Lower Valent Dialkylamides of Titanium and Vanadium

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Summary Novel dialkylamides of Ti^{III} which have alkylamido-bridged structures and exhibit fluxional behaviour and strong metal–metal interactions, together with the Ti^{II} derivatives obtained by disproportionation $2TiX(NR_2)_2 \longrightarrow TiX_2 + Ti(NR_2)_4$, afford valuable starting materials for the synthesis of bivalent and tervalent titanium complexes.

METAL DIALKYLAMIDES LMR_2 (where L represents the sum of all ligands other than one NR_2 group attached to the metal M) are interesting *inter alia* because (i) they are versatile intermediates in inorganic and organic syntheses,[1] (ii) the ligand(s) NR_2 may stabilise unusual co-ordination numbers (*e.g.* 3-co-ordinate Fe^{III} and Cr^{III}),[2,3] and (iii) their attempted preparation from $MCl_n/n LiNR_2$ may afford unusual[4] or rearranged[5] products.

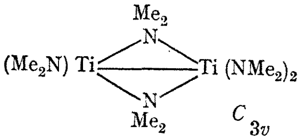
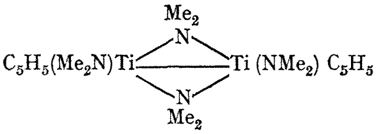
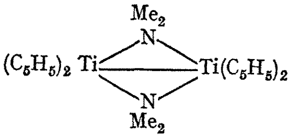
We now report on the novel Ti^{III} and, more briefly, the Ti^{II}, V^{IV}, and V^{III} dialkylamides. Some data on Ti^{III} amides (all analysed satisfactorily) are summarised in the Table. They may be used as reagents for obtaining other d^1-complexes; for example, $(\pi\text{-}C_5H_5)_2TiNMe_2$ reacts with several metal hydrides to give $(\pi\text{-}C_5H_5)_2Ti$–metal complexes.[6]

The reaction $LMCl_n/n LiNR_2$ gave $Ti(NR_2)_3$ (R = Me or Et, but *not* Pr^i or Bu^s) and $(\pi\text{-}C_5H_5)_2TiNMe_2$. Only one NMe_2 group was displaced from $Ti(NMe_2)_3$ by reaction with the protic compound HA, to yield $ATi(NMe_2)_2$ [A = $\pi\text{-}C_5H_5$, NEt_2, NPr^i_2, or $N(SiMe_3)_2$]; the significance of steric effects is further demonstrated by the failure of Pr^i_2NH to react with $Ti(NEt_2)_3$. Alcohols (MeOH or EtOH) readily displaced all NMe_2 groups from $Ti(NMe_2)_3$ (acacH→Ti $acac_3$), $\pi\text{-}C_5H_5Ti(NMe_2)_2$, $(\pi\text{-}C_5H_5)_2TiNMe_2$ (the C_5H_5 groups are also suceptible to displacement by ROH), or $V(NMe_2)_4$ to give the corresponding alkoxides. Carbon disulphide and $Ti(NEt_2)_3$, failed to yield the corresponding trisdithiocarbamate and gave instead $Ti(S_2CNEt_2)_4$ and $Ti(S_2CNEt_2)_2$. Disproportionation was also observed upon attempted distillation of $XTi(NMe_2)_2$; volatile[7] $Ti(NMe_2)_4$ and the black-green pyrophoric Ti^{II} compounds $(TiX_2)_n$ (X = NMe_2, NEt_2, NPr^i_2, or Cl) were obtained. Similarly, distillation of the products obtained by treating VCl_3 with $LiNR_2$ (3 mol., R = Me or Et) afforded the volatile[8] $V(NR_2)_4$.

In view of the current interest in Ti^{II} complexes,[9] the synthetic possibilities of (i) the volatility-controlled disproportionation $2TiL(NR_2)_2 \rightarrow TiL_2 + Ti(NR_2)_4$; and (ii) the $Ti(NR_2)_2$ compounds containing reactive titanium–nitrogen bonds are significant and are being explored.

It is interesting that complete replacement of all the

TABLE

Compound[a]	E.s.r. (g values)[b]	^{1}H n.m.r. (τ)[f]	Probable structure
$[(Me_2N)_3Ti]_2$	$g_{1,2,3} = 1{\cdot}98_9$[c]	6·79[g]	
$(Me_2N)_3,Ti,OEt_2$	$g_{1,2} = 1{\cdot}98_3$[d] $g_3 = 1{\cdot}91_4$	6·78[h]	
$[\pi\text{-}C_5H_5Ti(NMe_2)_2]_2$		6·84, 3·97	
$[(\pi\text{-}C_5H_5)_2TiNMe_2]_2$	$g_1 = 1{\cdot}99_9$[e] $g_2 = 1{\cdot}98_3$ $g_3 = 1{\cdot}95_9$	6·79, 4·17	

[a] Molecular weights were determined cryoscopically in C_6H_6; the compounds, except the brown powder $[(C_5H_5)TiNMe_2]_2$, are red-brown viscous liquids at ambient temperatures.

[b] Approx. 10^{-2}M-solutions; we thank Dr. A. Hudson and Mr. M. J. Kennedy for these data; the compounds are virtually diamagnetic.

[c] Benzene solution, room temperature and −196°.

[d] Ether solution, −196°.

[e] Benzene solution, −196°.

[f] 60 MHz., 37°; all peaks are singlets; benzene or C_6D_6 solution.

[g] At −80° in pentane peaks due to terminal and bridging NMe_2 are resolved, 2·2 Hz. apart.

[h] Also broad multiplets (OEt_2) centred at τ 6·7 and τ 8·2.

chloride ligands of MCl_3 by NPr^i_2 (from $LiNPr^i_2$) was not achieved for M = Ti or V, in contrast to M = Cr;[3] this may be related to the relative gain ($d^3 \gg d^1$ or d^2) in C.F.S.E. in forming trigonal $M(NPr^i_2)_3$ from tetrahedral $[ClM(NPr^1)_2]_2$.

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