Novel µ-methyl complexes of vanadium and their relevance to bimolecular deactivation of homogeneous imidovanadium polymerisation catalysts

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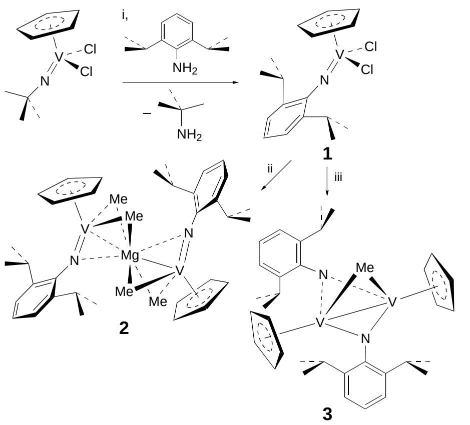
Attempted dimethylation of $[CpV(NC_6H_3Pr^i{}_2\text{-}2,6)]Cl_2$ using Grignard reagents affords novel µ-methyl complexes arising by reductive dimerisation; the structure of one of these products, $[CpV(NC_6H_3Pr^i{}_2\text{-}2,6)(\mu\text{-}Me)_2]_2(\mu\text{-}Mg)$ 2, reveals V–(µ-Me)–Mg, V–Mg, N–Mg and C–H···Mg interactions.

There is presently much interest in the development of new-generation 'non-metallocene' catalysts for the polymerisation of α-alkenes. These include, for example, alkoxide,[1] thiolate,[2] amide,[3] imide,[4] tetradentate Schiff-base[5] and macrocyclic procatalysts.[6] In recent work we have been investigating the isolobal relationship between group 4 metallocenes and group 5 half-sandwich imido species[7] and have found that vanadium complexes of the type $[CpV(NR)Cl_2]$ are particularly active amongst these group 5 metal pro-catalysts.[4a] Typically, they give high initial polymerisation activities but die over the course of a few minutes, a kinetic profile that is not uncommon in many homogeneous Ziegler-type polymerisation systems. In order to gain more insight into the deactivation process and to be able to control this behaviour, we set out to synthesise well defined cationic alkyl versions of these catalysts. Methyl derivatives were targeted since such species have proved to be suitable precursors in metallocene systems.[8] Here, we describe two highly unusual products arising from reactions of $[CpV(NAr)Cl_2]$ (Ar = $C_6H_3Me_2$-2,6) **1** with methylmagnesium halides under differing conditions of solvent and Grignard reagent. The products are structurally exceptional and provide insight into the bimolecular deactivation process occurring in [CpV(NR)] polymerisation systems.†

The synthesis of the starting complex **1** has been described previously by Teuben and coworkers.[9] During the course of our studies, we have found that **1** and related imido complexes can also be prepared by an imido exchange route according to Scheme 1, a methodology that appears to be quite general.[10] Thus treatment of $[CpV(NBu^t)Cl_2]$ with 2,6-diisopropylaniline in hot 1,2-dichloroethane affords $[CpV(NAr)Cl_2]$ **1** in high yield.



Scheme 1 *Reagents and conditions*: i, $(CH_2Cl)_2$, 75 °C, 10 d; ii, 2.5 MeMgBr, Et_2O, 12 h; iii, 3 MeMgCl in thf–Et_2O, 12 h

The paramagnetic magnesium-containing divanadium complex **2** was isolated from the reaction of **1** with excess MeMgBr in diethyl ether (Scheme 1). The molecular structure is shown in Fig. 1.‡ Complex **2** crystallises as a trimetallic V_2Mg cluster in the centrosymmetric space group $P2_1/c$, with the magnesium atom located at the centre of inversion. The structure consists of two methyl groups bridging between the vanadium atom of the [CpV(NAr)] fragment and the magnesium core. The V–Mg distance of 2.594(1) Å is similar to other proposed metal–Mg bonds[11,12] and therefore may be viewed as a direct V–Mg interaction. The N–Mg distance of 2.366(6) Å is within the range for a genuine bonding interaction,[13] although the V–N distance of 1.724(6) Å (1.60–1.68 Å in terminal imides,[14] 1.84–1.85 Å in bridging imides[3a,8,15]) and the V–N–C_{ipso} angle of 160.6(5)° suggest that this interaction is weak and that the imido unit behaves more as a terminal ligand to the vanadium centre than a bridging group between V and Mg. The carbon atoms of the bridging methyl groups are located slightly closer to the vanadium [V–C_{methyl} 2.200(7), 2.227(7) Å; Mg–C_{methyl} 2.382(7), 2.408(7) Å] and the V–C_{methyl} distances are longer than those reported for vanadium complexes with terminal alkyl groups (2.04–2.08 Å).[3,4,8,16] The two V–C_{methyl}–Mg angles are identical [68.4(2)°] and are typical for methyl groups bridging two metals.[11,16] The two highly distorted V–C–H angles (55, 77°) and the particularly short Mg–H separations (2.04, 2.35 Å) for H(18c) and H(19b) respectively,‡ indicate the presence of C–H···Mg agostic interactions [Fig. 1(*b*)]. The presence of the

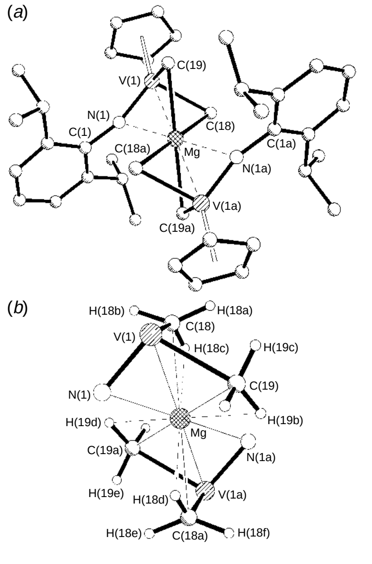


Fig. 1 (*a*) The molecular structure of **2** with key atoms labelled. H atoms are omitted for clarity. Selected dimensions (Å and °): V(1)–N(1) 1.724(6), V(1)–C(18) 2.200(7), V(1)–C(19) 2.227(7), V(1)–Mg 2.594(1), Mg–N(1) 2.366(6), Mg–C(18) 2.408(7), Mg–C(19) 2.382(7); N(1)–V–C(18) 100.5, N(1)–V–C(19) 101.3(3), C(18)–V–V(19) 91.0(3), N(1)–V–Mg 62.7(2), C(18)–V–Mg 59.6(2), C(19)–V–Mg 58.6(2), V(1)–N(1)–C(1) 160.6(5), V(1)–C(18)–Mg 68.4(2), V(1)–C(19)–Mg 68.4(2); (*b*) view of the magnesium core showing the agostic C–H···Mg interactions.

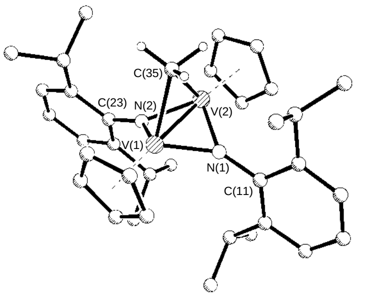


Fig. 2 The molecular structure of **3** with key atoms labelled. H atoms are omitted for clarity. Selected dimensions (Å and °): V(1)–N(1) 1.867(3), V(1)–N(2) 1.882(3), V(2)–N(1) 1.896(3), V(2)–N(2) 1.894(3), V(1)–C(35) 2.215(4), V(2)–C(35) 2.310(4), V(1)–V(2) 2.324(1); V(1)–C(35)–V(2) 61.8(1), V(1)–N(1)–V(2) 76.3(1), V(1)–N(2)–V(2) 76.9(1), V(1)–N(1)–C(11) 143.8(2), V(2)–N(1)–C(11) 139.9(2), V(1)–N(2)–C(23) 142.4(2), V(2)–N(2)–C(23) 141.6(2).

magnesium core with its attendant weak ligand interactions (bonding distances 2.366–2.594 Å) appears to lend significant stability to this unusual product.

By contrast, in the presence of diethyl ether and tetrahydrofuran, **1** reacts with an excess of MeMgCl to afford the paramagnetic mono μ-methyl complex **3** (Scheme 1, Fig. 2). The crystal structure of **3**‡ consists of a single methyl and two arylimido groups bridging between two [CpV] units. The distances V(1)–C(35) [2.310(4) Å], V(2)–C(35) [2.215(4) Å] and the V(1)–C(35)–V(2) angle [61.8(1)°] are comparable with **2**. In this case, however, there are no close interactions of the bridging methyl C–H bonds with the adjacent metal centres. The V–N distances [av. 1.885(4) Å] are longer than for **2** owing to the decreased bond order resulting from the fact that the imido substituents are bridging. The V(1)–V(2) distance of 2.324(1) Å is within the range for a bonding interaction,[17] and the V–Cp(centroid) vectors are almost coaxial with the V–V bond. Finally, the bridging methyl and imides are arranged around the V–V axis such that C(35), N(1) and N(2) are approximately 120° to each other. We note that Teuben and coworkers have reported a related tolylimido complex, [CpV(μ-NC_6H_4Me-*p*)Me]$_2$, which contains bridging imido ligands and terminal methyl groups.[18]

Since dialkylation of a dihalide precursor is the prevalent route to a well defined cationic alkyl catalyst species, these observations provide an explanation for the rapid deactivation of [CpV(NR)] procatalysts and are likely to be of general relevance to other rapidly deactivating catalyst systems.

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Footnotes and References

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† Satisfactory elemental analyses have been obtained.

‡ *Crystal data*: **2**: $C_{19}H_{28}Mg_{0.5}NV$, M_r = 333.52, orange-red irregular plate-shaped crystal (0.40 × 0.36 × 0.15 mm), monoclinic, space group, $P2_1/c$, a = 10.220(2), b = 9.909(2), c = 18.658(3) Å, β = 104.94(1)°, U = 1825.6(6) Å^3, Z = 4, T = 150(2) K, D_c = 1.213 g cm^{-3}, $F(000)$ = 712, μ = 0.556 mm^{-1}. 2184 unique reflections ($2\theta < 45°$) were measured on a Siemens P4 diffractometer with graphite monochromated Mo-Kα X-radiation (λ = 0.710 73 Å); no absorption correction was made. Structure solved (by Patterson methods) and refined using SHELXL-93. 2179 reflections were used in the full-matrix least-squares refinement. Refinement of positional parameters for all non-H atoms and anisotropic thermal parameters for V (91 parameters) converged to $R_1[I > 2\sigma(I)]$ = 0.0602 and $wR_2[I > 2\sigma(I)]$ = 0.0912 [$w = 1/(\sigma^2F_0{}^2 + 0.0003P^2)$ where $P = (F_o{}^2 + 2F_c{}^2)/3$] with S = 0.729. All bridging H atoms were found in the difference map but not refined. **3**: $C_{35}H_{47}N_2V_2\cdot 0.5C_6H_{12}$, M_r = 597.63, deep red diamond-shaped crystal (0.80 × 0.62 × 0.40 mm), monoclinic, space group, $P2_1/n$, a = 9.924(2), b = 21.653(4), c = 16.235(3) Å, β = 98.73°, U = 3448(1) Å^3, Z = 4, T = 150(2) K, D_c = 1.151 g cm^{-3}, $F(000)$ = 1268, μ = 0.565 mm^{-1}. 4865 unique reflections ($2\theta < 46.5°$) were measured on a Siemens SMART-CCD diffractometer with graphite monochromated Mo-Kα X-radiation (λ = 0.710 73 Å); no absorption correction was made. Structure solved (by direct methods) and refined using SHELXL-93. 4857 reflections were used in the full-matrix least-squares refinement. Refinement of positional and anisotropic thermal parameters for all non-H atoms (364 parameters) converged to $R_1[I > 2\sigma(I)]$ = 0.0531 and $wR_2[I > 2\sigma(I)]$ = 0.1476 [$w = 1/(\sigma^2F_o{}^2 + 0.0650P^2 + 5.1588P)$] with S = 1.208. Hexane solvent H atoms were not modelled. CCDC 182/609.

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