_6H_4) and 6.53 (s, 5H, Cp); Vc (CD_3OD) δ 6.60 (s, br, C_6H_3) 6.55 (s, Cp) and 2.17 (s, Me) (integration is not possible due to overlapping of the signals); Vd (CD_2Cl_2) δ 7.13 (m, 3H, C_6H_3), 6.52 (s, 5H, Cp) and 1.06 (s, 9H, $C(CH_3)_3$).

$CpZr(O_2Ar)Cl$ (VIb–d)

A suspension of 0.68 g (2 mmol) of IIb and 2 mmol of the appropriate catechol b–d in 75 ml of toluene was refluxed for 4 h then cooled to room temperature. The solid was filtered off, washed with toluene and hexane, and vacuum dried. Yield 75–80%.

^1H NMR data: VIb (DMSO-d_6) δ 6.40 (m, 4H, C_6H_4) and 6.20 (s, 5H, Cp); VId (CD_3OD) δ 6.55 (s, br, 3H, C_6H_3), 6.47 (s, 5H, Cp) and 2.2 (s, 3H, CH_3); VId ($CDCl_3$) δ 7.00–6.59 (m, 3H, C_6H_3), 6.47 (s, 5H, Cp) and 1.02 (s, 9H, $C(CH_3)_3$).

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