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Vanadium-Promoted Aldol Condensation and Pinacolic Coupling of Acetylpyrrole: Formation of Two New Potent Dinuclear Catalysts for Olefin Copolymerization

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Reaction of $VCl_3(THF)_3$ with 3 equiv of the potassium salt of acetylpyrrole, $K[\alpha\text{-}(CH_3CO)\text{-}C_4H_3N]$, afforded the dinuclear $\{V_2[K(THF)]_2[CH_3CO(C_4H_3N)]_2\}[(C_4H_3N)C(O)CH_2C(C_4H_3N)(CH_3)O]_2$ (**1**), where four acetylpyrrolide anions from two vanadium moieties have undergone an aldol condensation. The two pyrrolyl−acetylacetonate units so generated work as tetradentate binucleating ligands holding together the dinuclear structure. A similar reaction carried out on the divalent $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ salt afforded the dinuclear and trivalent $\{VK(THF)[(C_4H_3N)C(O)CH_3]\}_2[(C_4H_3N)(CH_3)(O)CC(O)(CH_3)(C_4H_3N)]\cdot 0.5(\text{toluene})$ (**2**), where two acetylpyrrolide ligands, one per vanadium atom, have undergone a reductive coupling to form a pinacol. Even in this case the dipyrrolylpinacol works as a tetradentate binucleating ligand holding together the dinuclear frame. Attempts to perform the same reaction on another V(II) salt such as $VCl_2(TMEDA)_2$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) afforded instead the corresponding divalent derivative $V(TMEDA)[(C_4H_3N)C(O)CH_3]_2$ (**3**), where the acetylpyrrolide anions remained intact. Both **1** and **2** are potent olefin copolymerization catalysts upon activation with diethyl aluminum chloride, while **3** displays low but not negligible activity.

Introduction

Most research in the field of Ziegler−Natta catalysis has traditionally focused on group IV elements and more recently on late metals, whereas group V derivatives have largely been ignored. Information about the performance of group V metal catalysts has been confined mainly within the patent literature.[1] Only recently has the appearance of a few reports rejuvenated interest in vanadium-based Ziegler−Natta catalysis.[2] Nonetheless, the field remains underdeveloped and the current paucity of this literature strikingly contrasts with the fact that vanadium catalysts are widely used for the industrial production of ethylene−propylene−diene elastomers (EPDM).[3]

The ability of vanadium catalysts to perform random or super-random copolymerizations makes these species well-suited for synthetic rubber manufacture.[4] The only

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drawback for using these catalysts is the rather endemic low activity, which typically is a few orders of magnitude lower than that displayed by group IV catalysts. While theoretical calculations have recently predicted that a particularly high level of activity should be expected for d^2 V(III) complexes,[5] an intrinsic instability of vanadium alkyls toward formation of inactive divalent vanadium species is likely to be responsible for the generally observed low activity of these catalysts.[6] Accordingly, we have recently shown that in the case of both the commercially used $V(acac)_3$[6] and the potent olefin polymerization catalyst VCl_2(diiminopyridinato)[7] the alkylation process indeed affords inactive low-valent vanadium complexes. In the particular case of the $V(acac)_3$ catalytic system, the catalyst deactivation is a direct consequence of the ability of the alkylaluminum cocatalyst to completely strip the vanadium atom of the acac ligands (leaching).[6] The abstraction of ligand diminishes the stability of the V−C function, and the consequent reduction to the divalent state is responsible for the deactivation observed with this and other vanadium-based catalytic systems.

Given this rationale, we have embarked on the preparation of new complexes of trivalent vanadium to relate catalytic activity to the stability of trivalent organometallic vanadium species. To this end, nitrogen-donor-based ligands seem to be particularly promising for improving the stability of the V−C bonds[7,8] and display a lower affinity for aluminum species with consequent reduced possibility of "leaching". However, recent studies have indicated that partial or complete replacement of the oxygen donor atoms with nitrogen, as in the so-called acnac or nacnac ligands,[9,10] resulted in a significant decrease of catalytic activity. On the other hand, a functionalized tridentate vanadium amidinate was recently reported to have a very promising level of activity.[11] Therefore, we became interested in examining the behavior of the N- and O-donor-based acetylpyrrolide chelating anion, which displays a low possibility of being leached. Like the acac ligands, it possesses a π-electron system, while the aromaticity of the pyrrolyl anion moiety may reasonably be expected to act as an electron-withdrawing group. Thus, by increasing the Lewis acidity of the metal center the acetylpyrrolide anion might ultimately promote the ability of vanadium to interact with olefins. Last but not least, should the pyrrolide anion adopt a η^5 bonding mode with respect to the metal center (Cp type), the vanadium catalyst might gain a geometry closely reminiscent of the tremendously successful single-site constrained-geometry catalysts.[12] Herein, we report our observations.

Experimental Section

All operations were performed under an inert atmosphere using standard Schlenk type techniques. $VCl_3(THF)_3$,[13] $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$,[14] and $VCl_2(TMEDA)_2$[15] were prepared according to published procedures. Diethylaluminum chloride (1.0 M solution in hexane), trimethylaluminum (1.0 M solution in toluene), dimethylaluminum chloride (2.0 M solution in toluene), ethyl trichloroacetate, and acetylpyrrole were obtained from Aldrich and were used as received. Propylene (99.5%, polymer grade, Praxair) and ethylene (99.5%, polymer grade, Praxair) were purified by passing through a gas purification system (P_2O_5 column and oxygen removal column). 1-Hexene and norbornene were distilled over metallic sodium. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox. NMR spectra were recorded on a Bruker DRX 500 instrument. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. Magnetic moments were calculated following standard methods,[16] and corrections for underlying diamagnetism were applied to the data.[17] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for the X-ray crystal structure determinations were collected on a Bruker AXS SMART 1k CCD diffractometer equipped with a Smart CCD area detector.

Synthesis of $K[\alpha\text{-}(CH_3CO)C_4H_3N]$. A solution of acetylpyrrole (2.0 g, 18.3 mmol) in THF (50 mL) was treated with KH (0.8 g, 19.9 mmol) at −78 °C. The solution was stirred for 1 h while being warmed to room temperature. The solution was filtered, concentrated, and slowly cooled to −30 °C. Colorless needles of the corresponding potassium salt separated, which were collected by filtration and thoroughly dried (2.2 g, 14.9 mmol, 81%). IR (Nujol mull, cm^{-1}): ν 3533 (m), 3172 (w), 2949 (s), 2868 (s), 2729 (w), 2671 (w), 1734 (w). 1716 (w), 1699 (m), 1684 (w), 1653 (m), 1616 (m), 1558 (s), 1464 (s), 1377 (s), 1338 (w), 1319 (w), 1267 (m), 1184 (w), 1153 (w), 1130 (w), 1068 (w), 1034 (m), 1018 (w), 966 (w), 914 (w), 881 (w), 870 (w), 839 (w), 798 (w), 766 (m), 746 (m), 735 (m), 721 (m), 694 (w), 667 (w), 633 (w), 625 (w). Anal. Calcd (found) for C_6H_6ONK: C, 48.95 (48.05); H, 4.11 (4.21); N, 9.51 (8.96). ^1H NMR (500 MHz, THF-d_8, 298 K): δ 7.03 (d, 1H, C−H pyr), 6.90 (d, 1H, C−H pyr), 6.00 (t, 1H, C−H pyr), 2.25 (s, 3H, CH_3). ^{13}C NMR (500 MHz, THF-d_8, 298 K): δ 188.72 (C=O), 141.18 (C pyr), 138.19 (C−H), 120.40 (C−H), 110.74 (C−H), 25.30 (CH_3).

Preparation of $\{V_2[K(THF)]_2[CH_3CO(C_4H_3N)]_2\}[(C_4H_3N)C(O)CH_2C(C_4H_3N)(CH_3)O]_2$ (1). A solution of $K[\alpha\text{-}(CH_3CO)C_4H_3N]$ (2.5 g, 16.9 mmol) in THF (50 mL) was treated with $VCl_3(THF)_3$ (1.3 g, 3.5 mmol). The resulting dark orange-red solution was filtered to eliminate a small amount of insoluble material. The solution was evaporated to dryness, and the residue was redissolved in ether. The solution was allowed to stand at room temperature for 4 days, upon which crystalline **1** separated (1.2 g, 1.2 mmol, 68%). IR (Nujol, cm^{-1}): ν 1591 (w), 1550 (vs), 1532 (s), 1498 (m), 1460 (vs), 1446 (vs), 1432 (w), 1384 (vs), 1368 (w), 1313 (m, sh), 1287 (vs), 1273 (w), 1203 (s), 1188 (s), 1154 (vs), 1121 (m), 1110 (m), 1063 (s), 1043 (vs), 1028 (s), 980 (m), 965 (w), 943 (vs), 920 (m), 891 (m), 867 (s), 831 (m), 795 (m), 757 (w), 744 (s), 728 (vs), 710 (w), 697 (s), 668 (s), 652 (m), 629 (m), 608 (s), 582 (s), 550 (m),

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Table 1. Polymerization Results

feed	T (°C)	activator	run time (min)	yield (g)	activity (g/((mmol of cat.)/h))	M_w ($\times 10^3$)	PD	% ethylene
			Complex **1**					
ethylene	25	DMAC	60	6.31	3786	54	25.5[a]	100
		DMAC	60	4.31	2590[b]			
		DEAC	20	2.70	1620			
ethylene/propylene	25	DMAC	20	2.61	2490	580	4.96	62
		DEAC	20	4.15	1566			
ethylene/propylene/ norbornylene	25	DMAC	20	2.75	1650	88	3.48	57
ethylene/norbornylene	25	DMAC	20	6.00	3600	65.4	2.51	87
ethylene/1-hexene	25	DMAC	20	3.21	1926	526	2.60	82
			Complex **2**					
ethylene	25	DMAC	60	5.78	3466	73	23[a]	100
	25	DMAC	60	14.21	8526[b]			
	25	DEAC	20	2.40	1600			
ethylene/propylene	25	DMAC	20	4.40	2933	1230	2.79	64
ethylene/propylene/ norbornylene	25	DMAC	20	3.84	2560	465	18.4[a]	51
ethylene/norbornylene	25	DMAC	20	5.58	3720	630	4.4	75
ethylene/1-hexene	25	DMAC	20	4.71	3140	295	6.17	71
			Complex **3**					
ethylene	25	DMAC	60	0.115	0.550	84	6.3	100
	25	DMAC	60	0.334	1.486[b]	135	4.3	100

[a] Bimodal distribution. [b] With 2 equiv of ETA (ETA = ethyl-1,1,1-trichloroacetate).

529 (m). Anal. Calcd (found) for $C_{44}H_{50}N_6O_8V_2K_2$: C, 54.43 (54.01); H, 5.19 (5.23); N, 8.66 (8.58). $\mu_{eff} = 4.19\ \mu_B$ per formula unit.

Preparation of {VK(THF)[(C_4H_3N)C(O)CH_3]}$_2$[(C_4H_3N)-(CH_3)(O)CC(O)(CH_3)(C_4H_3N)]·0.5(toluene) (2). A solution of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (2.0 g, 1.2 mmol) in THF (70 mL) was treated with K[α-(CH_3CO)C_4H_3N] (2.2 g, 14.8 mmol). The resulting dark brown greenish solution was centrifuged to eliminate KCl. After evaporation of the solvent in vacuo, the solid residue was redissolved in ether and the resulting brown solution was allowed to stand at room temperature for 4 days, upon which a burgundy red microcrystalline solid separated. The solid was collected and redissolved in toluene (10 mL). Reddish brown crystals of **2** were obtained upon cooling to −40 °C (0.9 g, 0.9 mmol. 38%). IR (Nujol, cm^{-1}): ν 1734 (w), 1684 (w), 1643 (s), 1547 (vs), 1506 (m), 1464 (vs), 1379 (vs), 1286 (vs), 1261 (s), 1236 (m), 1203 (m), 1182 (m), 1163 (w), 1147 (m), 1118 (m), 1107 (w), 1086 (m), 1039 (s), 987 (m), 956 (m), 929 (s), 912 (m), 841 (w), 802 (w), 754 (s), 744 (s), 727 (s), 696 (s), 687 (m), 650 (m), 621 (m), 604 (m), 550 (w). Anal. Calcd (found) for $C_{47.5}H_{56}N_6O_8K_2V_2$: C, 55.98 (55.76); H, 5.54 (5.48); N, 8.25 (8.19). $\mu_{eff} = 5.88\ \mu_B$ per formula unit.

Preparation of V(TMEDA)[(C_4H_3N)C(O)CH_3]$_2$ (3). Method A. A light blue solution of $VCl_2(TMEDA)_2$ (1.8 g, 5.1 mmol) in THF (100 mL) was treated with K[α-(CH_3CO)-C_4H_3N)] (2.5 g, 17 mmol). The resulting dark blue solution was evaporated to dryness, and the resulting residue was redissolved in ether (75 mL). The solution was filtered and allowed to stand at −20 °C, upon which blue crystals of **3** separated (0.9 g, 2.3 mmol, 45%). IR (Nujol, cm^{-1}): ν 1734 (w), 1685 (m), 1637 (s), 1539 (s), 1462 (vs), 1377 (vs), 1279 (vs), 1259 (s), 1199 (m), 1138 (m), 1097 (s), 1063 (s), 1032 (s), 1003 (s), 955 (m), 924 (s), 889 (m), 870 (m), 796 (s), 739 (s), 696 (s), 667 (w), 644 (m), 613 (m), 588 (w). Anal. Calcd (found) for $C_{18}H_{28}N_4O_2V$: C, 56.39 (56.27); H, 7.36 (7.28); N, 14.61 (14.55). $\mu_{eff} = 3.68\ \mu_B$.

Method B. A solution of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (2.0 g, 1.2 mmol) in THF (70 mL) was treated with K[α-(CH_3CO)C_4H_3N] (1.4 g, 9.5 mmol). The resulting dark blue solution was centrifuged to eliminate KCl and subsequently treated with TMEDA (0.6 g, 4.9 mmol). The solvent was evaporated in vacuo, and the residue was redissolved in ether (20 mL). The solution was centrifuged, concentrated, and allowed to stand at −20 °C, upon which dark blue crystals of analytically pure **3** separated (yield 33%).

General Polymerization Procedure. Catalysts were evaluated for homo- and copolymerization of ethylene with other α-olefins reported in Table 1. Polymerization experiments were carried out in 150 mL of anhydrous toluene in magnetically agitated glass reactors using a continuous flow of 1000 sccm of ethylene and/or 1000 sccm of propylene or in the presence of the appropriate amount of another comonomer. The total working pressure was 30 psi. After equilibration with the feed, 0.2 mmol of aluminum alkyl cocatalyst was added, followed by addition of 5 μmol of the vanadium complex. During experiments where ethyl trichloroacetate (Aldrich) was used as reactivator, the total amount of reactivating substance added to the reaction mixture was 20 μmol. Polymerization reactions were carried out for either 20 or 60 min, followed by addition of 5 mL of ethanol and depressurization. The polymers were recovered by either filtration or solvent evaporation and were then washed and sonicated in dilute HCl and dried at 60 °C. The polymer composition was determined by FTIR using the ratio of peak heights after calibration with standard samples. The molecular weights were determined using either a Waters GPCV 2000 or a Polymer Laboratory PL-GPC-220 instrument equipped with a refractive index detector. Samples for analysis were dissolved in 13.0 mL of trichlorobenzene (TCB) containing 300 ppm w/w Ionol (4-methyl-2,6-di-*tert*-butylphenol). The solutions were shaken at 160 °C for 2 h and then filtered while hot using a 0.5 μm stainless steel filter. A polystyrene/polyethylene universal calibration was carried out using narrow molecular weight distribution polystyrene standards from Polymer Laboratories with Ionol as the flow marker. Polymerization results are summarized in Table 1. Molecular weights are reported as polystyrene equivalents.

X-ray Crystallography. Suitable crystals were selected and mounted on thin glass fibers using paraffin oil or epoxy adhesive and cooled to the data collection temperature. Data were collected using 0.3° ω-scans at 0, 90, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The molecule was located at a 2-fold rotation axis in **2** and at an inversion center in **1**. Attempts to model several peaks located away from the molecule in **2** as a chemically reason-

Table 2. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$K_2V_2C_{44}H_{50}N_6O_8$	$K_2V_2C_{47.5}H_{56}N_6O_8$	$VC_{18}H_{28}N_4O_2$
fw	970.98	1020.26	383.38
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pbcn$	$P2_1/n$
a (Å)	11.348(1)	16.267(4)	10.485(3)
b (Å)	15.675(2)	16.905(4)	14.218(4)
c (Å)	12.780(1)	21.523(5)	14.129(4)
β (deg)	103.618(2)		105.679(5)
V (Å^3)	2209.4(4)	5919(2)	2027.8(9)
Z	2	4	4
radiation (Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
T (K)	203(2)	203(2)	293(2)
D_{calcd} (g cm^{-3})	1.460	1.145	1.256
μ_{calcd} (cm^{-1})	6.71	5.00	5.07
F_{000}	1008	2126	812
R1, wR2, GOF[a]	0.0400, 0.0868, 1.023	0.0784, 0.1990, 1.095	0.0524, 0.1126, 1.065

[a] For all data, $R1 = \sum|F_o| - |F_c|/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, and $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$.

able, cocrystallized solvent molecule failed. The data were thus modified using the SQUEEZE filter in the PLATON package[18] with solvent accessible void space of 1953.6 Å^3 and electron count/cell = 244, suggesting a half-molecule of toluene solvent per compound dimer, as consistent with noncrystallographic data. All remaining non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library (Sheldrick, G. M. Bruker AXS, Madison, WI, 1997). Crystal data for the three complexes are given in Table 2 while selected bond distances and angles are given in Table 3.

Complex 1. The complex is dinuclear and consists of two identical V(acetylpyrrolide) units bridged by two 1,3-bis(α-pyrrolyl)-3-hydroxybutan-1-one trianions (Figure 1). Two potassium atoms, each solvated by one molecule of THF, complete the dinuclear structure. The coordination geometry around each vanadium is distorted octahedral (O(1)−V(1)−N(1) = 82.25(11)°, O(1)−V(1)−N(3) = 108.40(11)°, O(1)−V(1)−O(2) = 92.30(10)°, O(1)−V(1)−N(2) = 164.17(11)°, O(1)−V(1)−O(3) = 89.89(10)°) and is defined by one intact acetylpyrrolide ligand which occupies two adjacent coordination sites with the nitrogen of the pyrrolide ring (V(1)−N(3) = 2.030(3) Å) and the oxygen atom of the acetyl group (V(1)−O(3) = 2.135(3) Å). The oxygen atom also bridges one potassium atom (K(1)−O(3) = 2.871(3) Å). The two tetradentate 1,3-bis(α-pyrrolyl)-3-hydroxybutan-1-one trianions bridge the two vanadium centers. Each trianion uses the N atom of one of the two pyrrolyl rings and the carbonyl group (C(11)−O(2) = 1.275(4) Å) to bond to the first vanadium (V(1)−N(2) = 2.111(3) Å, V(1)−O(2) = 2.077 (2) Å) and the N atom of the second pyrrolyl ring and the contiguous deprotonated hydroxyl oxygen atom to bond to the second vanadium atom (V(1A)−N(1A) = 2.024(3) Å, V(1A)−O(1A) = 1.890 (2) Å). Overall, the *fac*-octahedral coordination geometry of each vanadium is defined by three nitrogen atoms of three σ-bonded pyrrolyl moieties and three oxygens (one oxygen/nitrogen couple from the intact acetylpyrrolide and the other two from two (pyrrolyl)hydroxybutanone ligands). Each potassium atom is π-bonded to one butanone pyrrolyl ring σ-bonded to one vanadium and to the three oxygen atoms bonded to the second vanadium, forming a planar V_2K_2 tetrametallic core (V−K−V−K torsion angle 0°).

Complex 2. This complex is a symmetry-generated dimer with two identical V(acetylpyrrolide)$_2$ units bridged by one 2,3-bis(α-pyrrolyl)-2,3-butanediolate tetraanion (Figure 2). The coordination geometry around each vanadium atom is slightly distorted octahedral (O(1)−V(1)−N(1) = 81.0(2)°, O(1)−V(1)−N(3) = 103.4(2)°, O(1)−V(1)−O(2) = 97.0(2)°, O(1)−V(1)−O(3) = 89.1(2)°, O(1)−V(1)−N(2) = 172.3(2)°) and is defined by the oxygen and nitrogen atoms of two σ-bonded acetylpyrrolyl ligands and by one oxygen atom and one nitrogen atom of the bridging tetraanion (V(1)−N(3) = 2.045(6) Å, V(1)−N(2) = 2.119(6) Å, V(1)−O(3) = 2.123(4) Å, V(1)−O(2) = 2.070(5) Å). The bridging interaction is realized with the four donor atoms with one set of contiguous N and O atoms bonding each vanadium (V(1)−O(1) = 1.859(4) Å, V(1)−N(1) = 2.041(5) Å). Thus, even in this case, three oxygen and three nitrogen atoms define the overall *fac*-octahedral coordination geometry of each vanadium. Each of the potassium atoms is connected to the three oxygen atoms attached to one vanadium and π-bonded to one pyrrolyl ring, which is in turn σ-bonded to the second vanadium atom. The bridging interaction creates a tetrametallic V_2K_2 cluster with a planar core.

Complex 3. The complex is formed of discrete monomeric units containing vanadium in a distorted-octahedral environment (O(1)−V−N(2) = 97.1(2)°, O(1)−V−O(2) = 173.7(1)°, O(1)−V−N(1) = 77.8(2)°, O(1)−V−N(4) = 96.9(2)°, O(1)−V−N(3) = 88.7(2)°) (Figure 3). The coordination geometry around the metal is defined by the oxygen (V−O(1) = 2.12(4) Å, V−O(2) = 2.11(3) Å) and nitrogen (V−N(1) = 2.12(5) Å, V−N(2) = 2.11(4) Å) donor atoms of two intact acetylpyrrolide anions and the two nitrogen atoms of one TMEDA molecule (V−N(3) = 2.25(5) Å, V−N(4) = 2.23(4) Å). The two oxygen atoms are located on the axes, while the four N atoms form the equatorial plane (N(4)−V−N(3) = 81.4(2)°, N(4)−V−N(2) = 163.7(2)°, N(4)−V−N(1) = 91.3(2)°). The bond distances and angles of the coordinated anions compare well with those in complexes **1** and **2**.

Results and Discussion

The potassium salt K(THF)[α-$(CH_3CO)C_4H_3N$] was readily prepared via reaction of acetylpyrrole with KH in THF. The reaction was accompanied by vigorous gas evolution, and the salt was isolated in good yield and in crystalline form as colorless needles. The crystals rapidly desolvate upon drying, and meaningful analytical data in agreement with the formulation K[α-$(CH_3CO)C_4H_3N$] were obtained only from samples previously exposed to vacuum for a few hours. The ^1H NMR spectrum showed the expected pattern with three slightly broadened singlets for the pyrrolyl CH groups and one sharp singlet for the methyl group with the correct relative intensities. The ^{13}C NMR spectrum also showed the expected six-line spectrum.

Given the excellent activity and versatility of the commercially used V(acac)$_3$ catalyst, attempts to prepare a monomeric V(acetylpyrrolide)$_3$ complex of similar octahedral structure were initially carried out by reacting the potassium salt of acetylpyrrole, K[α-$(CH_3CO)C_4H_3N$], with $VCl_3(THF)_3$ in THF at room temperature and by using a stoichiometric ligand to vanadium ratio of 3:1. The reaction afforded instead the complex $\{V_2[K(THF)]_2[CH_3CO(C_4H_3N)]_2\}[(C_4H_3N)C(O)CH_2C(C_4H_3N)(CH_3)O]_2$ (**1**) (Scheme 1). The two 1,3-bis(α-pyrrolyl)-3-hydroxybutan-1-one trianionic ligands bridging the two vanadium centers arise from the aldol condensation of two acetylpyrrole units. Although this type of process typically requires the intervention of a base, we found no sign for this transformation during the initial deprotonation of acetylpyrrole by KH. In contrast, reaction of analytically pure K[α-$(CH_3CO)C_4H_3N$] with VCl_3-

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[18] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

Table 3. Selected Bond Distances (Å) and Angles (deg)

1	2	3
O(1)−V(1)−N(1) = 82.25(11)	O(1)−V(1)−N(1) = 81.0(2)	O(1)−V−N(2) = 97.1(2)
O(1)−V(1)−N(3) = 108.40(11)	O(1)−V(1)−N(3) = 103.4(2)	O(1)−V−O(2) = 173.7(1)
O(1)−V(1)−O(2) = 92.30(10)	O(1)−V(1)−O(2) = 97.0(2)	O(1)−V−N(1) = 77.8(2)
O(1)−V(1)−N(2) = 164.17(11)	O(1)−V(1)−O(3) = 89.1(2)	O(1)−V−N(4) = 96.9(2)
O(1)−V(1)−O(3) = 89.89(10)	O(1)−V(1)−N(2) = 172.3(2)	O(1)−V−N(3) = 88.7(2)
V(1)−N(3) = 2.030(3)	V(1)−N(3) = 2.045(6)	V−O(1) = 2.12(4)
V(1)−O(3) = 2.135(3)	V(1)−N(2) = 2.119(6)	V−O(2) = 2.11(3)
K(1)−O(3) = 2.871(3)	V(1)−O(3) = 2.123(4)	V−N(1) = 2.12(5)
C(11)−O(2) = 1.275(4)	V(1)−O(2) = 2.070(5)	V−N(2) = 2.11(4)
V(1)−N(2) = 2.111(3)	V(1)−O(1) = 1.859(4)	V−N(3) = 2.25(5)
V(1)−O(2) = 2.077 (2)	V(1)−N(1) = 2.041(5)	V−N(4) = 2.23(4)
V(1A)−N(1A) = 2.024(3)	C(5)−O(1) = 1.433(7)	N(4)−V−N(3) = 81.4(2)
V(1A)−O(1A) = 1.890 (2)	C(17)−O(3) = 1.284(8)	N(4)−V−N(2) = 163.7(2)
	C(11)−O(2) = 1.277(8)	N(4)−V−N(1) = 91.3(2)
	K(1)−O(4) = 2.674(6)	

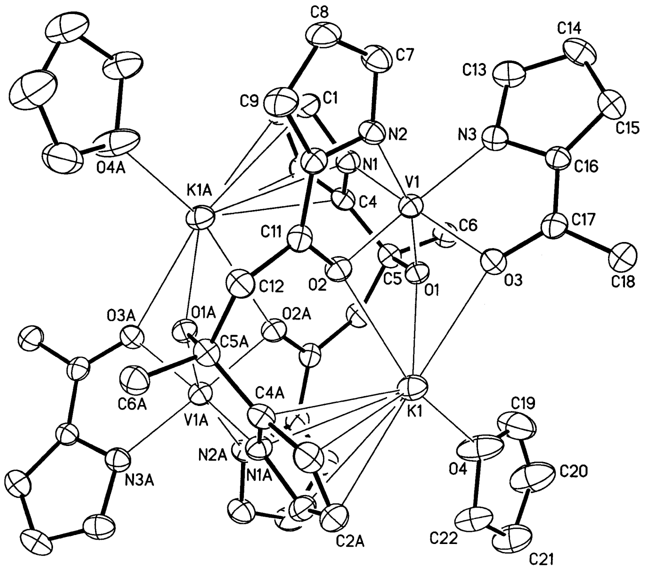


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms and angles in degrees.

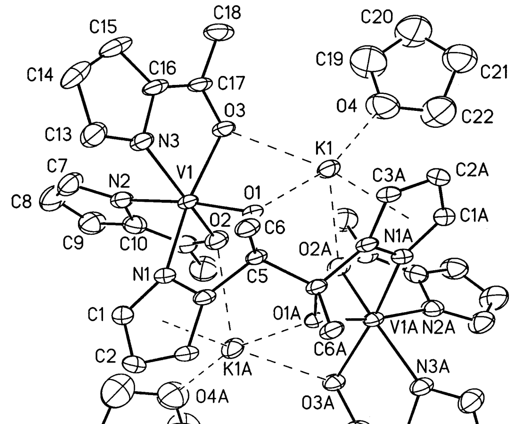


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms and angles in degrees.

(THF)$_3$ yielded **1** as the only product which could be isolated and identified from the reaction mixtures. This suggests that vanadium acts as a templating agent by triggering the aldol condensation of two of the three acetylpyrrolide anions. Furthermore, the formal elimination of one proton from the acetylpyrrolide anion, as required by the aldol condensation, can be obtained only with the intervention of a base, and which in this particular case is provided by a *fourth* equivalent of potassium acetylpyrrolide (Scheme 1). Accordingly,

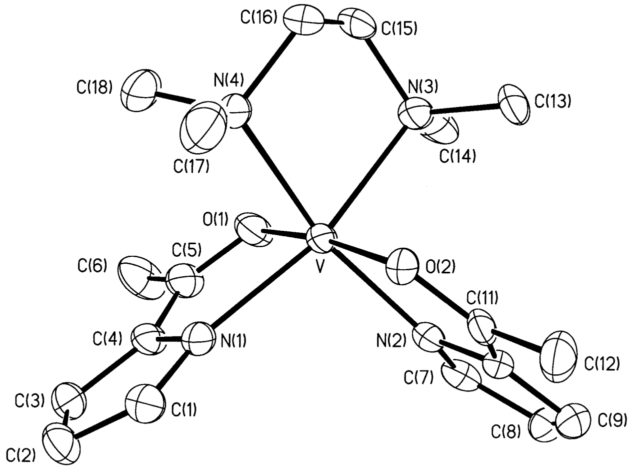
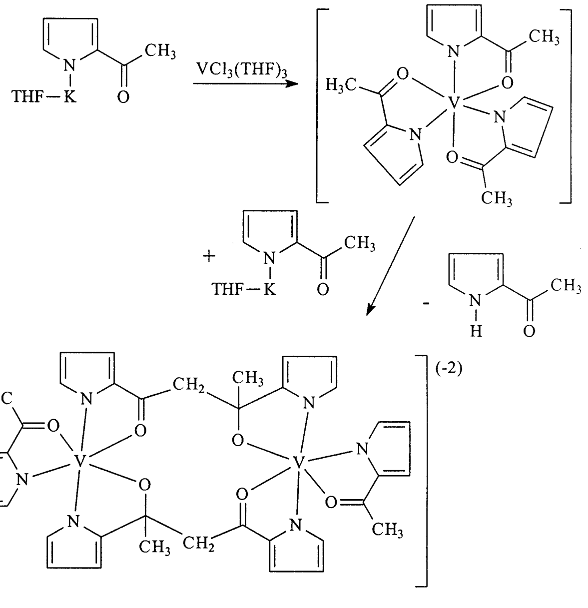


Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms and angles in degrees.

Scheme 1



1

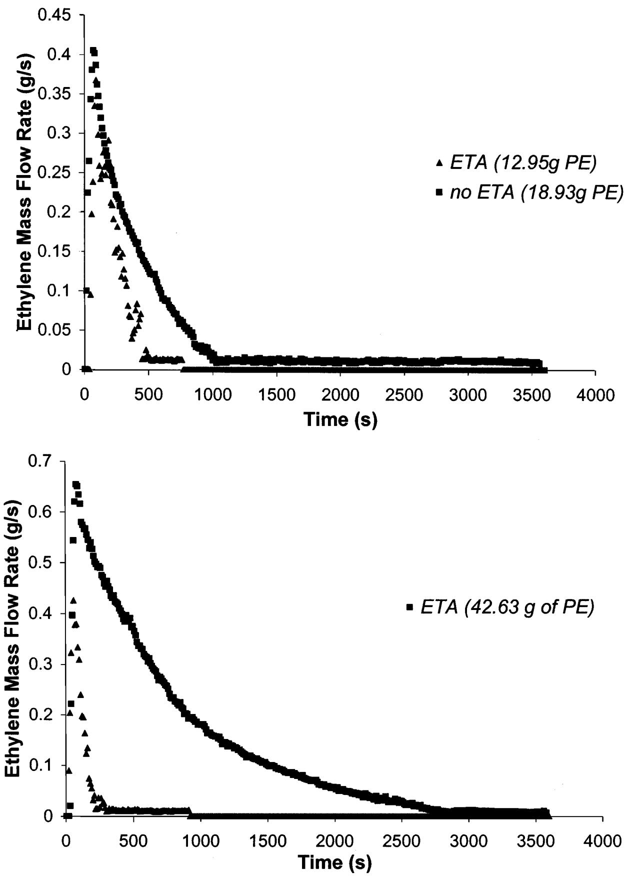


Figure 4. Diagram of the ethylene uptake versus time for **1** and **2** with and without addition of ETA.

reactions carried out with excess $K[\alpha\text{-}(CH_3CO)C_4H_3N]$ gave a substantial improvement of the reaction yield (from 25% to 68%).

Complex **1** is a versatile catalyst for ethylene homo-, co-, and terpolymerization (Table 1). For this study the investigation was limited to propylene, norbornene, and 1-hexene as comonomers. The activity of the catalyst activated by either diethylaluminum chloride (DEAC) or dimethylaluminum chloride (DMAC) and calculated on the basis of the amount of isolated polymer places this complex among the most active vanadium catalysts reported so far.[1,6−9] In addition, the average molecular weight of the polymer was substantially higher, while the polydispersity and composition remained comparable. As expected, the polyethylene samples were unexciting, displaying rather low molecular weight and broad polydispersity. The diagram of the ethylene uptake as a function of time recorded for an ethylene homopolymerization experiment (Figure 4) clearly indicated that the catalyst was active only in the first 16−17 min, after which no activity was longer observed. By assuming that even in this case the deactivation was the result of the reduction of the vanadium center to the divalent state, attempts to extend catalyst life were done by carrying out polymerization experiments in the presence of ethyl trichloroacetate (ETA) as a reactivating substance. The role of this particular compound in the chemistry of $V(acac)_3$ is believed to be that of reoxidizing intermediate V(II) species to a trivalent state capable of re-entering the catalytic cycle. To our surprise, the activity was substantially *decreased*, indeed indicating that a complete and irreversible catalyst deactivation occurred after only 8 min. Accordingly, the amount of polymer produced was also substantially lower. The detrimental effect of ETA suggests that (a) the divalent species resulting from the deactivation process either is not reoxidized by ETA or produces an inactive species upon oxidation and (b) the striking difference of behavior with the $V(acac)_3$ catalyst (where the employment of ETA is necessary to optimize catalyst performance) can only be ascribed to the presence of the acetylpyrrolide ligand, which therefore is likely to remain connected to the vanadium center. Finally, the nature of the aluminum alkyl cocatalyst (DMAC versus DEAC) has a rather strong influence on the activity. We speculate that this behavior is determined by the relative stability of the corresponding intermediate vanadium alkyl initiators (i.e. a V−Me function is likely to have a longer lifetime than the corresponding V−Et).

The rapid drop in catalytic activity of **1**, observed after the initial burst, is a rather common feature among vanadium-based Ziegler−Natta catalysts.[7] As mentioned above, this behavior is usually attributed to reduction of the metal center to the inactive divalent state, whose formation is in turn ascribed to poor stability of the vanadium organometallic functions formed during the catalytic cycle. In an attempt to verify these hypotheses or at least to gain some insight into the reactivation process of deactivated catalyst by mild oxidizing agents, we have attempted the synthesis of novel divalent vanadium complexes of the acetylpyrrolide ligand system. The aim was 2-fold: (a) to verify the inability of the divalent state to promote olefin polymerization under Ziegler−Natta conditions and (b) to understand the anomalous behavior of **1** with respect to the oxidation by ETA.

The reaction of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ with $K[\alpha\text{-}(CH_3CO)C_4H_3N]$ proceeded in two different manners, depending on the reaction stoichiometry. Reactions carried out with an excess of ligand afforded the dinuclear trivalent vanadium complex $\{VK(THF)[(C_4H_3N)C(O)CH_3]\}_2[(C_4H_3N)(CH_3)(O)CC(O)(CH_3)(C_4H_3N)]\cdot 0.5(toluene)$ (**2**) (Scheme 2). The $[(C_4H_3N)(CH_3)(O)CC(O)(CH_3)(C_4H_3N)]^{4-}$ tetraanion which bridges the two vanadium centers is the result of the pinacolic condensation of two acetylpyrrolide ligands. Given the strength of divalent vanadium as reductant, the reduction of one acetylpyrrolide ligand to the corresponding pinacol is not particularly surprising.[19] Thus, it is conceivable that a divalent species produced by the normal deactivation process may undergo an internal reoxidation reaction at the expense of the acetylpyrrolide ligand, re-forming a trivalent complex ready to re-enter the catalytic cycle. As a fascinating possibility, the high catalytic activity of **1** might be a direct consequence of this behavior. Accordingly, complex **2** also is an active catalyst for ethylene homo- and copolymerization, although it is slightly less active than **1** (Table 1). However, the kinetic profile of the ethylene polymerization reaction showed that the catalyst is active only during *the first 3 min*, after which the activity suddenly comes to an end

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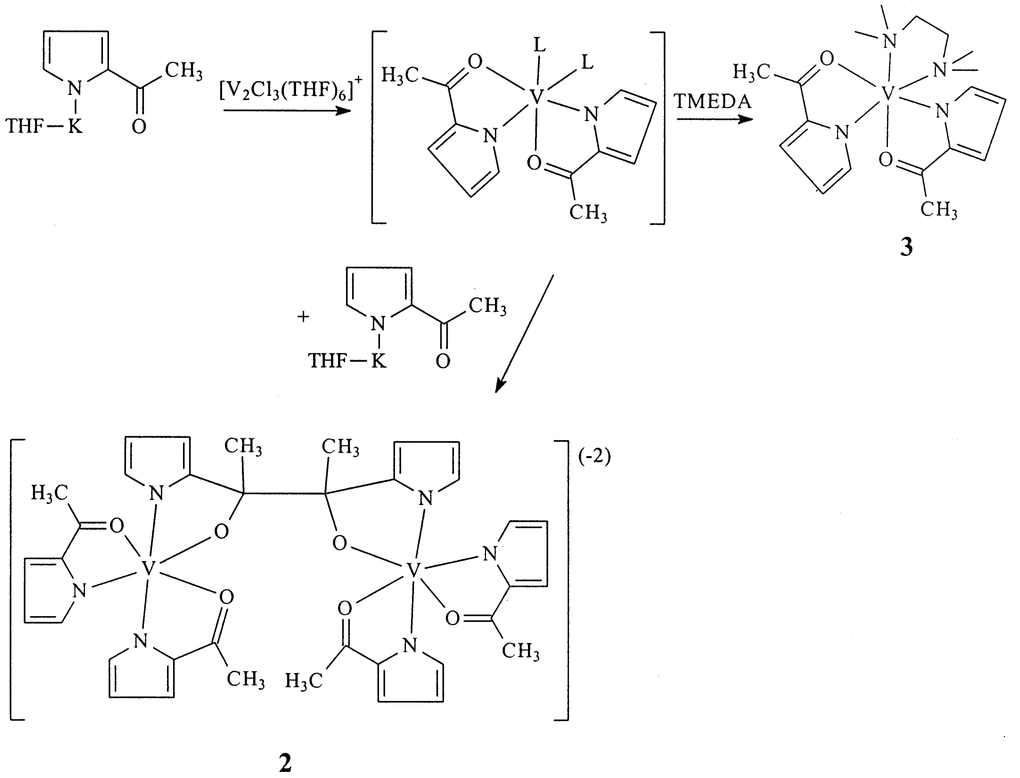
(19) (a) Hirao, T.; Hatano, B.; Imamoto, Y.; Ogawa, A. *J. Org. Chem.* **1999**, *64*, 7665. (b) Ogawa, A. *J. Org. Chem.* **1998**, *63*, 9604. (c) Hirao, T. *J. Org. Chem.* **1998**, *63*, 9421. (d) Ogawa, A. *J. Org. Chem.* **1998**, *63*, 2812.

Scheme 2



(Figure 4). Furthermore, when the polymerization reaction was carried out in the presence of ETA as a reactivating substance, the catalyst remained active for up to 45−46 min and the production of polyethylene was the highest ever observed for a vanadium catalyst (8526 g/(mmol/h)), comparable to that of the recently reported vanadium amidinate derivative.[11] The contrasting behavior between **1** and **2** with respect to the treatment with ETA dismisses the possibility that **2** may be generated by a divalent species, as obtained from the deactivation of **1**. Complexes **1** and **2** seem to be unrelated from a catalytic point of view, despite the structural similarities.

When the preparation of **2** was carried out with a stoichiometric ligand to V ratio of 2:1, a blue solution was obtained, possibly indicating that the vanadium atom was present in the divalent state. Unfortunately, attempts to grow crystals of suitable size only afforded microcrystalline material which was analyzed as $V[\alpha\text{-}(CH_3CO)C_4H_3N]_2(THF)_2$. The complex was derivatized via treatment with TMEDA, affording the mononuclear and divalent $V(TMEDA)[\alpha\text{-}(CH_3CO)C_4H_3N]_2$ (**3**). Analytical data were in agreement with the formulation of the complex, as obtained from the X-ray crystal structure. The magnetic moment was also as expected for the high-spin d^3 electronic configuration of vanadium. The isolation of a divalent compound in significant yield clearly indicates that *in the absence of excess acetylpyrrolide* no reductive coupling to form a pinacol may occur and that Lewis bases such as THF or TMEDA are necessary to stabilize the divalent species.

To our surprise, complex **3** displayed, despite the divalent state, a non-negligible catalytic activity in terms of ethylene polymerization, thus breaking the paradigm that divalent complexes should be inactive. However, the activity (550 g/(mol/h)) was indeed substantially lower than that of complexes **1** and **2**, whereas higher activity (1486 g/(mol/h)) was obtained via previous treatment of **3** with ETA.

Unfortunately, repeated attempts to isolate intermediate complexes derived from the direct interaction between the three complexes reported in this paper and a variety of alkylaluminum derivatives and even $AlCl_3$ as a model only afforded noncrystalline materials. Therefore, we can only speculate about the identity of the intermediate species and the factors responsible for the high activity of **1** and **2**. At this stage and on the basis of the different qualities of the produced polymers, we can only conclude that complexes **1** and **2** are not part of the same catalytic cycle and that their unusually high catalytic activity is the result of ligand resistance to leaching with consequent improved stability of the V−C bond. It is also tempting to speculate that the dinuclear nature of these complexes may also play an important role in improving the activity of the catalyst. The reduction of **1** to the divalent state, as usually occurring during the olefin polymerization reaction promoted by vanadium, cannot be responsible in the present case for the observed complete deactivation. In fact, a simple pinacolic type of reaction will regenerate another active catalyst that, by being more robust and more resistant to oxidizing agents, may last even longer. In addition, the fact that the divalent **3** is also catalytically active opens interesting perspectives for further research and mechanistic investigations.

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Supporting Information Available: Tables giving complete crystallographic data for complexes **1**–**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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