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Theory Predicts Anchimeric Assistance in Olefin Polymerization with Imidovanadium(V) Model Catalysts[†]

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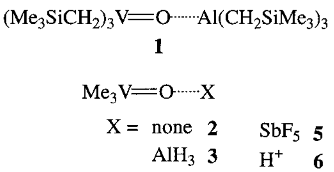
Summary: Gradient-corrected levels of density functional theory have been used to compute the barriers for insertion of ethylene into a V−C bond of $V(NR)Me_3$ *(R = H, tBu,* $C(CF_3)_3$*,* C_6H_5*, p-*C_6H_4OMe*, p-*$C_6H_4NO_2$*, o,p-*$C_6H_3(NO_2)_2$*, o-*$C_6H_4(COMe)$*). For the dinitroaryl derivative a notable lowering of the insertion barrier is predicted (to 18.5 kcal/mol) due to stabilization of the transition state by intramolecular chelate formation of the o-nitro group with the metal center, suggesting that experimentally accessible analogues should be active polymerization catalysts.*

Tailoring of transition-metal-based catalysts is often achieved by appropriate variations in the ligand sphere. Transition-metal NMR spectroscopy is a powerful tool to monitor subtle electronic and steric properties of the ligands, and in some systems catalytic activities or enantioselectivities have been correlated with the chemical shifts of the metal.[1,2] A similar NMR/reactivity correlation has recently been predicted for **1**, a moderately active catalyst for ethylene polymerization,[3] on the basis of computations for model compounds **2**−**6** (Chart 1).[4] In this series, lower ethylene insertion barriers ΔE_a are associated with more deshielded ^{51}V resonances, which should permit a screening of suitable cocatalysts X by ^{51}V NMR, also in the "real" system **1**: more active catalysts should be idetifiable by more deshielded ^{51}V resonances.

Chart 1



Similar, but much smaller, changes in the insertion barrier have been found upon variation of the terminal π ligand itself:[5] on the basis of $\delta(^{51}V)$ and ΔE_a values computed for the parent imidovanadium(V) model $V(NH)Me_3$ (**7**; δ 791), it would appear that alkylimido species such as $V(NtBu)(CH_2SiMe_3)_3$ (**8**; δ 877)[6] would not be active as olefin-polymerizing catalysts. (Arylimido)vanadium(V) species, on the other hand, are characterized by more deshielded ^{51}V nuclei, e.g. $V\{N(p\text{-}C_6H_4Me)\}(CH_2SiMe_3)_3$ (**9**; δ 1048),[7] and might thus be more promising candidates for catalysis. A systematic study of imidovanadium(V) derivatives, $V(NR)Me_3$, is now presented, calling special attention to the substituent effects on the computed ΔE_a and $\delta(^{51}V)$ values. Interesting neighboring-group effects are revealed, allowing one to suggest modifications of known compounds in order to make them active polymerization catalysts.

Ethylene-insertion barriers ΔE_a and ^{51}V chemical shifts of $V(NR)Me_3$ species, computed at BP86/I and GIAO-B3LYP/I levels, respectively,[8] are collected in Table 1. In comparison to the parent **7**, the alkyl derivative **10** shows a slightly higher insertion barrier, whereas a somewhat smaller one (by 1 kcal/mol) is computed for the perfluoro compound **11.** This sequence is consistent with the buildup of negative charge at nitrogen in the transition state (e.g. −0.62e for the parent transition state **7(TS)** vs. −0.59e for the reactant **7**),[9] similar to what has been found for the oxygen ligands in **2** and **3**.[4] Electron-releasing and withdrawing substituents tend to respectively increase and decrease the barrier.

A phenyl group could serve as acceptor for this excess charge in the transition state and should thus also lower the barrier. This expectation is borne out by the result for **12**, but quantitatively the effect is small (0.6 kcal/mol, compare data for **10** and **12** in Table 1). The acceptor properties of the phenyl group are also apparent in the ground-state reactant, as evidenced by the deshielding of the ^{51}V nucleus in **12** vs. **10.** The computed difference, $\Delta\delta = 172$, agrees excellently with corresponding experimental data involving bulkier alkyl substituents at vanadium, e.g. **9** vs. **8**, $\Delta\delta = 171$. Introducing a methoxy substituent at the para position in **12** leaves both the ^{51}V chemical shift and insertion barrier virtually unchanged. The effects of a *p*-nitro group are more noticeable but are still small; in particular, the insertion barrier is little affected (see entry **14** in Table 1). Including estimated zero-point corrections, ΔE_a values between 24.2 and 22.5 kcal/mol are

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[†] Dedicated to Prof. Dr. W. von Philipsborn on the occasion of his 70th birthday.

(1) (a) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R.; von Philipsborn, W.; Egolf, T. *J. Organomet. Chem.* **1984**, *272,* 231−249. (b) Bender, R. B.; Koller, M.; Nanz, D.; von Philipsborn, W. *J. Am. Chem. Soc.* **1993**, *115*, 5889−5890. (c) Fornica, R.; Görls, H.; Seeman, B.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1479−1480.

(2) Review: von Philipsborn, W. *Chem. Soc. Rev.* **1999**, 95−106.

(3) Feher, F. J.; Blanski, R. L. *Organometallics* **1993**, *12*, 958−963.

(4) Bühl, M. *Angew. Chem.* **1998**, *110*, 153−155; *Angew. Chem., Int. Ed.* **1998**, *37,* 142−144.

(5) Bühl, M. In *Modeling NMR Chemical Shifts*; Facelli, J., DeDios, A., Eds.; ACS Symposium Series 732; American Chemical Society: Washington, DC, in press.

(6) Preuss, F.; Becker, H. *Z. Naturforsch.* **1986**, *41B*, 185−190.

(7) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109,* 7408−7416.

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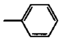
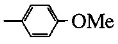
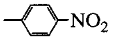
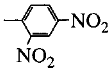
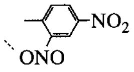
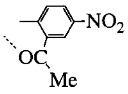
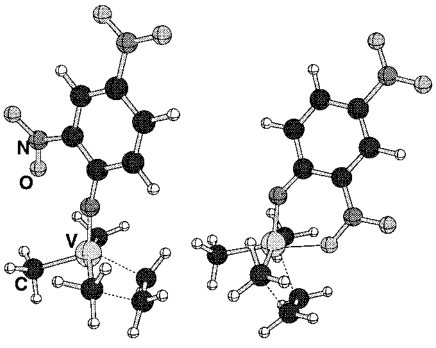
Table 1. Ethylene-Insertion Barriers ΔE_a (kcal/mol)[a] and ^{51}V Chemical Shifts (ppm)[b] of Imidovanadium(V) Compounds V(NR)Me$_3$

Compd.	R	ΔE_a	$\delta(^{51}V)$
7	H	23.4	791
10	CMe$_3$	24.2	774
11	C(CF$_3$)$_3$	22.5	972
12		23.6	946
13		23.6	949
14		23.1	1028
15a		25.9	1226
15b[c]		18.5	1658
16b[c]		20.9	1449

[a] BP86/I level, corrected for estimated zero-point energy.[8] [b] GIAO-B3LYP/I level employing BP86/I geometries.[8] [c] Oxygen atom of ortho substituent coordinated to vanadium.[10]



15a(TS) **15b(TS)**

Figure 1. BP86/I optimized transition structures **15a(TS)** (left) and **15b(TS)** (right). Note the V···O contact in the latter.

obtained for **7** and **10−14.** When these data are compared to the theoretical results for the related oxovanadium(V) model catalysts,[4] i.e. $\Delta E_a = 19.1$ kcal/mol for **3** (experimental counterpart **1** moderately active) and $\Delta E_a = 22.2$ kcal/mol for **2** (experimental counterpart not active), one can predict that simple alkyl- and arylimido complexes V(NR)R′$_3$, for which **10−14** could serve as models, should not be active as catalysts for olefin polymerization.

For the *o,p*-dinitro derivative **15**, two transition states for ethylene insertion have been located, **15a(TS)** and **15b(TS)** (Figure 1). In **15a(TS)** the *o*-nitro group is placed opposite to the incoming olefin. The corresponding reactant **15a** with an essentially linear V═N−C(Ar) arrangement is characterized by an additional deshielding of the metal with respect to that in **12** ($\Delta\delta = 198$, Table 1), but also by a larger ΔE_a value via **15a(TS)** (1.8 kcal/mol higher that for 12). Apparently, the excess negative charge at the imido nitrogen in **15a(TS)** is destabilized by the nearby nitro group with its electron-rich oxygen atoms. Consistent with this interpretation, the *o*-nitro group in **15a(TS)** is somewhat twisted out of planarity with the aromatic ring (by ca. 22°). When the nitro group is placed such that it points toward the incoming olefin, **15b(TS)** is obtained (Figure 1). Quite surprisingly, the optimization has afforded a structure with a strongly bent V═N−C(Ar) unit (143°), a contact between vanadium and a nitro oxygen (2.168 Å), and a significantly lower energy (8 kcal/mol below **15a(TS)**).

Subsequently, the corresponding reactant minimum **15b** was located, which shows essentially the same characteristics, namely a V···O contact (2.234 Å) and a bent V═N−C(aryl) moiety (144°). At the BP86/I level, **15b** is more stable than **15a** by 1.5 kcal/mol (by 0.2 kcal/mol employing the larger basis II′).[10] The stabilization due to intramolecular V···O contact formation is thus considerably larger in the transition state than in the reactant, resulting in a substantial *anchimeric assistance* of the *o*-nitro group. The lowering of the barrier is paralleled by a large deshielding of the ^{51}V resonance (Table I). From the total insertion barrier of 18.5 kcal/mol estimated for **15b,** it can be predicted that experimentally accessible counterparts such as V{N(*o,p*-C$_6$H$_3$-

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(8) The same methods and basis sets as in the previous studies[4,5] were employed; i.e., geometries have been fully optimized employing the gradient-corrected exchange-correlation functionals of Becke (Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100) and Perdew (Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824; **1986**, *34*, 7406), denoted BP86, and basis I, i.e. Wachters' (14s11p6d)/[8s7p4d] all-electron basis augmented with one additional diffuse d and two 4p functions for V (Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033−1036. Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377−4384) and a standard 6-31G* basis for all other elements (e.g.: Hehre, W.; L. Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986). It is known that these types of density functionals afford reliable descriptions of geometries, vibrations, and energetics for transition-metal complexes (see, e.g.: Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743−761). Zero-point corrections to the insertion barriers, computed from analytical harmonic frequencies, were found to be virtually identical for **7** and **12**, namely increasing the barrier by 4.1 kcal/mol; this correction has been applied to all other computed barriers, which are thus reported at the BP86/I + ZPE(estimated) level. Magnetic shieldings have been computed with a recent implementation (Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996,** *104*, 5497−5509) of the GIAO (gauge-including atomic orbitals)-DFT method employing basis I and Becke's three-parameter hybrid functional (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5642) together with the correlation functional of Lee, Yang, and Parr (Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789), denoted B3LYP, for the BP86/I optimized geometries. Chemical shifts are reported relative to VOCl$_3$, the experimental standard, with a computed absolute shielding of $\sigma = -2317$ at the same level. This particular combination of density functionals has proven to be particularly well suited for the computation of ^{51}V chemical shifts (Bühl, M.; Hamprecht, F. A. *J. Comput. Chem.* **1998**, *119*, 113−122). All computations have been performed with the Gaussian 94 program (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C. ; Pople, J. A. Gaussian 94; Gaussian, Inc., Pittsburgh, PA, 1995).

(9) From natural population analysis: Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(10) Basis II′ is a well-tempered [14s15p11d] basis on V (Huzinaga, S.; Klobukowski, M. *J. Mol. Struct.* **1988**, *167*, 1−210), contracted from the 20s13p10d set and augmented with two additional p shells and one additional d- shell of the well-tempered series, and IGLO-basis II (Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Princ. Prog.* **1990**, *23*, 165−262) for the ligands except hydrogen, for which the corresponding double-ζ basis is used.

$(NO_2)_2\}(CH_2SiMe_3)_3$ (**17**)[11] should be active catalysts for ethylene polymerization.

Neighboring-group participation is not restricted to nitro groups. For an *o*-carbonyl derivative **(16b),** both a minimum and a transition state could be located with the same salient features as those of **15b** and **15b(TS)**. However, anchimeric assistance of the carbonyl group in **16b** is less pronounced, as apparent from the more shielded $\delta(^{51}V)$ value and a larger barrier (by ca. 2.4 kcal/mol), with respect to **15b** (Table I).

The electronic structure of **15b** is interesting: topological analysis of the total BP86/II′ electron density[12] not only confirms the bonding interaction between vanadium and oxygen (presence of a bond critical point with $\rho = 0.05$ au and $-\nabla^2\rho = 0.23$ au)[13] but also reveals a valence-shell charge concentration in the V═N−C(aryl) plane, indicative of a free lone pair at nitrogen.[14] If this lone pair is available for coordination of Lewis acids, the insertion barrier could perhaps be further reduced, in analogy to the oxovanadium species **2−6.** Indeed, protonation of the imido nitrogen in **15b** affords **18b**[15] with a strongly deshielded ^{51}V nucleus (computed δ 2383) and an estimated insertion barrier of only 11.7 kcal/mol, very similar to the data for the protonated oxo species **6**.[4] At this point, however, the steric demand of the aryl group makes it unclear to what extent larger, more realistic Lewis acids could be bound to the imido nitrogen in **15b.**

Even in the limit of **18b,** compounds of the type $V\{N(X)Ar\}R_3$ (X = Lewis acid) could probably not match the highest olefin-polymerizing activities presently achievable with homogeneous catalysts.[16] Other imidovanadium(V) species are among the more promising catalysts based on vanadium, for instance $V\{N(p\text{-}C_6H_5Me)\}(C_5H_5)Cl_2$ (**19**) activated by methylalumoxane,[17] but they are still only moderately active.[18] In the light of the present results it would seem possible that the activity of catalysts derived from **19** could be enhanced by appropriate modification of the imido substituent, i.e. by introducing nitro or carbonyl groups in an ortho position.

Inspection of the data in Table 1 reveals that by and large, smaller ΔE_a values are associated with larger ^{51}V chemical shifts. This trend extends to protonated **18b,** as illustrated in Figure 2. From an examinination of experimental systems and the energetic data discussed above, one can estimate that (arylimido)vanadium(V) species should be active polymerization catalysts when their ^{51}V resonances are higher than δ 1600. Note, however, that the anchimeric chelates responsible for both barrier reduction and deshielding need not be fully formed in the reactant (cf. the small energy difference between **15a** and **15b).** Note also the deviation of **15a** due to the above-mentioned destabilization of **15a(TS)**, suggesting that the NMR/reactivity correlation would only apply in the absence of additional strain in the transition state.

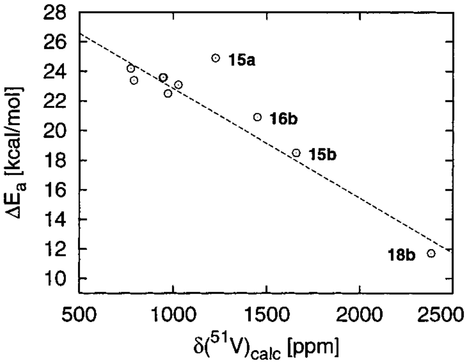

Figure 2. 2. Plot of ΔE_a vs. $\delta(^{51}V)$ in imidovanadium(V) species **7**, **10−16**, and **18**. **15a** has been excluded from the linear regression.

In summary, density-functional computations have led to proposed modifications of (arylimido)vanadium(V) species $V(NAr)R'_3$ in order to turn them into catalysts for ethylene polymerization, at least with moderate activity. This should be achieved by introducing substituents in the ortho position at the aryl group which are suitable for anchimeric assistance in the transition state, for instance a nitro group. To the extent that the barrier-lowering chelatization takes place also in the reactant, active catalysts could be identified by ^{51}V NMR, since a trend towards lower barriers with more deshielded $\delta(^{51}V)$ values is predicted for a number of model compounds. It would appear worthwhile to test experimentally if the same derivatization would also increase the activity of other, known vanadium-based catalysts bearing an arylimido moiety.

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Supporting Information Available: Gaussian archive entries for optimized minima of **7**, **10−16**, and **18** and the corresponding transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] A suitable reaction sequence could be alkylation[7] of $V\{N(o,p\text{-}C_6H_3(NO_2)_2\}Cl_3$ (analogous to the *p*-nitro derivative: Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 3069−3070), which could be prepared[7] from $VOCl_3$ and *o,p*-dinitrophenyl isocyanate (Naegeli, T.; Tyabji, *C. Helv. Chim. Acta* ***1938,*** *21,* 1127-1138).

[12] Topological analysis in the atoms-in-molecules framework (Bader, R. W. F. *Atoms In Molecules: A Quantum Theory;* Clarendon Press: Oxford, U.K., 1990) has been performed using the MORPHY program (Popelier, P. L. A. *Comput. Phys. Commun.* **1996,** *93,* 212−240).

[13] A bcp is also found in **15a** between the imido nitrogen and an oxygen atom of the *o*-nitro group, indicative of a repulsive interaction (cf. the values of $\rho = 0.02$ au and $-\nabla^2\rho = 0.07$ au).

[14] A search for natural localized MOs in the natural bond orbital scheme[9] also affords such a lone pair localized at the imido nitrogen.

[15] Protonation of any one of the nitro groups is computed to be less favorable by at least 10 kcal/mol.

[16] E.g.: Britovsek, G. J. P.; Gibson, V.; Wass, D. F. *Angew. Chem.* **1999**, *111,* 448−468; *Angew. Chem., Int. Ed.* **1999**, 38, 428−447.

[17] Coles, M. P.; Gibson, V. C. *Polym. Bull.* **1994**, *33,* 529−533.

[18] Catalyst stability is also a problem, see e.g.: (a) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1997**, 2345−2346. (Arylimido)vanadium(V) alkyls can be stable enough for structural characterization: (b) Murphy, V. J.; Turner, H. *Organometallics* **1997**, *16,* 2495−2497.