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Vanadium-Catalyzed Ethylene−Propylene Copolymerization: The Question of the Metal Oxidation State in Ziegler−Natta Polymerization Promoted by (β-diketonate)$_3$V

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Four different (β-diketonate)$_3$V complexes [β-diketonate = 2,4-pentanedione (*acac*), 2-acetylcyclohexanone (*Cy-acac*), 2,2,6,6-tetramethyl-3,5-heptanedione (*t-Bu-acac*), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (*F-acac*)] have been prepared and tested as catalysts for propylene−ethylene copolymerization with the aim of gaining insights into the structure of the active species. Data on polymer composition and catalyst activity indicate that one of the roles of the Al cocatalyst is to trigger a major ligand scrambling around the transition metal. Attempts to isolate the catalytically active species afforded a compound formulated as $\{[(\beta\text{-diketonate})AlCl_2][VCl_2][(\beta\text{-diketonate})_2AlCl]\}$. This species, which displayed only a minor catalytic activity, arises from a parasite process (catalyst deactivation). The formulation was supported by chemical degradation experiments with THF, which afforded a mixture of $[V_2Cl_3(THF)_6][AlCl_4]$ and $[(acac)_2Al(THF)_2][Al\ Cl_4]$ (**5**). Two unprecedented V(II) complexes (R-*acac*)$_2$V(TMEDA) [R = H(**7a**), Cy(**7b**), t-Bu (**7c**)] have been prepared and reacted with halocarbons to model the reactivation process. The results indicated that the primary role of reactivating substances, commonly employed in the industrial processes, is to reoxidize V(II) to the trivalent state. The reaction formed the catalyst precursor (R-*acac*)$_2$VCl(TMEDA), which was characterized on the basis of analytical and spectroscopic data. In agreement with this proposal, a trapping experiment carried out with $ZnCl_2$ or oxidation with CuCl allowed the isolation and characterization of (t-Bu-*acac*)$_2$V(TMEDA)][X] [X = $ZnCl_4^-$ (**8**), $CuCl_2^-$ (**9**)]. The structures of **5**, **7a**, **8,** and **9** have been elucidated by X-ray diffraction. Crystal data are as follows. **5:** triclinic space group $P\bar{1}$, $a = 8.916(3)$ Å, $b = 9.802(3)$ Å, $c = 15.390(5)$ Å, $\alpha = 88.156(4)°$, $\beta = 86.041(4)°$, $\gamma = 82.710(4)°$, $Z = 2$. **7a:** triclinic space group $P\bar{1}$, $a = 7.896(1)$ Å, $b = 10.032(2)$ Å, $c = 13.134(2)$ Å, $\alpha = 75.265(2)°$, $\beta = 88.520(2)°$, $\gamma = 71.445(2)°$, $Z = 2$. **8:** orthorhombic space group *Pbcn*, $a = 18.723(7)$ Å, $b = 19.675(7)$ Å, $c = 18.836(7)$ Å, $Z = 4$. **9:** monoclinic space group $C2/c$, $a = 13.676(5)$ Å, $b = 19.521(3)$ Å, $c = 13.206(3)$ Å, $\beta = 98.47(3)°$, $Z = 4$.

Introduction

The Ziegler−Natta olefin polymerization certainly is among the most famous catalytic processes discovered in this century. It is widely used worldwide for the large-scale production of polymers important to modern society. The process is very efficient, and a remarkable wealth of technology has been developed to improve even further its efficiency and stereoselectivity.[1] However, despite the enormous commercial interest involved in this science, the understanding of the mechanism remains limited. Major breakthroughs in this direction were obtained with the discovery of the cationic Ziegler−Natta catalysts[2] and, more recently, with the discovery that a cationic aluminum alkyl derivative may catalyze olefin polymerization in the absence of transition metals.[3] Today it is well established that an enhanced Lewis acidity and the employment of a large excess of Al-based cocatalyst are the recipe of a successful and efficient catalytic system. However, the recent discovery that some electron-rich late transition metal complexes may also act as powerful Ziegler−Natta catalysts[4] has rejuvenated the academic and industrial interest for a better understanding of these remarkable systems.

The main stream of research in this field has relatively ignored group V metals, and information remained mainly limited to the patent literature[5] until recently, when the appearance of a few reports[6] indi-

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[1] For recent review-articles on this vast topic see for example: (a) Toto, M.; Cavallo, L.; Corradini, P.; Moscardi, G.; Resconi, L.; Guerra, G. *Macromolecules* **1998**, *31*, 3431. (b) Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I.; Destro, M. *Macromolecules* **1998**, *31*, 3409. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (d) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118,* 1045.

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cated a revival of interest for vanadium-based Ziegler–Natta catalysis.[7] In fact, the current paucity of this literature is in striking contrast with the fact that vanadium catalysts are widely used for the industrial production of ethylene–propylene–diene elastomers (EPDM).[8] The most surprising peculiarity of this vanadium-based catalytic system consists of the employment of a coordinatively saturated V(β-diketonate)$_3$ complex containing vanadium in the trivalent oxidation state. Given its d^2 electronic configuration and the medium oxidation state, this species certainly cannot be considered as an "acidic" complex and somewhat deviates from the usual Ziegler–Natta paradigm. Therefore, the excellent activity of this particular catalytic system poses some fascinating mechanistic questions. The fact that the catalyst is coordinatively saturated implies that one of the functions of the Al cocatalyst is to trigger a major molecular reorganization around the transition metal. It is reasonable to assume that at least one of the *acac* ligands is abstracted by the Al cocatalyst to form a coordinatively unsaturated vanadium alkyl. On the other hand, it is well established that the chlorine content of the cocatalyst is a determining factor for the activity of the catalyst.[8] Thus, other questions arise about the structure of the catalyst and the role of the halogen. Is the active complex ionic with a positive charge on the transition metal or is it instead a species containing both vanadium and aluminum in the same molecular aggregate?[9]

The second point of interest concerns the oxidation state of the vanadium center during the catalytic cycle. The +3 oxidation state of vanadium is a fairly stable one, and a few examples of stable homoleptic alkyl derivatives have been reported in the literature.[10] On the other hand, the aluminum alkyl cocatalyst certainly has the sufficient reducing strength to lower the oxidation state of vanadium to the +2 state.[11a] In agreement with this idea, a recent report has suggested the possibility that an in situ generated V(II) alkyl complex might work as a catalyst precursor.[11b] In addition, some V(II) salts have been reported to be active ethylene polymerization catalysts.[11c] Conversely, ESR experiments have indicated that the oxidation state +2 might be inert toward polymerization, in agreement with the observation that vanadium catalysts typically die over the course of few minutes after displaying initially high polymerization rates.[12] Thus, the possible reduction of the V(β-diketonate)$_3$ catalyst is commonly regarded as a deactivating process.[11d] This idea is further supported by the fact that the employment of mild oxidizing agents (chlorinated esters or halocarbons) as catalyst reactivators is critical for the optimization of the catalytic cycle. The role of these substances is debated since in addition to reoxidizing the metal center to a higher

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oxidation state (+3 or +4) that is able to restart the cycle, they also react in a destructive manner with the cocatalyst. Since the catalyst oxidation state and the role of the reactivators remain speculative, we have carried out the present study with the aim to gain some insight into both the catalyst structure and the metal oxidation state of the catalytically active species.

Herein we describe our findings.

Experimental Section

All operations were performed under inert atmosphere with the use of standard Schlenck techniques or in a nitrogen-filled drybox. $VCl_2(TMEDA)_2$,[13] $VCl_3(THF)_3$,[14] V(*acac*)$_3$,[15] and $[V_2Cl_3(THF)_6][AlCl_4]$[16] were prepared according to published procedures. Solvents were dried by following standard procedures. NMR spectra were recorded on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a drybox. Ethyl trichloroacetate, 1,1,2-trichloroethane, 2,4-pentanedione (*acac*), 2-acetylcyclohexanone (*Cy-acac*), 2,2,6,6-tetramethyl-3,5-heptanedione (*t-Bu-acac*), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (*F-acac*) were purchased from Aldrich and dried using activated molecular sieves. Infrared spectra were recorded on Mattson 3000 FTIR spectrometer. Nujol mulls were prepared in the drybox. $Et_3Al_2Cl_3$, Et_2AlCl (DEAC), MeLi, and i-BuLi (Aldrich) were used as received. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods,[17] and corrections for underlying diamagnetism were applied to the data.[18]

Synthesis of V(*Cy-acac*)$_3$ (2). In a modification of a previously reported preparation[12e] an ether solution of MeLi (7.8 mL, 1.4 M) was added dropwise and under vigorous stirring at −78 °C to a solution of 2-acetylcyclohexanone (1.54 g, 11.0 mmol) in THF (100 mL). Stirring was continued for 1 h. After warming the reaction mixture to room temperature, the addition of $VCl_3(THF)_3$ (1.37 g, 3.7 mmol) resulted in a dark brown color. The reaction mixture was stirred overnight. The solvent was evaporated in vacuo, and the residual brown solid was resuspended in hexane (350 mL). After filtration of LiCl and partial removal of the solvent, the resulting solution was allowed to stand at −30 °C for 2 days, upon which brown microcrystals of **2** (1.0 g, 2.2 mmol, 59%) separated. Anal. Calcd (Found) for $VC_{24}H_{33}O_6$: C 61.53 (61.12), H 7.10 (7.33). IR (Nujol mull, cm^{-1}) ν: 1568(br, s), 1460(br, s), 1375(sh), 1261(m), 1166(m), 994(m), 962(m), 825(w), 711(w). $\mu_{eff} = 2.89\ \mu_B$.

Synthesis of V(*t-Bu-acac*)$_3$ (3). An identical procedure as per **2** was followed by using *t-Bu-acac*H (1.3 mL, 6.2 mmol) in THF (150 mL) and MeLi (4.5 mL 1.4 M). Yield: 0.70 g, 1.2 mmol, 57%. Anal. Calcd (Found) for $VC_{33}H_{57}O_6$: C 65.98 (65.17), H 9.56 (9.13). IR (Nujol mull, cm^{-1}) ν: 1539(s), 1501(s), 1462(s), 1382(s), 1357(s), 1224(m), 1175(m), 1144(m), 1021(m), 873(m), 795 (m), 761(w), 740(w), 628(m). $\mu_{eff} = 2.86\ \mu_B$

Synthesis of V(*F-acac*)$_3$ (4). An identical procedure as for **2** was followed by using *F-acac*H (0.9 mL, 6 mmol) in THF (150 mL) and MeLi (4.3 mL, 1.4 M) at −78 °C. Yield: 0.55 g, 0.82 mmol, 41%). Anal. Calcd (Found) for $VC_{15}H_3F_{21}O_6$: C 24.71 (25.08), H 0.41 (0.42). IR (Nujol mull, cm^{-1}) ν: 1596(s), 1524(s), 1456(s), 1419(s), 1381(s), 1358(s), 1275(m), 1190(w), 1163(m), 1020(m), 962(m), 825 (m), 711(m), 667(s). $\mu_{eff} = 2.90\ \mu_B$.

Reaction of (*acac*)$_3$V with $AlCl_3$. Preparation of [Al(*acac*)$_2$(THF)$_2$][$AlCl_4$] (5). Solid V(*acac*)$_3$ (0.97 g, 2.8 mmol) was dissolved in THF (150 mL) and treated with $AlCl_3$ (0.75 g, 5.6 mmol). The resulting solution slowly changed color from reddish brown to light yellow. After concentration to a small volume, the resulting solution was allowed to stand at −78 °C for 2 days, upon which colorless crystals of [Al(*acac*)$_2$(THF)$_2$][$AlCl_4$] separated (0.40 g, 0.74 mmol, yield 28%). Anal. Calcd (Found) for $Al_2C_{18}H_{30}O_6Cl_4$: C 40.17 (39.66), H 5.62 (5.67). IR (Nujol mull, cm^{-1}) ν: 1574(s), 1538(s), 1459(s), 1399(s), 1377(s), 1345(m), 1295(m), 1198(w), 1021(s), 953(m), 872(s), 808(s), 702(m), 660(m), 620(m). ^1H NMR (THF-d_8, 500 MHz, ppm) δ: 5.78 (2H, CH *acac*), 3.58 (CH_2 THF), 2.03 (12H, CH_3 *acac*), 1.74 (CH_2, THF). ^{13}C NMR (THF-d_8, 125.7 MHz, ppm) δ: 195.22 (C=O, *acac*), 103.92 (CH, *acac*), 68.598 (CH_2, THF), 26.855 (CH_3, *acac*), 26.351 (CH_2, THF). ^{27}Al NMR (THF-d_8, 130.3 MHz, ppm) δ: 102.57 (sharp s, [Al(*acac*)$_2$(THF)$_2$]$^+$), 3.01 (very broad, $[AlCl_4]^-$).

Reaction of V(*acac*)$_3$ with $EtAlCl_2$. The addition of a hexane solution of $EtAlCl_2$ (18 mL 1.0 M) to a solution of V(*acac*)$_3$ (2.1 g, 6.0 mmol) in toluene (150 mL) at room temperature changed instantaneously the color from reddish brown to brown. An insoluble light brown precipitate appeared almost immediately (2.6 g, 4.7 mmol, 78%) and was filtered after the mixture was stirred for 2 h. Redissolving the solid in THF (100 mL) turned the color light green. After filtration and concentration to small volume, the resulting solution was allowed to stand at −78 °C for 2 days, upon which a mixture of colorless crystals [Al(*acac*)$_2$(THF)$_2$][$AlCl_4$] (**5**) and light green crystals of $[V_2Cl_3(THF)_6][AlCl_4]$ (**6**) separated**.** The large size of the crystals allowed physical separation under the microscope, and analytically pure samples of **5** (0.5 g, 0.93 mmol, yield 10%) and **6** (0.7 g, 0.88 mmol, yield 29%) were obtained. Both compounds were identified by comparison of their spectroscopic data, crystallographic cell parameters, and combustion analysis data with those of analytically pure samples prepared according to literature procedures.[16]

Synthesis of V(*acac*)$_2$(TMEDA) (7a). A solution of *acac*H (0.58 mL, 5.7 mmol) in THF (150 mL) was treated with a solution of MeLi in ether (4.1 mL, 1.4 M) at −78 °C. Gas evolution took place, and the mixture was maintained under vigorous stirring for 1 h while warming to room temperature. $VCl_2(TMEDA)_2$ (0.88 g, 2.8 mmol) was added to the mixture. The resulting dark violet-blue solution was stirred for several hours. The solution was evaporated to dryness and the residual solid redissolved in hexane (50 mL). A small amount of insoluble and colorless material was eliminated by filtration, and the filtrate was allowed to stand at −30 °C for 2 days. Dark violet-blue crystals of **7a** separated (0.51 g, 1.4 mmol, yield 50%). Anal. Calcd (Found) for $VC_{16}H_{30}N_2O_4$: C 52.60 (52.68), H 8.28 (8.33), N 7.67 (7.34). IR (Nujol mull, cm^{-1}) ν: 1576(s), 1522(s), 1457(s), 1376(s), 1283(s), 1190(s), 1124(m), 1017(s), 953(s), 924(s), 796(s), 756(s), 654(s). $\mu_{eff} = 3.58\ \mu_B$.

Synthesis of (*Cy-acac*)$_2$V(TMEDA) (7b). An identical procedure as per **7a** was followed by using freshly distilled *Cy-acacH* (1.47 mL, 11.3 mmol) in THF (100 mL) and NaH (0.27 g, 11.3 mmol) at room temperature. Yield: 1.49 g, 3.34 mmol, 59%. Anal. Calcd (Found) for $VC_{20}H_{38}N_2O_4$: C 57.00 (56.86), H 9.09 (9.01), N 6.65 (6.65). IR (Nujol mull, cm^{-1}): 1571(s), 1510(m), 1462(m), 1411(s), 1378(s), 1327(m), 1285(m), 1256(m), 1167(m), 1078(m), 1027(m), 1005(w), 993(w), 920(m), 853(m), 722(w), 652(m), 566(w). $\mu_{eff} = 3.79\ \mu_B$.

Synthesis of (*t-Bu-acac*)$_2$V(TMEDA) (7c). An identical procedure as per **7a** was followed by using freshly distilled *t-Bu-acacH* (2.36 mL, 11.3 mmol) in THF (100 mL) and NaH (0.27 g, 11.3 mmol) at room temperature. Yield: 1.69 g, 3.16 mmol, 56%. Anal. Calcd (Found) for $VC_{28}H_{52}N_2O_4$: C 63.02 (62.99), H 10.20 (10.14), N 5.25 (5.17). IR (Nujol mull, cm^{-1}):

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Table 1.

	V(*acac*)$_3$ (**2**)		V(*Cy-acac*)$_3$ (**2**)		V(*t-Bu-acac*)$_3$ (**3**)		V(*F-acac*)$_3$ (**4**)	
	DEAC	EASC	DEAC	EASC	DEAC	EASC	DEAC	EASC
activity[a]	994	980	1168	990	746	622	762	800
$M_w \times 10^3$	219	702	218	716	290	1265	277	801
M_w/M_n	2.3	2.5	2.3	2.2	2.2	2.4	2.2	2.3
% ethylene	62	52	59	53	65	57	63	54

[a] Kg EP elastomer produced in 30 min by 1 mol of vanadium catalyst; DEAC = Et_2AlCl, EASC = $Et_3Al_2Cl_3$.

1559(s), 1510(s), 1456(m), 1398(s), 1376(s), 1285(m), 1256(m), 1188(m), 1125(m), 1099(m), 1058(m), 1005(s), 955(m), 920(m), 797(m), 755(m), 722(w), 652(m), 566(w). $\mu_{eff} = 3.82\ \mu_B$.

Reaction of (*acac*)$_2$V(TMEDA) with 1,1,2-Trichloroethane. A solution of V(Cy-acac)$_2$(TMEDA) (2.0 g, 4.5 mmol) in toluene (100 mL) was treated with 1 equiv of 1,1,2-trichloroethane (0.42 mL, 4.5 mmol). The color of the solution immediately changed from dark blue to reddish brown. After stirring the mixture overnight, the solvent was evaporated in vacuo, affording a green precipitate of (*Cy-acac*)VCl$_2$(TMEDA) (0.77 g, 2.0 mmol, 45%). Anal. Calcd (Found) for $VC_{14}H_{27}O_2N_2Cl_2$: C, 44.58 (44.63); H, 7.21 (7.19); N, 7.43 (7.38). IR (Nujol mull, cm^{-1}): 1572 (s), 1463.7 (s), 1414 (s), 1378 (s), 1365(s), 1352(s), 1322(s), 1279(s), 1251(s), 1172(s), 1135(m), 1121(w), 1101(w), 1074(w), 1061(w), 1043(m), 1031(m), 1018(s), 997(s), 963(s), 952(s), 928(m), 901(w), 887(m), 859(m), 817(m), 803, 765(w), 722(m), 709(s), 657(m) 636(w), 591(w), 570(w). $\mu_{eff} = 2.77\ \mu_B$.

The mother liquor was evaporated to dryness under reduced pressure and the residual solid redissolved in freshly distilled ether (100 mL). (*Cy-acac*)$_3$V precipitated after concentration of the solution and cooling to −20 °C (0.8 g, 1.7 mmol, 38%). The compound was identified by comparison of the analytical and spectroscopic properties with those of an analytically pure sample.

Synthesis of [(*t-Bu-acac*)$_2$V(TMEDA)]$_2$[ZnCl$_4$] (8). A mixture of [(*t-Bu-acac*)$_2$V(TMEDA)] (1 g, 1.8 mmol) with excess ZnCl$_2$(THF)$_2$ was added to a dry toluene solution (100 mL) containing 3 equiv of ethyl trichloroacetate (0.75 mL, 5.4 mmol). Stirring for 12 h resulted in a drastic color change from dark blue to a reddish brown. After partial removal of the solvent in vacuo, the solution separated as red cubic crystals of **8** (0.22 g, 0.17 mmol, 19%) upon standing at room temperature for a few hours. Anal. Calcd (Found) for $V_2C_{56}H_{108}O_8N_4ZnCl_4$: C, 52.77 (52.82); H, 8.54 (8.55); N, 4.40 (4.41). IR (Nujol mull, cm^{-1}): 1561(s), 1510(s), 1456(m), 1376(s), 1286(m), 1186(m), 1125(m), 1098(m), 1057(m), 1003(s), 953 (m), 920(m), 798(m), 755(m), 722(w), 654(m), 566(w); $\mu_{eff} = 2.82\mu_B$.

Synthesis of [(*t-Bu-acac*)$_2$V(TMEDA)][CuCl$_2$] (9). A crystalline sample of **8** (2.00 g, 3.3 mmol) was dissolved in toluene (100 mL). Upon addition of excess anhydrous CuCl (0.49 g, 4.9 mmol), there was no immediate color change. The mixture was stirred and heated at 110 °C for 12 h, upon which a dark burgundy red solution was formed. The solution was filtered to eliminate some colloidal copper and excess CuCl. The solution was concentrated in vacuo and allowed to stand overnight at room temperature. Burgundy red crystals of [(*t-Bu-acac*)$_2$V(TMEDA)]$^+$[CuCl$_2$]$^-$ separated (0.80 g, 1.2 mmol, yield 36%). Anal. Calcd (Found) for $VC_{28}H_{54}N_2O_4CuCl_2$: C 50.33 (50.21), H 8.15 (8.09), N 4.19 (4.13). IR (Nujol mull, cm^{-1}): 1582(s), 1531(s), 1456(s), 1376(s), 1327(m), 1286(m), 1172(m), 1036(s), 921(m), 853(s), 722(m), 668(m). $\mu_{eff} = 3.92\ \mu_B$.

General Polymerization Procedure. Catalysts were evaluated by copolymerizing ethylene−propylene in cyclohexane solutions at 2 bar total pressure and 22 °C. Experiments were carried out in 200 mL of cyclohexane in magnetically agitated glass reactors using a continuous flow of 1000 sccm ethylene and 1000 sccm propylene. After equilibration of the cyclohexane with the EP feed, 0.2 mmol of cocatalyst were added followed by 5 μmol of V(β-diketonate)$_3$ containing a chlorinated ester such as ethyl trichloroacetate. The total amount of reactivating substance added to the reaction mixture was 20 μmol. Polymerization reactions were carried out for 30 min followed by addition of 5 mL of ethanol and depressurization. The EP rubber was recovered by solvent evaporation and dried in a vacuum oven at 60 °C. The polymer composition was determined by FTIR using the ratio of peak heights of the bands at 1155 and 720 cm^{-1} after calibration with standard samples. The molecular weights were determined by GPC at 140 °C by using trichlorobenzene as a solvent. The molecular weights are reported as polystyrene equivalents.

Structural Studies. Suitable crystals were mounted with cooled, viscous oil on thin, glass fibers. Data were collected on a Bruker SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. No absorption corrections were required. The reflection data for **9** were uniquely consistent for the reported space group. No symmetry higher than triclinic was observed for **7a** and **5**. The reflection data for **5** were consistent for *Cc* and *C*2/*c*. For **7a**, **5,** and **8**, solutions in the centric option yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with subsequent Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2.

The copper atom of **9** and the zinc atom of **8** are located on 2-fold axes of symmetry. Two, symmetry-unique, half-molecules of the cation in **5** are each located on an inversion center. One of the two half-cations has a coordinated molecule of THF that is disordered in two contributing conformational forms with a 60/40 site occupancy distribution.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned with idealized geometry and constrained with an isotropic riding model. Crystallographic details are presented in Table 2. Selected bond distances and angles are given in Table 3. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1997, WI).

Complex 5. The structure consists of two distinct ionic fragments (Figure 1). The cation is formed by an octahedral aluminum atom sorrounded by two *acac* ligands [Al(1)−O(3) = 1.846(4) Å, Al(1)−O(4) = 1.843(4) Å] and two molecules of THF [Al−O(6) = 1.953(4) Å] in an overall regular octahedral coordination geometry [O(3)−Al(1)−O(4) = 92.8(2)°, O(3)−Al−O(6) = 90.1(2)°, O(4)−Al−O(6) = 90.1(2)°, O(3)−Al(1)−O(4a) = 87.2(2)°]. The two *acac* ligands define the symmetry-generated equatorial plane of the octahedron [O(3)−Al(1)−O(3a) = 180.0°, O(4)−Al(1)−O(4A) = 179.997(1)°], while the two molecules of THF are lying trans to each other on the vertical axis [O(6)−Al(1)−(O6a) = 180.0°]. The anion is a regular tetrahedral AlCl$_4^-$ anion [Al(3)−Cl(1) = 2.100(3) Å°, Cl(1)−Al(3)−Cl(2) = 109.6(2)°]. The structure of **5** is another of the few examples of cationic aluminum species.[3,19]

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Table 2. Crystal Data and Structure Analysis Results

	5	7a	8
formula	$Al_2C_{18}H_{30}O_6Cl_4$	$VC_{16}H_{30}N_2O_4$	$C_{56}H_{108}N_4O_8V_2ZnCl_4$
fw	538.18	365.36	1274.51
space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	orthorhombic, *Pbcn*
a (Å)	8.916(3)	7.896(1)	18.723(7)
b (Å)	9.802(3)	10.032(2)	19.675(7)
c (Å)	15.390(5)	13.134(2)	18.836(7)
α (deg)	88.156(4)	75.265(2)	
β (deg)	86.041(4)	88.520(2)	
γ (deg)	82.710(4)	71.445(2)	
V (Å^3)	1330.7(7)	952.1(3)	6939(4)
Z	2	2	4
radiation (Kα, Å)	0.71073	0.71073	0.71073
T (K)	213(2)	173(2)	213(2)
D_{calcd} (g cm^{-3})	1.343	1.274	1.220
μ_{calcd} (cm^{-1})	5.40	5.40	8.08
F_{000}	560	390	2720
R, R_w^2,[a] GoF	0.1288, 0.2114, 1.114	0.0786, 0.1921, 1.089	0.0636, 0.1722, 1.010

[a] $R = \sum F_o - F_c/\sum F_o R_w = [(\sum(F_o - F_c)^2/\sum wF_o^2)]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 5, 7a, and 8

5	7a	8
Al(1)−O(4) = 1.843(4)	V−O(4) = 2.042(4)	V−O(3) = 1.936(4)
Al(1)−O(3) = 1.846(4)	V−O(2) = 2.051(4)	V−O(4) = 1.957(4)
Al(1)−O(6) = 1.953(4)	V−O(1) = 2.057(4)	V−O(2) = 1.961(4)
Al(3)−Cl(1) = 2.100(3)	V−O(3) = 2.065(4)	V−O(1) = 1.963(4)
Al(3)−Cl(2) = 2.119(3)	V−N(2) = 2.239(4)	V−N(2) = 2.169(6)
Al(3)−Cl(3) = 2.125(3)	V−N(1) = 2.243(5)	V−N(1) = 2.172(6)
Al(3)−Cl(4) = 2.130(3)	O(4)−V−(2) = 91.4(2)	O(1)−C(5) = 1.272(8)
O(4a)-Al(1)−O(4) = 179.997(1)	O(4)−V−O(1) = 94.2(2)	O(2)−C(7) = 1.307(8)
O(4a)-Al(1)−O(3) = 92.8(2)	O(2)−V−O(1) = 88.0(2)	O(3)−C(16) = 1.285(9)
O(4)−Al(1)−O(3a) = 87.2(2)	O(4)−V−O(3) = 88.4(2)	O(4)−C(18) = 1.289(8)
O(4a)-Al(1)−O(3) = 87.2(2)	O(2)−V−O(3) = 179.8(2)	Zn−Cl(1) = 2.277(2)
O(4)−Al(1)−O(3) = 92.8(2)	O(1)−V−O(3) = 92.0(2)	Zn−Cl(2) = 2.279(2)
O(3)−Al(1)−O(3) = 180.0	O(4)−V−N(2) = 92.6(2)	O(3)−V−O(4) = 87.82(18)
Cl(1)−Al(3)−Cl(3) = 109.6(2)	O(2)−V−N(2) = 87.4(2)	O(3)−V−O(2) = 87.97(19)
Cl(1)−Al(3)−Cl(4) = 109.8(2)	O(1)−V−N(2) = 171.9(2)	O(4)−V−O(2) = 173.87(18)
Cl(2)−Al(3)−Cl(4) = 108.23(13)	O(3)−V−N(2) = 92.6(2)	O(3)−V−O(1) = 96.03(18)
Cl(1)−Al(3)−Cl(3) = 110.08(14)	O(4)−V−N(1) = 173.3(2)	O(4)−V−O(1) = 88.71(18)
	O(2)−V−N(1) = 90.6(2)	O(2)−V−O(1) = 87.31(18)
	O(1)−V−N(1) = 92.2(2)	O(3)−V−N(2) = 90.3(2)
	O(3)−V−N(1) = 89.7(2)	O(4)−V−N(2) = 93.8(2)
	N(2)−V−N(1) = 81.1(2)	O(2)−V−N(2) = 90.7(2)
		O(1)−V−N(2) = 173.3(2)
		O(3)−V−N(1) = 172.6(2)
		O(4)−V−N(1) = 91.5(2)
		O(2)−V−N(1) = 93.3(2)
		O(1)−V−N(1) = 91.3(2)
		N(2)−V−N(1) = 82.4(2)

Complex 7a. The crystal structure is composed of discrete monomeric units containg a vanadium atom in a slightly distorted octahedral environment. Two *acac* ligands [V−O(1) = 2.057(4) Å, V−O(2) = 2.051(4) Å, V−O(3) = 2.065(4) Å, V−O(4) = 2.042(4) Å] and one TMEDA [V−N(1) = 2.243(5) Å, V−N(2) = 2.239(4) Å] defined the coordination octahedron [O(1)−V−O(2) = 88.0(2)°, O(1)−V−N(1) = 92.2(2)°, O(1)−V−O(3) = 92.0(2)°, O(1)−V−O(4) = 94.2(2)°, O(1)−V−N(1) = 92.2(2)°, O(1)−V−N(2) = 171.9(2)°] (Figure 2).

Complex 8. The structure consists of three separate ionic units. The two identical cationic vanadium moieties are octahedral, with two *acac* ligands and one TMEDA defining the vertexes of a distorted octahedron [O(1)−V−O(2) = 87.31(18)°, O(1)−V−O(3) = 96.03(18)°, O(1)−V−O(4) = 88.71(18)°, N(1)−V−N(2) = 82.4(2)°, O(1)−V−N(1) = 91.3(2)°, O(1)−V−N(2) = 173.3(2)°]. Both the V−N and V−O bond distances [V−N(1) = 2.172(6) Å, V−O(1) = 1.963(4) Å, V−O(2) = 1.961(4) Å] and angles are as expected and compare well with those of (*acac*)$_3$V.[15] The anion is formed by a zinc atom surrounded by four chlorine atoms defining a rather regular tetrahedron with normal bond distances [Zn−Cl(1) = 2.277(2) Å] and angles [Cl(1)−Zn−Cl(2) = 11.07(8)°] (Figure 3). The relatively large thermal parameters of some of the methyl carbon atoms and of the TMEDA CH$_2$ groups are probably indicative of some rotational and conformational disorder.

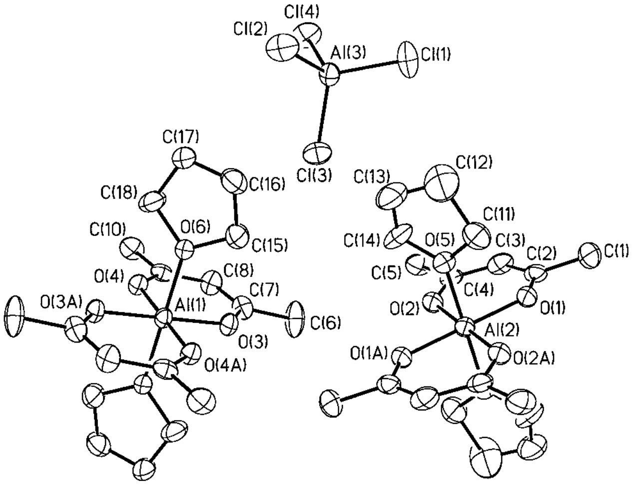
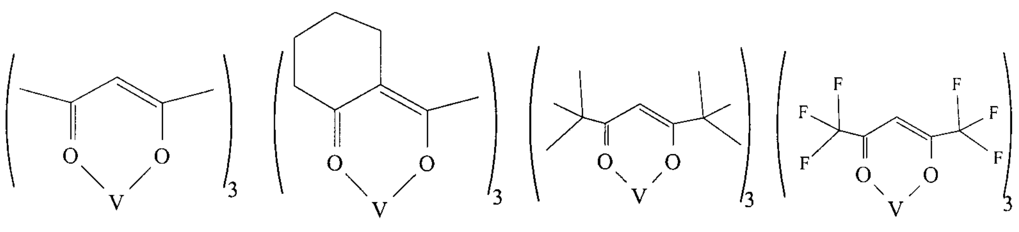


Figure 1. Thermal ellipsoid plot of **5**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 1



acac **1** *Cy-acac* **2** *t-Bu-acac* **3** *F-acac* **4**

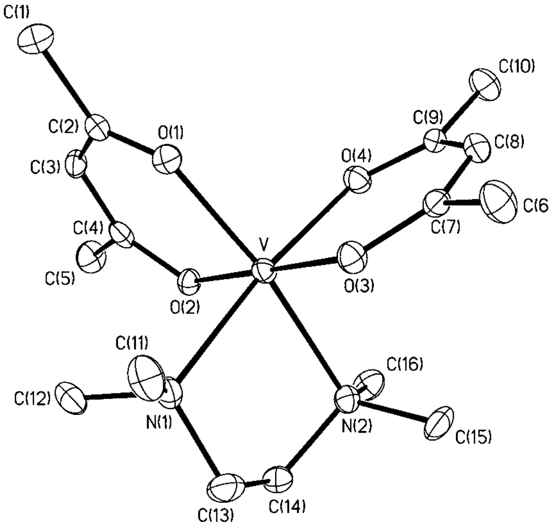


Figure 2. Thermal ellipsoid plot of **7a**. Thermal ellipsoids are drawn at the 30% probability level.

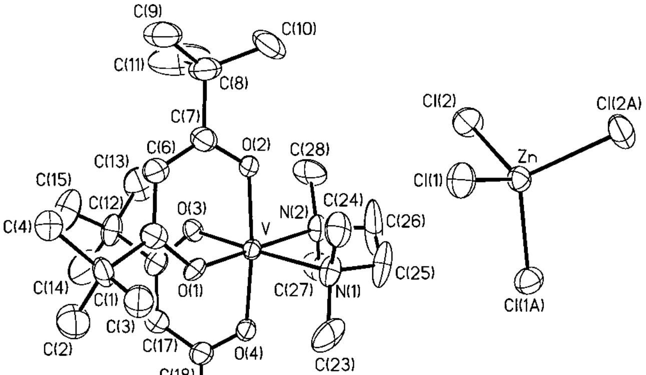


Figure 3. Thermal ellipsoid plot of **8**. Thermal ellipsoids are drawn at the 30% probability level.

Complex 9. The complex is isomorphous with **8** except for the anionic fragment which consists of a linear $CuCl_2$ anion [Cu−Cl(1) = 2.0863(13) Å, Cl(1)−Cu−Cl(1a) = 180.00(8)°] (for further details on this crystal structure see the Supporting Information).

Results and Discussion

Four (R-*acac*)$_3$V complexes were prepared (Scheme 1) in order to study the effect of the steric and electronic features of the various ligands on catalyst activity. By selecting the *Cy-acac* ligand we expected to obtain higher solubility while preserving almost unchanged the steric and electronic properties of the basic *acac* ligand. It was hoped that higher solubility would give better chances for isolating the catalytically active species in crystalline form. By using the *t-Bu-acac* ligand we expected to be able to evaluate the influence of steric factors on the catalytic process. The fluorinated *F-acac* ligand was expected to modify mainly the electronic features while maintaining the steric bulk of the catalyst very close to that of *t-Bu-acac*. The vanadium dionate complexes employed in this study were prepared following standard procedures and were characterized by combustion analysis, IR spectroscopy, and single-crystal X-ray analysis. Magnetic moments consistent with the high-spin d^2 electronic configuration were obtained in all cases.

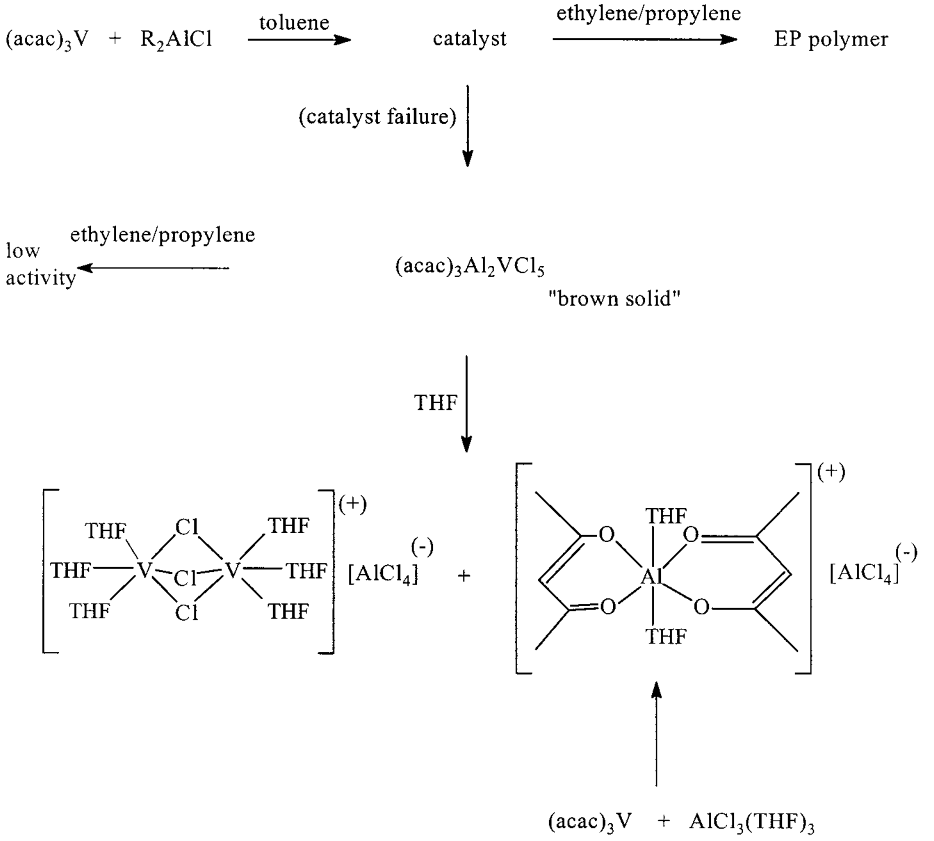
The catalytic activity of the various complexes was tested for ethylene−propylene copolymerization in the presence of catalyst reactivator. The results are summarized in Table 1.

The results clearly indicated that the activities of **1** and **2** are comparable in the presence of DEAC and EASC and are only slightly higher with respect to the two more crowded **3** and **4**. Surprisingly, the chlorine content of the cocatalyst and the steric hindrance of the *R-acac* ligand have only minor effects on the catalytic activity. Even more surprising, complexes of the two bulky *t-Bu-acac* and *F-acac* ligands show comparable activity despite considerably different electronegativity. Examination of the data in Table 1 reveals that the propylene content in the EP elastomers decreases in the case of the sterically encumbered **4** and **3** catalysts but, again, only to a very modest extent.

The insensitivity of both the catalyst activity and polymer composition to a large variation of ligand steric hindrance and electronic features strongly indicates that the catalytic site is widely open and probably far from the β-diketonate ligand. Thus, a primary role of the aluminum cocatalyst is that of abstracting at least two if not all three *acac* ligands from the vanadium center. The variation of only 5−10% in polymer composition observed by changing the cocatalyst Lewis acidity is also in line with this rationale. A relatively minor increase of the Lewis acidity of the cocatalyst as in the case of EASC probably increases the extent of migration of the *acac* ligand from vanadium, thus decreasing further the selectivity.

The polymerization reactions were typically carried out in hydrocarbon solvents since the employment of coordinating solvents such as ethers is well-known to quench the polymerization. For this reason, attempts to isolate and characterize the catalytically active species were carried out by mixing together catalyst and

Scheme 2



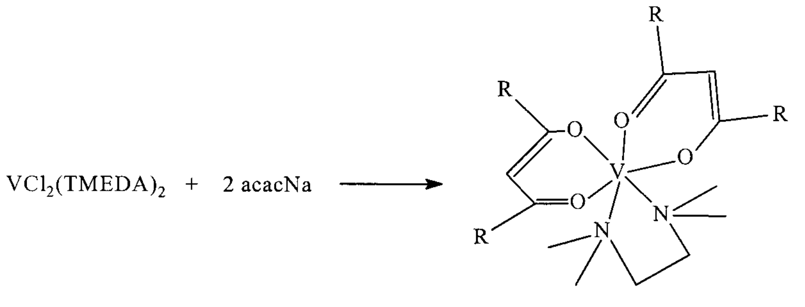
cocatalyst in toluene with variable ratios and without exposure to reactivators. Similar results were also obtained in hexane. This was of course an oversimplification of the real catalytic system which *requires* the presence of reactivating substances for higher catalyst productivity. Nevertheless, we felt that this strategy might help to evaluate the intriguing role of these substances and to shed some light on the structure of the catalyst.

Different from the catalytic system where a large excess of cocatalyst is imperative to enhance catalyst efficiency, the nature of the isolated product proved to be rather insensitive to the stoichiometric ratio. Typically, reactions carried out with the ratio of 1:1, 1:3 or higher produced the same poorly soluble, brown and paramagnetic material in 78% yield based on the proposed formulation (Scheme 2). The magnetic moment of this compound [$\mu_{\mathrm{eff}} = 3.75\ \mu_{\mathrm{B}}$] is also consistent with the d^3 electronic configuration of a V(II) center. This solid is pyrophoric and reacts with moisture to yield negligible amounts of ethane. Although combustion analysis data were inconclusive due to the extreme air-sensitivity of this solid, XRF data consistently yielded a V/Cl/Al ratio of 1:5:2. The IR spectrum clearly indicated the presence of the *acac* ligand. Once placed in cyclohexane or toluene and exposed to a mixture of ethylene and propylene, this solid displayed a minimal polymerization activity without need of additional cocatalyst and of catalyst reactivator. Further addition of cocatalysts did not affect the catalytic activity.

These observations together with the high yield indicate that the brown solid is a deactivated catalyst. Unfortunately, repeated attempts to grow suitable crystals for X-ray analysis were frustrated by the low solubility in hydrocarbon solvents. Therefore, we have attempted to indirectly identify the nature of this species via degradation (Scheme 2). Treatment of the "brown solid", obtained from the direct reaction of the catalyst with the aluminum cocatalyst, with THF yielded a bright green solution, from which a green crystalline mass, mixed together with white crystals, was obtained. In the case of the *acac* ligand (complex **1**) the structures of both compounds were elucidated by X-ray analysis. The green crystals are $[V_2Cl_3(THF)_6][AlCl_4]$ containing vanadium in the formal oxidation state +2 and whose crystal structure was previously reported.[16] The white crystals are the unprecedented ionic $[(acac)_2Al(THF)_2][AlCl_4]$ complex. This species was also conveniently prepared in analytically pure form by reacting $(acac)_3V$ with $AlCl_3$ or, more simply, through direct treatment of $AlCl_3(THF)_3$ with 1 equiv of *acac*Na in THF.

These findings indicate that the cocatalyst plays the dual role of (1) *completely* abstracting the *acac* ligands from the vanadium center and (2) reducing vanadium to its divalent state. In fact, the treatment of the "brown solid" with THF is unlikely to trigger a redox process, although the possibility that the divalent **6** might be generated by a disproportionation reaction cannot be categorically excluded at this stage. However, the neatness of the reaction and the fact that the visible region of the UV–vis spectrum of the mother liquor was basically identical to that of **6** discourage the idea that other high-valent vanadium species may be present in significant amount in the reaction mixture. By reducing vanadium, the aluminum cocatalyst deactivates the catalyst. On the basis of the XRF and the results of the above degradation experiment, we speculate that the

Scheme 3

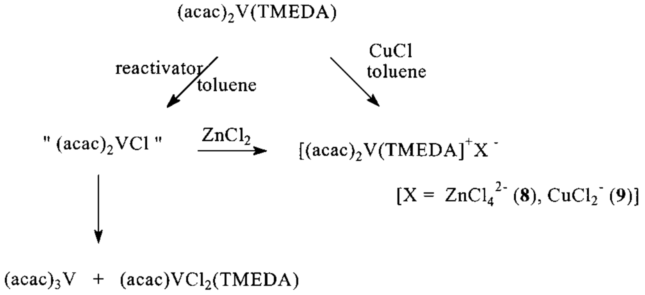


[R = H, **7a**; Cy, **7b**; t-Bu, **7c**]

brown deactivated catalyst has the formulation {[(β-diketonate)$AlCl_2$][VCl_2][β-diketonate$)_2$AlCl]}. The reduction of the vanadium center can be envisioned as occurring via β-hydrogen elimination from the corresponding V(III) alkyl derivative (Scheme 2). This is suggested by the presence of small amounts of hydrogen and ethane in the reaction mixtures obtained upon reacting in preparative scale the catalyst with a stoichiometric amount of cocatalyst. Obviously the structures of both catalyst and deactivated catalyst are purely putative. However, they are consistent with all the findings described above. They contain the appropriate ratio of heavy elements. The absence of *acac* ligands on the vanadium center is furthermore consistent with the relative insensitivity of the catalyst activity and polymer composition to the nature of the *acac* ligand.

Since the brown product isolated from the reaction catalyst/cocatalyst is a very poor catalyst, at first glance this seems to contradict the claims that V(II) species might be active catalysts.[11b] We have tested the activity of [$V_2Cl_3(THF)_6$][$AlCl_4$] and of other V(II) derivatives [e.g., $VCl_2(TMEDA)_2$, $V_2Cl_5(TMEDA)_3^+$, $V(BH)_4(THF)_3$] under the usual reaction conditions, finding only a negligible amount of polymerization in comparison to the β-diketonate V(III) complexes used in this work. Some activity was observed in the presence of reactivator, but the overall polymerization capability always remained very low. While it is very possible that the presence of THF in the coordination sphere of vanadium is responsible in this particular case for the lack of catalytic activity, on the other hand, the “brown solid” is a much less efficient catalyst in comparison with the catalysts prepared in situ. Therefore, the “brown solid” is a deactivated form of the catalyst, and since vanadium is present in this species in the oxidation state +2, reduction of the metal center indeed corresponds to catalyst deactivation. In an attempt to substantiate this hypothesis, we have attempted the preparation of a V(II) complex containing the *acac* ligand and to study its behavior in the presence of cocatalysts and with or without reactivators. The (*R-acac*$)_2$V(TMEDA) complexes [*R* = H (**7a**), Cy (**7b**), t-Bu (**7c**)] were prepared as described in Scheme 3 via straightforward chlorine replacement reaction on $VCl_2(TMEDA)_2$ by the corresponding β-diketonate sodium salt. The complexes were isolated in good yield and crystalline form after suitable workup. These unprecedented species were characterized on the basis of combustion analysis data, while the connectivity was elucidated by an X-ray crystal structure in the case of **7a**. The complex displays a value of the magnetic moment as expected for the d^3 electronic configuration.

Scheme 4



Complexes **7** are certainly not an ideal substrate to model the catalyst reactivation process. Two ligands are still attached to the vanadium atom, while this is unlikely to happen during the catalytic cycle, where the transition metal probably retained no more than one *acac* (if any). Furthermore, the presence of coordinated TMEDA in the coordination sphere of vanadium, necessary to prevent rapid disproportionation toward the formation of (*acac*$)_3$V, could be detrimental to the catalytic process. Nevertheless, we expected that TMEDA would be easily abstracted by the excess cocatalyst, thus overturning its undesirable presence. Also, the presence of the β-diketonate ligand is certainly necessary to the catalytic cycle since simple vanadium(II) and -(III) halide salts display much lower or no activity.[11c]

As expected, complex **7** does not polymerize olefins under the usual reaction conditions in the presence of cocatalyst and in the absence of reactivating substances. This reinforces the idea that V(II) species, formed during the catalytic cycle, are unreactive or only poorly reactive toward polymerization, and thus their formation indeed accounts for the catalyst failure during the cycle. Conversely, treatment of toluene solutions of complexes **7** with reactivator (for example, 1,1,2-trichloroethane) suddenly changed color from blue to brown-red, and subsequent addition of excess DEAC gave a moderate polymerization activity (153 kg polymer/ cat./20 min) despite the detrimental presence of 1 equiv of TMEDA in the mixture (Scheme 4). Attempts to isolate the product of the reaction were carried out in the case of **7b.** The reaction with ethyl trichloroacetate yielded a mixture of the green (*Cy-acac*)VCl_2(TMEDA) and the red-brown (*Cy-acac*$)_3$V, which were separated and identified. We propose that both products arise from ligand disproportionation of the intermediate (*acac*$)_2$VCl-

(TMEDA). In fact, a similar reaction of **7a** with reactivators carried out in the presence of $ZnCl_2$ afforded red crystals of $[(acac)_2V(TMEDA)]_2[ZnCl_4]$ (**8**). This new compound is paramagnetic and provides satisfactory analytical data consistent with the formulation revealed by the X-ray crystal structure.

Similarly, oxidation of **7a** with excess CuCl in hot toluene led to the formation of an ionic complex $[(acac)_2V(TMEDA)][CuCl_2]$ (**9**) also containing the same cation of complex **8**.

Conclusions

While further work will be necessary in the future to elucidate the structure of the catalyst and fully understand the reactivation step in the catalytic cycle, the results described above have allowed the clarification of some aspects of the vanadium-catalyzed ethylene−propylene copolymerization. The nature of the *acac* ligand has a surprisingly minor effect on the catalyst activity, thus indicating that an almost complete migration of the ligand from the vanadium center occurs during the process. With this respect, one of the roles of the aluminum cocatalyst is certainly that of abstracting the ligand from the metal center. This work reiterated the idea that V(II) species, largely produced during the polymerization process, are inactive in polymerization. The role of the reactivating substances is that of restoring the original trivalent oxidation state of vanadium and perhaps to reform the $(acac)_3V$ catalyst via ligand scrambling.

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Supporting Information Available: Listing of atomic coordinates, thermal parameters, and bond distances and angles for **5**, **7a,** and **8**. Crystallographic details and ORTEP plot for **9**.

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