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Preliminary communication

STABILISATION OF TRANSITION METALS IN A LOW COORDINATIVE ENVIRONMENT USING THE BIS(TRIMETHYLSILYL)METHYL LIGAND; A MONOMERIC Cr^{III} ALKYL, $Cr[CH(SiMe_3)_2]_3$, AND RELATED COMPLEXES

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Summary

$(Me_3Si)_2CHLi(RLi)$ and $CrCl_3$ in Et_2O at 0° yield bright-green, air-sensitive, crystalline monomeric $(C_6H_6)CrR_3$, which has a magnetic moment of 3.7 B.M., shows *g* values (ESR) at ca. 2 and ca. 4, and is diamagnetic red $CrR_3 \cdot NO$ with NO or $Ph_3C\cdot$ with Ph_3CCl; the following stable alkyls are reported; $MR_3 \cdot 2THF$ (M = Sc or Y), $M'R_3$ (M' = Y, Ti, or V), $ClM''R_3$ (M'' = Zr or Hf), and Cp_2TiR.

Thermally-stable binary (homoleptic) alkyls of the early transition metals have recently been reported, using $Me_3SiCH_2^-$ (R'^-) as ligand [1]. These are tetrahedral or distorted tetrahedral d^0 to d^2 complexes of formula MR'_4 (M = Ti, Zr, Hf, V, or Cr) or $(MR'_3)_2$ (M = Mo or W). For Group IIIA metals, stability was achieved only by incorporation into the metal coordination sphere of extra ligands, viz., $MR'_3 \cdot 2THF$ (M = Sc or Y) [2].

We now show that, using the more bulky $(Me_3Si)_2CH^-$ (R^-) [3] presumed trigonal or distorted trigonal d^0 to d^3 complexes MR_3 (M = Y, Ti, V, or Cr) become accessible. Scandium and yttrium compounds have also been obtained as the adducts, $MR_3 \cdot 2THF$, and Zr and Hf species as $ClMR_3$ (from $ZrCl_4$ or $HfCl_4$ and an excess of LiR). Whereas Cp_2TiCl_2 and LiR' gave $Cp_2TiR'_2$ [4], LiR gave $(Cp_2TiCl)_2$ (with 1 mol of LiR) or Cp_2TiR (with 2 mol of LiR).

It is evident that for bulky ligands of the type R and R', the metal coordination number is affected primarily by the nature of the ligand rather than the electronic configuration of the metal. Similarly, whereas the 1-norbornyl ligand (R'') has yielded four-coordinate species MR''_4 (M = Ti, Zr, Hf, V, Cr, Mn, Fe, or Co), the related but more crowded 2,2,3-trimethyl-1-norbornyl (R''') is found in CrR'''_3 [5]. Three-coordination is also a feature of $(Me_3Si)_2N^-$ complexes [6], and of the stable radical SnR_3 [7].

A typical synthetic procedure involved addition of bis(trimethylsilyl)methyllithium, LiR, in diethyl ether to $CrCl_3$ at 0° to give bright-green, air-sensitive crystals of CrR_3. This gave satisfactory microanalytical results. It is a monomer in C_6H_6 (cryoscopy) and has $\nu(CrC_3)$ at 403 and 449 cm^{-1}. The ESR spectrum (frozen toluene solution or solid) showed g values at ca. 2 and ca. 4, appropriate [8] for Cr^{III} in a trigonal environment. The magnetic moment (Gouy) is 3.7 B.M. at 20°, and showed (by NMR [9] insignificant temperature dependence over the range +30 to −60°. CrR_3 did not sublime in vacuo; decomposition took place at ca. 80° with formation of $(Me_3Si)_2CH_2$. The chromium atom in CrR_3 appears to be highly shielded by the bulky ligands, because there was no reaction with severally $(Me_3Si)_2NH$, C_5H_5N, or CO_2. However, with 1 equivalent of NO in hexane, a diamagnetic deep red solution was formed, presumed to be $CrR_3 \cdot NO$ [$\nu(NO)$ 1672 cm^{-1}] (cf. [10], the behaviour of $Cr[N(SiMe_3)_2]_3$). Trityl chloride afforded $Ph_3C\cdot$ (ESR) and a purple solution believed to contain $ClCrR_3$. Hydrolysis or reaction with glacial HOAc afforded $(Me_3Si)_2CH_2$ (100%) and $Cr(OH)_3$ or $Cr(OAc)_3$. Some data for the other compounds are in Table 1.

TABLE 1

TRIS[BIS(DIMETHYLSILYL)METHYL]METAL COMPLEXES

Alkyl precursor [a] (solvent)	Product (appearance) [b]	$\nu(MC_3)$ (cm^{-1})	τ values (ppm) [$(CH_3)_3Si$, CH]
$ScCl_3$ (THF/Et_2O)	$ScR_3 \cdot 2THF$ (white)	415	9.31; 10.16
YCl_3 ($PhCH_3$/Et_2O)	YR_3 (white)	402	9.60; 10.53 [e]
YCl_3 (THF/Et_2O)	$YR_3 \cdot 2THF$ (white)	—	9.36; 10.43 [e]
$TiCl_3 \cdot 2Me_3N$ (Et_2O)	TiR_3 (green-blue)	432, 403	[f]
$VCl_3 \cdot 2Me_3N$ (Et_2O)	VR_3 (green-blue)	460, 400	
$CrCl_3$ (Et_2O)	CrR_3 (bright green)	449, 403	[g]
Cp_2TiCl_2 (Et_2O)	Cp_2TiR (green-brown)	463	[h]
$ZrCl_4$ (Et_2O)	$ClZrR_3$ (white)	443, 415 [c]	9.50; 8.80
$HfCl_4$ (Et_2O)	$ClHfR_3$ (white)	424, 414 [d]	9.51; 9.51

[a] + RLi. [b] All products crystalline. [c] $\nu(ZrCl)$ 368 cm^{-1}. [d] $\nu(HfCl)$ 350 cm^{-1}. [e] $^2J(YH)$ 2.5 Hz. [f] g(ESR) 1.968. [g] g(ESR) 2.0 and 3.9, μ_{eff} 3.7 B.M. [h] g(ESR) 1.960.

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