σ and π Organometallic Derivatives of Titanium(III) and Vanadium(III) bonded to a Dibenzotetramethyltetra-aza[14]annulene Ligand

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Reaction of $MCl_3(thf)_3$ (thf = tetrahydrofuran; M = Ti or V) with Li_2(tmtaa) (tmtaa = 7,16-dihydro-6,8,16,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetra-azacyclotetradecinato dianion) led to [M(tmtaa)(Cl)] complexes, which can be transformed into the corresponding organometallic derivatives [(tmtaa)V(mes)] (mes = mesityl) and [(tmtaa)M(η^5-C_5H_5)] (M = V or Ti), whose structure was proven by *X*-ray analysis.

The organometallic derivatives of early transition metals and studies of their chemical behaviour are mainly limited to cyclopentadienyl derivatives.[1,2] The extension of the so-called macrocyclic stabilization effect on M–C bonds to early transition metals is practically non-existent, with the exception of one recent report.[3] Among the polydentate ligands, which normally impose a square planar geometry around the metal ion, our attention was attracted by the dianion 7,16-dihydro-6,8,16,17-tetramethyldibenzo[*b,i*][1,4,8,11]-tetra-azacyclotetradecinato (tmtaa),[4] which has a saddle shape conformation. It defines a cavity around the metal and determines a *cis*-arrangement of the additional ligands,[5,6] as found for the bent $[(cp)_2M]$ (cp = η^5-C_5H_5 or η^5-C_5Me_5) fragment.[1,2] Such structural properties affect the chemistry of the M–C bond. We report here the use of tmtaa as ancillary ligand for organic derivatives of vanadium(III) and titanium(III). The hitherto unknown starting materials were synthesised by the reaction of Li_2(tmtaa) in tetrahydrofuran (thf) with the corresponding metal(III) halide (Scheme 1).

Complexes (**1**) and (**2**) which contain LiCl of crystallization,† have been fully characterized and their structures

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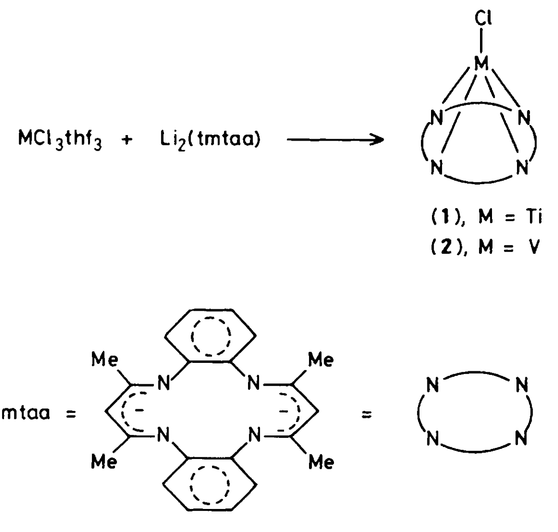
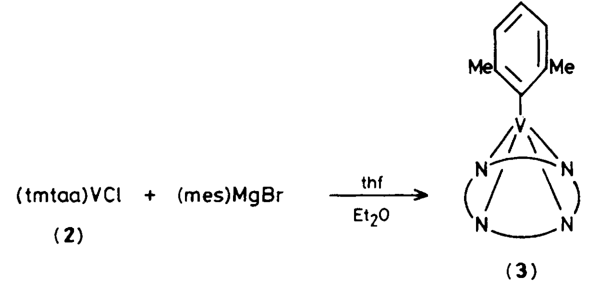
† Complexes (**1**) and (**2**) have the general formula [(tmtaa)M-Cl]·$[Li_2(\mu\text{-}Cl)_2(thf)_4]_{0.5}$ (M = Ti or V).



Scheme 1



Scheme 2. mes = 2,4,6-$Me_3C_6H_2$.

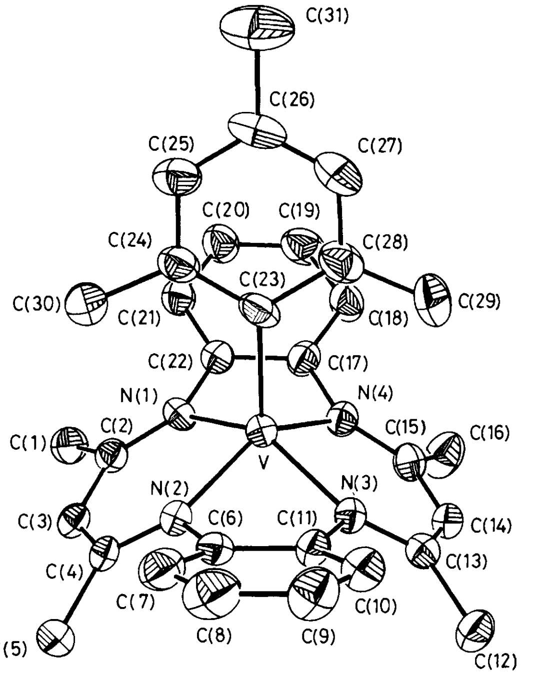
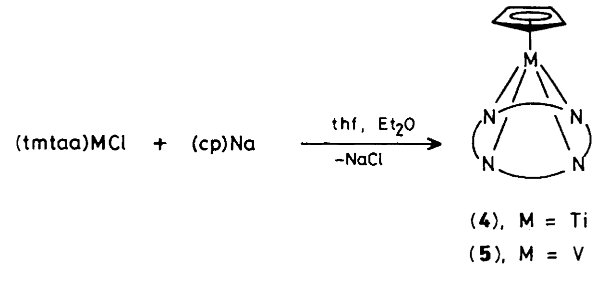


Figure 1. An ORTEP view of complex (**3**), [(tmtaa)V(mes)]. Bond distances (Å): V–N(1), 2.009(5); V–N(2), 2.003(8); V–N(3), 2.009(6); V–N(4), 2.002(8); V–C(23), 2.085(8). Bond angles (°): N(1)–V–C(23), 104.8(3); N(2)–V–C(23), 109.9(3); N(3)–V–C(23), 109.7(2); N(4)–V–C(23), 108.4(3).



Scheme 3

determined.[6] They are alkylated by various reagents. Structural support, which we believe essential for defining the nature of these paramagnetic materials, has so far been obtained only for complex (**3**),‡ which was synthesised by a conventional method (Scheme 2). Complex (**3**) co-crystallized with the magnesium salt (*ca.* 30%)§¶ ($\mu_{eff.}$ = 2.90 μ_B at 293 K).

An ORTEP view of complex (**3**) is in Figure 1 with selected bond distances and angles. The ligand is saddle shaped owing to the steric interactions of the tmtaa methyl groups with the hydrogen atoms of the benzenoid rings,[5,7] with the metal out of the N(1), N(2), N(3), N(4) plane by 0.626 Å, binding the phenyl group at 2.085(8) Å, which is shorter than the few other V–C σ bonds known thus far.[3,8] The phenyl ring of the mesityl ligand is almost parallel to the benzene rings of the tmtaa. The V–N distances vary from 2.002(8) to 2.009(6) Å. The other structural parameters are similar to those found in complexes (**1**) and (**2**)[6] and in other derivatives of the same ligand.[5,7] Compound (**3**) and analogous titanium and vanadium derivatives are very reactive either at the metal or at the M–C bond, and their chemistry is under investigation.

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‡ *Crystal data:* complex (**3**), $C_{31}H_{35}N_4V\cdot 1/2[MgCl_{1.56}Br_{0.44}(thf)_4]\cdot thf$, M = 798.09, triclinic, space group $P\bar{1}$, a = 12.671(4), b = 13.501(5), c = 14.613(4) Å, α = 113.58(3), β = 93.80(3), γ = 109.79(3)°, U = 2096(3) Å^3, Z = 2, D_c = 1.25 g cm^{-3}, $F(000)$ = 838, $\mu(\text{Cu-}K_\alpha)$ = 75.09 cm^{-1} (λ = 1.54178 Å), crystal dimensions 0.39 × 0.56 × 0.17 mm. Intensities of 5598 reflections were measured at 298 K on a Nicolet R3m diffractometer using Cu-K_α radiation, resulting in 5281 independent reflections. The structure was solved by the heavy method and refined by full-matrix least-squares. All calculations were carried out using the SHELX-TL program. For 3116 observed reflections [$I > 3\sigma(I)$] the final R value was 0.0747 (R_w = 0.1002).

Complex (**4**), $C_{27}H_{27}N_4Ti$, M = 455.4, orthorhombic, space group $Pbca$, a = 8.747(2), b = 17.765(3), c = 28.532(7) Å, U = 4434(2) Å^3, Z = 8, D_c = 1.365 g cm^{-3}. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined anisotropically by blocked full-matrix least-squares. For 1920 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 130°$ (Cu-K_α radiation) the R value is 0.064 (R_w = 0.066). An absorption correction was applied (μ = 34.4 cm^{-1}). Most of the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX 76.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been depositied at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

§ Satisfactory elemental analyses have been obtained.

¶ Complex (**3**) crystallizes as $[(tmtaa)V(mes)]\cdot[MgX_2(thf)_4]_{0.5}(thf)$. Microanalysis and structural analysis agree with a composition having 78% of Cl and 22% of Br.

The electron deficient [M(tmtaa)] fragment can bind organic fragments which can provide a significant number of electrons. The reaction in Scheme 3 was carried out by adding a thf solution of (cp)Na (cp = η^5-C_5H_5) to a suspension of (**1**) or (**2**) in the same solvent. Sodium chloride was removed from the resulting solution, which was concentrated, then Et_2O was added. Complexes (**4**) and (**5**) were isolated as crystalline solids (yield *ca.* 60%).§

Complex (**4**) has one unpaired electron ($\mu_{eff.}$ 1.81 μ_B at 292 K), and (**5**) has two unpaired electrons ($\mu_{eff.}$ 2.76 μ_B at 292 K). The sixteen-electron vanadium(III) in (**5**) is in the high-spin state, as in many $(cp)_2V$–X derivatives.[9] The structure of (**4**), which is a brown crystalline solid, has been determined by *X*-ray analysis. A view of the structure with some selected bond distances and angles is in Figure 2. The Ti(tmtaa) fragment has the usual features, with the metal out of the N(1),N(2),N(3),N(4) plane by 0.889(1) Å. The Ti–N bond distances range from 2.101(5) to 2.124(6) Å. The cp ligand is η^5-bonded to titanium, with Ti–C bond distances ranging from 2.373(10) to 2.425(3) Å and a Ti–cp distance of 2.072(9) Å.

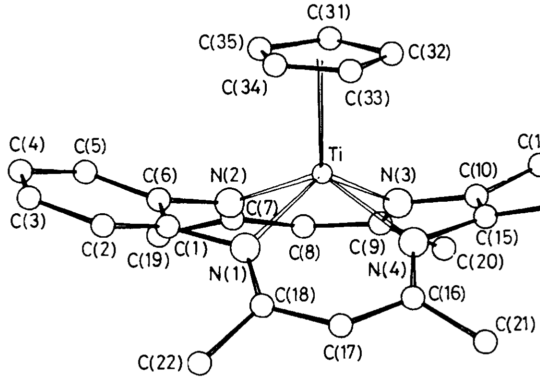

Figure 2. A view of complex (**4**), [(tmtaa)Ti(cp)]. Bond distances (Å): Ti–N(1), 2.124(5); Ti–N(2), 2.101(5); Ti–N(3), 2.107(6); Ti–N(4), 2.122(6); Ti–cp(1), 2.072(9). Bond angles (°): N(1)–Ti–N(2), 75.2(2); N(1)–Ti–N(4), 83.9(2); N(2)–Ti–N(3), 84.9(2); N(3)–Ti–N(4), 75.1(2); N(1)–Ti–cp(1), 116.4(3); N(2)–Ti–cp(1), 112.7(3); N(3)–Ti–cp(1), 114.8(3); N(4)–Ti–cp(1), 115.6(3). cp(1) refers to the centroid of the cyclopentadienyl ring.

From the results reported, the ligand tmtaa seems particularly suitable for an entry into the organometallic and low oxidation state chemistry of early transition metals.

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