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Linked Cyclopentadienyl-Amide Complexes of Divalent, Trivalent, and Tetravalent Vanadium: A Vanadium "Constrained Geometry Catalyst"[†]

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Summary: Paramagnetic complexes of V(II), V(III), and V(IV) with a linked cyclopentadienyl-amide ancillary ligand were prepared and structurally characterized. The V(IV) dichloride 4, when activated by MAO cocatalyst, polymerizes ethene with a lower productivity than that of its Ti(IV) congener 5 and gives polyethene with a considerably lower molecular weight.

When used in combination with group 4 metals, the linked cyclopentadienyl-amide dianionic ancillary ligand system[1] has yielded highly interesting "constrained geometry" catalysts for olefin polymerization (and in particular for ethene/α-olefin copolymerization).[2,3] These systems are more electron-deficient and sterically less encumbered when compared to the well-known group 4 metallocene catalysts. For these reasons they seem particularly suitable to study the effect on catalyst performance of features such as the interaction of the counterion with the cationic active center and the electronic configuration of the metal center. For the latter, it is required to prepare suitable non-d^0 catalyst precursors of the type (Cp-amide)MCl$_2$.

For the attachment of cyclopentadienyl-amide ligands to early transition metals a range of methods is available, with the route of choice depending strongly on the specific combination of ligand and metal. These methods include salt metathesis,[1,2,4] amine elimination from metal amides,[5] and elimination of HCl from metal chlorides in the presence of a base.[6] Previously we reported the first Cp-amide vanadium complex, the V(V) compound [h^5,h^1-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]V(Nt-Bu)Cl, obtained through the amine elimination route.[7] Here we describe a versatile entry into the chemistry of Cp-amide compounds of V(II), V(III), and V(IV). The synthesis of the V(IV) dichloride [h^5,h^1-C$_5$H$_4$(CH$_2$)$_2$Ni-

Scheme 1

Pr]VCl$_2$ allows a comparison in olefin polymerization performance between isostructural 3d^0 (Ti) and 3d^1 (V) Cp-amide catalysts, of which the first results are presented.

Various ways to attach the [C$_5$H$_5$(CH$_2$)$_2$Ni-Pr]-ligand to V(III) and V(IV) were explored, and we were successful in preparing a V(III) derivative using a stepwise salt metathesis approach. The ligand C$_5$H$_5$(CH$_2$)$_2$NHi-Pr[5b] was monolithiated in situ by reaction with 1 equiv of MeLi in THF, after which this solution was added to a THF solution of VCl$_3$(PMe$_3$)$_2$. This yields the purple-blue paramagnetic cyclopentadienyl-amine derivative [h^5,h^1-C$_5$H$_4$(CH$_2$)$_2$NHi-Pr]VCl$_2$(PMe$_3$) (**1**, Scheme 1), which was characterized by X-ray diffraction.[8] The coordination geometry around V strongly resembles that of square pyramidal CpVCl$_2$(PMe$_3$)$_2$[9] but with one phosphine replaced by the amine ligand which is intramolecularly coordinated trans to the PMe$_3$ ligand (V–N = 2.290(2) Å, V–P = 2.5140(8) Å). Reaction of **1**

(1) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.
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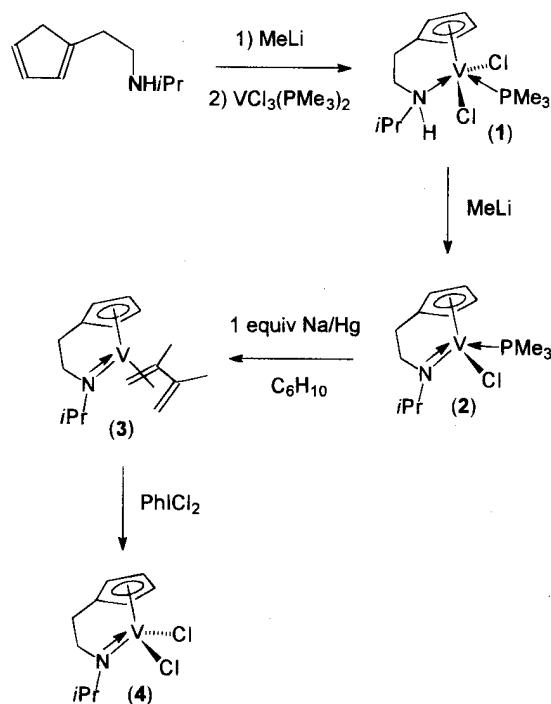(3) For a recent review, see: McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.
(4) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.
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(6) Sinnema, P.-J.; Van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245.
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(8) Details of the structure determinations of compounds **1** and **2** can be found in the Supporting Information.
(9) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.

with MeLi in THF resulted in elimination of LiCl and methane to give the green paramagnetic V(III) cyclopentadienyl-amide complex [h,[5]h[1]-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]-VCl(PMe$_3$) (**2**, Scheme 1). A single-crystal structure determination[8] of **2** shows a three-legged piano-stool structure with a V-N(amido) distance (1.873(2) Å) that is substantially shorter than the V-N(amine) distance in **1**, and a V-P distance (2.4791(8) Å) slightly shorter than in **1**.

Attempts to oxidize **2** cleanly to a V(IV) derivative using PCl$_3$[10] was unsuccessful. We therefore tried a two-step approach, first performing a one-electron reduction to V(II), followed by introduction of "Cl$_2$" to yield the desired V(IV) dichloride. A suitable V(II) derivative was readily obtained by reduction of **2** with 1 equiv of Na (as Na/Hg) in THF in the presence of 2,3-dimethyl-1,3-butadiene. The resulting paramagnetic, green V(II) diene complex   [h,[5]h[1]-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]V(h[4]-C$_6$H$_{10}$)   (**3**, Scheme 1) could also be obtained (in 63% overall yield) from a one-pot synthesis starting from VCl$_3$(THF)$_3$.[11] Compound **3** was characterized by single-crystal X-ray diffraction (Figure 1).[12] Despite conformational disorder in the (CH$_2$)$_2$ bridge around a crystallographic mirror plane, it can be seen that the diene is h[4]-coordinated to the metal center with a *prone* orientation relative to the Cp ligand. The diene ligand seems to have very little metallacyclopentene character, and the compound should be able to serve as a good precursor for the V(II) [h,[5]h[1]-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]V-fragment.

The V(II) diene complex **3** reacts with the mild chlorinating agent PhICl$_2$[13] in THF at low temperature under release of the diene (as seen by GC/MS) to yield the brown-red paramagnetic V(IV) dichloride [h,[5]h[1]-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]VCl$_2$ (**4**, Scheme 1).[14] The compound was obtained as single crystals by slow diffusion of pentane vapor into a THF solution of the compound. The crystal structure of **4** (Figure 2)[15] shows that it is practically isostructural with its Ti(IV) analogue **5**.[6] The
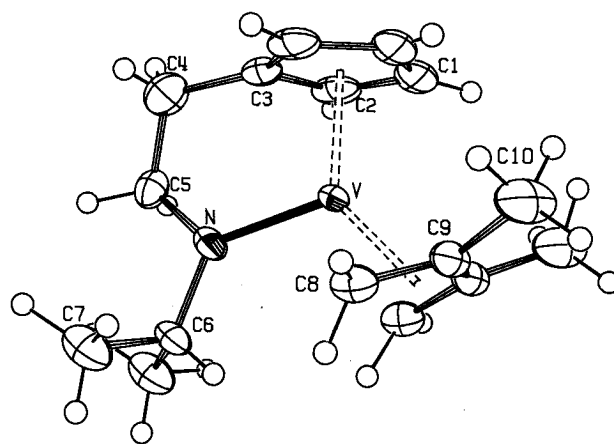

Figure 1. Molecular structure of **3**. Selected interatomic distances (Å) and angles (deg): V-N = 1.924(4), V-C(8) = 2.192(4), V-C(9) = 2.246(3), C(8)-C(9) = 1.412(5), C(9)-C(9´) = 1.397(5), V-C(8)-C(9) = 73.5(2).
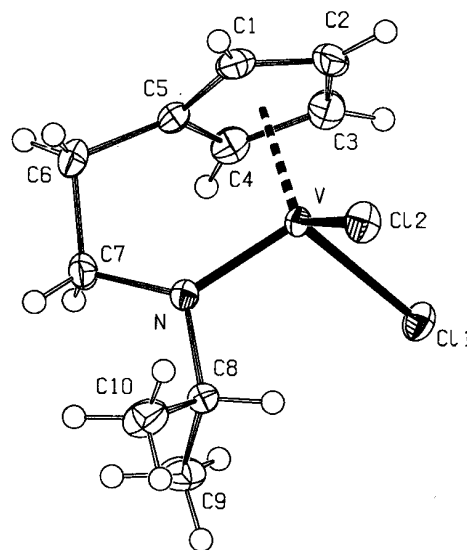

Figure 2. Molecular structure of **4**. Selected interatomic distances (Å) and angles (deg): V-Cl(1) = 2.2879(5), V-Cl(2) = 2.2958(4), V-N = 1.831(1), Cl(1)-V-Cl(2) = 95.61(2), V-N-C(7) = 130.0(1), V-N-C(8) = 112.61(8), C(7)-N-C(8) = 117.0(1).

somewhat smaller radius of V(IV) is reflected in the shorter N-M distance (1.831(1) Å versus 1.864(2) Å for **5**) and Cp(centroid)-M distance (1.934(1) Å versus 2.008(4) Å for **5**). The main difference is found in the Cl-M-Cl angle, which in **4** (95.61(2)°) is significantly smaller than in **5** (103.01(4)°), whereas the M-Cl

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(11) Synthesis of **3** (all manipulations were performed under inert N$_2$ atmosphere using Schlenk techniques): To a suspension of VCl$_3$(THF)$_3$ (6.59 g, 17.6 mmol) in 150 mL of THF was added PMe$_3$ (4.0 mL, 38.6 mmol), and the solution was stirred for 1 h at room temperature. To a solution of C$_5$H$_5$CH$_2$CH$_2$N(H)i-Pr (2.71 g, 17.6 mmol) in 20 mL of THF was added 20 mL of a 0.88 M MeLi solution (17.6 mmol) in diethyl ether at 0 °C, and the mixture was stirred for 30 min. The VCl$_3$ solution was cooled to -50 °C, and the solution of the monolithiated ligand was slowly added. After stirring for 1 h, the solution was brought to room temperature and stirred overnight. The purple solution was then cooled to -30 °C, and 20 mL of a 0.88 M MeLi solution in ether (17.6 mmol) was added over 5 min. After 30 min the green solution was brought to room temperature and stirred for 2 h. Then, 2.5 mL of 2,3-dimethyl-1,3-butadiene (22.1 mmol) was added and, subsequently, an amalgam made of 0.40 g of Na-sand (17.6 mmol) and 140 g of Hg. After stirring for 4 h, the dark green solution was decanted and the residual Hg was extracted twice with 20 mL of THF. The volatiles were removed in vacuo from the combined solutions, and the resulting dark solid was stripped of residual THF by stirring twice with 15 mL of pentane, which was subsequently pumped off. The solid was then extracted twice with 30 mL of pentane, and the extract was cooled to -60 °C. Yield: 3.15 g (11.2 mmol, 63%) of dark green crystalline **3** isolated in several crops.

(12) Structure of **3**. Crystal data: C$_{16}$H$_{25}$NV; space group *Pnma*; orthorhombic; a = 13.906(1) Å, b = 10.917(1) Å, c = 9.826(1) Å, V = 1491.7(2) Å^3 at 130 K, Z = 4. Final refinement on F^2 converged at $R_w(F^2)$ = 0.1428 for 1714 reflections with $F_o^2 \geq 0$ and 139 parameters, and $R(F)$ = 0.0556 for 1195 reflections with $F_o \geq 4.0$ $s(F_o)$.

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(14) Synthesis of **4** (all manipulations were performed under inert N$_2$ atmosphere using Schlenk techniques): Onto a solid mixture of 0.30 g of **3** (1.1 mmol) and 0.30 g of PhICl$_2$ (1.1 mmol) was condensed 20 mL of THF at liquid nitrogen temperature. Subsequently the mixture was thawed out. Upon melting of the THF, a green solution formed, which then quickly changed to brown. After reaching room temperature, the solution was stirred for an additional hour. The volatiles were removed in vacuo, and the solid was stripped of remaining volatiles by stirring with 15 mL of toluene, which was subsequently pumped off. The solid was extracted with hot toluene. Cooling the extract to -25 °C yielded 0.17 g (0.63 mmol, 57%) of **4** as red-brown crystals.

(15) Structure of **4**. Crystal data: C$_{10}$H$_{15}$Cl$_2$NV; space group *P*2$_1$/*c*; monoclinic; a = 10.346(1) Å, b = 10.674(1) Å, c = 11.899(1) Å, b = 115.251(6)°, V = 1188.5(2) Å^3 at 130 K, Z = 4. Final refinement on F^2 converged at $R_w(F^2)$ = 0.0573 for 2588 reflections with $F_o^2 \geq 0$ and 187 parameters, and $R(F)$ = 0.0216 for 2418 reflections with $F_o \geq 4.0$ $s(F_o)$.

distances in both species are nearly identical. These features may relate to the presence of the single 3d electron in **4**.

Comparative ethene homopolymerization experiments were carried out with the isostructural d^1 and d^0 complexes [$\boldsymbol{h}$,$^5\boldsymbol{h}^1$-C$_5$H$_4$(CH$_2$)$_2$Ni-Pr]MCl$_2$ (M = V, **4**; Ti, **5**), using methylalumoxane (MAO) activator, under identical conditions (15 **m**mol dichloride complex, 500 equiv of MAO, 250 mL of toluene, 50 °C, 3 bar ethene with continuous supply of the monomer, 30 min run time). Under these conditions the V system has a productivity of 209 kg PE (mol V)$^{-1}$ h^{-1} bar^{-1}, which is noticeably lower than that of the Ti system, 532 kg PE (mol Ti)$^{-1}$ h^{-1} bar^{-1}. The largest difference between the two systems is found, however, in the molecular weight of the polyethene produced. This is substantially lower for V (M_w = 14900, M_n = 4900, M_w/M_n = 3.0) than for Ti (M_w = 139000, M_n = 59500, M_w/M_n = 2.3). The polyethene prepared by **4**/MAO under these conditions is soluble in hot C$_2$D$_2$Cl$_4$, and ^{1}H NMR spectroscopy showed only CH$_2$=CH-CH$_2$- groups as olefinic end groups. By integration, a slight excess of methyl end groups was observed, indicating that some chain transfer to MAO occurs as well. The ratio between unsaturated versus saturated chains was determined by NMR to be 100:15. Thus, $\boldsymbol{b}$-H transfer appears to be the dominant chain-transfer route, suggesting that the observed lower molecular weight for the V system stems

largely from an intrinsically faster $\boldsymbol{b}$-H transfer process for this system relative to its Ti congener. First experiments indicate also that the V system is reluctant to effect homopolymerization of propene, whereas the Ti system under the same conditions readily produces atactic polypropene.[16]

In conclusion, we have gained access to (paramagnetic) cyclopentadienyl-amido vanadium complexes for the di-, tri-, and tetravalent oxidation state of the metal. Compounds **2**-**4** should provide convenient starting materials for Cp-amido organovanadium chemistry. Especially the V(IV) dichloride species **4** is of interest, as it allows comparative studies on the olefin polymerization behavior of isostructural "constrained geometry" catalysts with d^1 versus d^0 metal centers. This aspect, including the possibility for copolymerization of ethene with various other olefins, is currently under investigation by both experimental and theoretical methods.

Supporting Information Available: Text giving full experimental procedures and characterization data for the reported compounds. Details of the structure determinations of **1**-**4** including tables of crystal data, positional and thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9903184

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