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Novel Scorpionate and Pyrazole Dioxovanadium Complexes, Catalysts for Carboxylation and Peroxidative Oxidation of Alkanes

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Abstract: The dioxovanadium(V) complexes $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (pz = pyrazolyl), $[VO_2\{SO_3C(pz)_3\}]$ (**2**), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) and $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**), bearing pyrazole or scorpionate ligands, were obtained by reaction of triethyl vanadate $[VO(OEt)_3]$ with hydrotris(3,5-dimethyl-1-pyrazolyl)methane $[HC(3,5\text{-}Me_2pz)_3]$ or 3,5-dimethylpyrazole (3,5-Me_2Hpz; **1**), lithium tris(1-pyrazolyl)methanesulfonate {$Li[SO_3C(pz)_3]$, **2**}, potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate {$K[HB(3,5\text{-}Me_2pz)_3]$, **3**} and hydrotris(1-pyrazolyl)-methane $[HC(pz)_3$, **4**], respectively. Treatment of $[VO(OEt)_3]$ with potassium hydrotris(1-pyrazolyl)borate {$K[HB(pz)_3]$} led to the mixed η^3-tris(pyrazolyl)-borate and η^2-bis(pyrazolyl)borate oxovanadium(IV) complex $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}$, **5**]. The compounds were characterized by elemental analyses, IR, NMR and EPR spectroscopy, FAB and ESI mass spectrometry, cyclic voltammetry and, for **5**, also by single crystal X-ray diffraction analysis. All complexes exhibit catalytic activity in the single-pot carboxylation [in trifluoroacetic acid/potassium peroxodisulfate ($CF_3COOH/K_2S_2O_8$)] of gaseous alkanes (methane and ethane) to carboxylic acids (yields up to 40%, TONs up to 157) and in the peroxidative oxidation [in water/acetonitrile (H_2O/NCMe)] of liquid alkanes (cyclohexane and cyclopentane) to the corresponding alcohols and ketones (yields up to 24%, TONs up to 117), under mild conditions.

Keywords: alkanes; carboxylation; C–H bond activation; oxovanadium complexes; peroxidative oxidation; scorpionate ligands

Introduction

The coordination chemistry of vanadium, in particular with multidentate ligands, is receiving much attention on account of its involvement in various biological processes: in the active site of metalloenzymes such as vanadium nitrogenase[1] and haloperoxidases,[2] as a metabolic regulator,[3] as a mitogenic activator and especially as an insulin-mimicking agent;[4] vanadium complexes can also affect the cardiac abnormality associated with diabetes mellitus[5] and exhibit anticancer activity.[6] Moreover, catalytic applications have also stimulated the coordination chemistry of vanadium, and the search for novel V complexes with pharmacological and catalytic significance is a matter of a high current interest.[6,7]

Poly(1-pyrazolyl)borates,[8] the parent compounds within the so-called scorpionate ligands (Figure 1), and their coordination chemistry have been extensively developed[8,9] with particular significance for the control of the steric and electronic environment of the metal centre upon variation of the pyrazolyl groups. The neutral hydrotris(1-pyrazolyl)methane $HC(pz)_3$ (pz = pyrazolyl) and derivatives are formally related to the corresponding hydrotris(1-pyrazolyl)borate $HB(pz)_3^-$ species by replacing the central boron

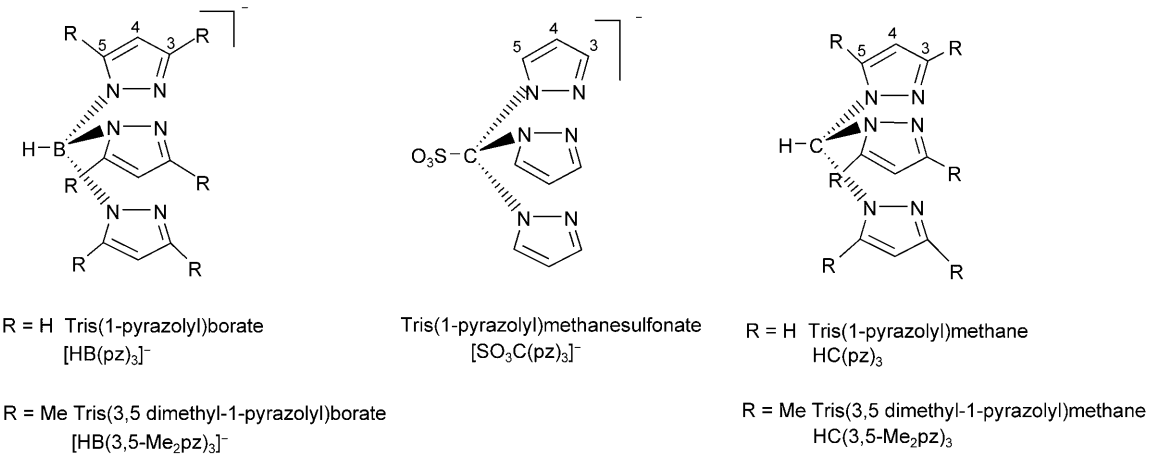


Figure 1. Tris(1-pyrazolyl)scorpionates.

atom with a carbon,[10] but their coordination chemistry, in particular at V centres and contrasting with that of tris(pyrazolyl)borates, has so far been reported only rarely.[9a,11] This arises from the relatively small number of such ligands, the difficulties and the usually low yields associated with their syntheses. A particular case is the sulfonate derivative tris(pyrazolyl)methanesulfonate $SO_3C(pz)_3^-$ (Tpms)[12] which, in contrast to hydrotris(1-pyrazolyl)methane, is almost exclusively soluble in water and moderately soluble in methanol. Another distinct behaviour relative to $HC(pz)_3$ and especially to hydrotris(1-pyrazolyl)borate concerns the stability of $SO_3C(pz)_3^-$ over a wide range of pH in aqueous solution.

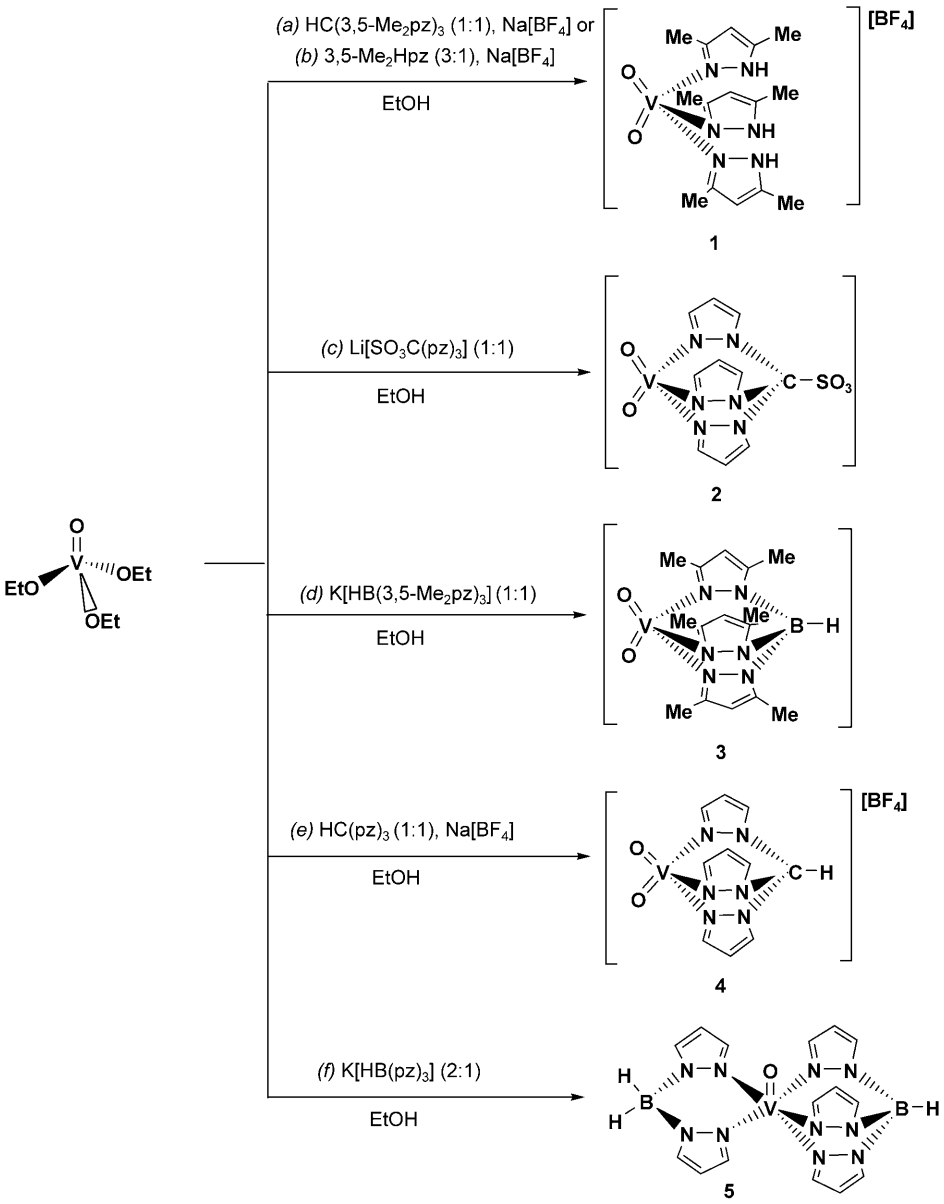
In view of the significance of vanadium chemistry with poly(pyrazolyl)borate ligands towards mimicking biocatalytic behaviour and also in pursuit of our interest on transition metal complexes bearing scorpionate ligands,[13] we have, in the current study, embarked upon the syntheses of oxovanadium complexes with such ligands and with those of the related, but still very little studied, tris(pyrazolyl)methane family. Hence, the work has allowed us to extend the still limited number of known complexes with the $HC(pz)_3$ and $SO_3C(pz)_3^-$ ligands, and in particular afforded the first dioxovanadium complex bearing the latter ligand. We have also observed the conversion of the disubstituted hydrotris(1-pyrazolyl)methane $HC(3,5\text{-}Me_2pz)_3$ into the corresponding dimethylpyrazole, and of the related hydrotris(1-pyrazolyl)borate into the corresponding bis(1-pyrazolyl)borate, the latter affording a mixed η^3-tris(pyrazolyl)borate and η^2-bis(pyrazolyl)borate oxovanadium(IV) complex. On the other hand, by investigating the redox behaviour of the obtained vanadium products, we have also gained an insight into the net electron-donor ability of such ligands and in the redox V(V)V(IV) or V(IV)/V(III) interplay, essential for the versatility of vanadium as a catalyst.

Recently, we have observed that a few scorpionate chlorovanadium complexes exhibit a good catalytic efficiency[13b,14] in the partial oxidation of cyclohexane (to cyclohexanol and cyclohexanone), a reaction of industrial importance. Hence, also taking into account that high oxidation state dioxovanadium species containing the VO_2^+ moiety have been used as models of vanadium haloperoxidases,[6a–c] and with the aim of extending the search for efficient scorpionate vanadium compounds in the catalytic functionalisation of light alkanes, we present here the application of the above dioxovanadium(V) complexes, bearing scorpionate ligands, as catalysts for the single-pot carboxylation of methane and ethane and for the peroxidative oxidation of cyclopentane and cyclohexane, under mild conditions.

Results and Discussion

Synthesis and Characterization of the Complexes

Reaction of triethyl vanadate, a convenient starting material in oxovanadium coordination chemistry,[15] in refluxing ethanol, with hydrotris(3,5-dimethyl-1-pyrazolyl)methane, $HC(3,5\text{-}Me_2pz)_3$ (in 1:1 stoichiometric amounts), followed by addition of $Na[BF_4]$, led to $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ **1** (reaction *a*, Scheme 1) which was isolated as an air-stable brown solid (45% yield), soluble in DMSO, dichloromethane and chloroform. The formation of **1** involves the rupture of a C(sp^3)–N(pyrazolyl) bond in $HC(3,5\text{-}Me_2pz)_3$. Other cases of metal-induced cleavage of such a type of bond have been reported, namely the C–N bond rupture in $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ by the benzoylhydrazido rhenium(V) chelate $[ReCl_2\{\eta^2\text{-}N,O\text{-}N_2C(O)Ph\}(PPh_3)_2]$[13f] or in bis(pyrazolyl)propane $(CH_3)_2C(pz)_2$ by Pt(II) complexes,[16] namely $[PtCl_2(RCN)_2]$ (R = Me or Ph) or $K_2[PtCl_4]$. Such a behav-



Scheme 1.

iour, to the best of our knowledge, had not been previously shown for vanadium. In all the reported cases, the manner of the cleavage reaction occurs has not been established. Complex **1** is also obtained upon reaction of $[VO(OEt)_3]$ with 3,5-dimethylpyrazole (50% yield, reaction *b*, Scheme 1).

Reactions of $[VO(OEt)_3]$ with the anionic Li^+ salt, lithium tris(1-pyrazolyl)methanesulfonate $Li[SO_3C(pz)_3]$, the related disubstituted potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate salt, i.e., $K[HB(3,5\text{-}Me_2pz)_3]$, or the neutral hydrotris(1-pyrazolyl)methane $HC(pz)_3$ (always in 1:1 stoichiometric amounts), the latter followed by addition of $Na[BF_4]$, led to the formation of the scorpionate dioxovanadium(V) compounds $[VO_2\{SO_3C(pz)_3\}]$ (**2**), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) and $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**), respectively (reactions *c*–*e*, Scheme 1). They were isolated (42–52% yields) as green (**2** and **4**) or brown (**3**) air-stable solids and (as well as the other complexes obtained in this study) were characterised by elemental analysis, IR and NMR, FAB- and ESI-mass spectrometry and electrochemical methods.

Compounds **1** and **2** represent, to the best of our knowledge, the first examples of dioxovanadium complexes bearing the pyrazole or $SO_3C(pz)_3^-$ ligand; in **2** the ligated scorpionate shows the typical *N,N,N*-coordination mode. Moreover, $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) is the first mononuclear tris(1-pyrazolyl)borate to be isolated and characterised. A related dinuclear vanadium complex $[V_2O_4\{HB(pz)_3\}_2]$ was recently report-

ed[17] and considered to consist of two identical VO{HB(pz)$_3$} groups connected by two μ-O atoms.

The mixed η^3-tris(pyrazolyl)borate and η^2-bis(pyrazolyl)borate complex [VO{HB(pz)$_3$}{H$_2$B(pz)$_2$}] (**5**) is obtained upon reaction of [VO(OEt)$_3$] with a twofold molar amount of hydrotris(1-pyrazolyl)borate (reaction *f*, Scheme 1), in refluxing ethanol. In this case, fragmentation of the tris(pyrazolyl)borate occurred along the reaction course, to afford the dihapto bis(pyrazolyl) ligand. The B–N bond rupture has been previously observed in K[HB(3,5-Me$_2$pz)$_3$] with Ru(II) complexes[18] such as [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$. The molecular structure of **5** (Figure 2) was established by X-ray diffraction (see below). This compound appears to have been obtained recently by others[19] using VOSO$_4$ as the starting vanadium material, but the reported structure, in contrast to ours, doubles the cell edge *c* and, consequently, the cell volume.

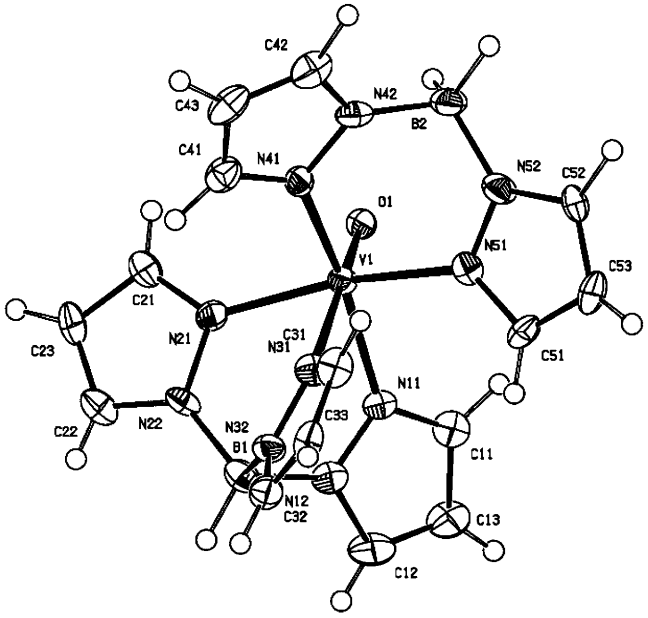


Figure 2. ORTEP diagram of the neutral complex [VO{HB(pz)$_3$}{H$_2$B(pz)$_2$}] **5**, indicating the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The IR spectra of complexes **1**–**5** exhibit ν(C=C) and ν(C=N) of the pyrazolyl or pyrazole rings at the usual[13,20] range of 1618–1503 cm^{-1}. ν(N–H) (**1**), ν(C–H) (**4**) and ν(B–H) (**3** and **5**) also appear at the characteristic[13,20,21]frequencies of 3141, 3127 and 2412–2365 cm^{-1}, respectively, also the ν(S=O) or ν(C–S) vibrations of the methanesulfonate group (**2**) which are observed at the common[12,13a,b,e] ranges of 1046–1015 and 647–638 cm^{-1}, respectively. Moreover, all the dioxovanadium(V) complexes (**1**–**4**) exhibit two sharp bands corresponding to the symmetrical VO$_2$ stretch (951–912 cm^{-1}) and the antisymmetric VO$_2$ stretch (888–839 cm^{-1}) of the *cis*-[VO$_2^+$] structural unit.[2b,15,22] The ν(V=O) value in **5** is comparable to those quoted for several oxovanadium(IV) complexes bearing the tris(pyrazolyl)borate ligand, such as [VOCl{HB(3,5-Me$_2$pz)$_3$}(Me$_2$Hpz)].[21,23]

In **1**, the equivalence of the pyrazole groups is indicated by both ^{1}H and ^{13}C{^{1}H} NMR spectra which display a single resonance for each type of protons or carbons, i.e., for the 3, 4 or 5 position in the rings. Moreover, the C resonances of the pyrazole rings are very similar to those observed for pyrazole Re[13e,f] complexes such as [ReCl$_2$\{NNC(O)C$_6$H$_5$\}(Hpz)-(PPh$_3$)$_2$]. The methine group was not detected for **1**, in accord with its formulation as a pyrazole compound.

In the ^{1}H NMR spectra, the methine hydrogen of **4** appears at $\delta = 8.96$ in accord with the reported data, e.g., for the tris(pyrazolyl)methane chloro-complexes [MCl$_n$\{HC(pz)$_3$\}] (M = V,[13b] Fe[13b] or Re,[13e] n = 2 or 3) or [ReCl$_2$\{HC(pz)$_3$\}(PPh$_3$)][BF$_4$].[13f] The corresponding resonance, i.e., B–H, of **3** is observed at $\delta = 8.50$ and is comparable to that reported[24] for hydrotris(pyrazolylborate) complexes of other metals.

In the ^{13}C{^{1}H} NMR spectra of complexes **2**–**4**, the three carbon atoms from the pyrazolyl rings appear as singlets, and the methine carbon resonances (in **2** and **4**, at 80.1 and 82.3 ppm, respectively) are comparable to those quoted, e.g., for our scorpionate complexes [MCl$_n$\{HC(pz)$_3$\}] (M = Fe[13b] or Re,[13e] n = 2 or 3, respectively), [ReCl$_2$\{HC(pz)$_3$\}(PPh$_3$)][BF$_4$][13f] or [ReO$_3$\{SO$_3$C(pz)$_3$\}][13f] and [Cu\{SO$_3$C(3-Phpz)$_3$\}L] [L = MeCN, PTA (1,3,5-triaza-7-phosphaadamantane) or HMT (hexamethylenetetramine)].[13a]

Compounds **1**–**4** exhibit strong ^{51}V NMR resonances in the −490 to −556 ppm range, relative to VOCl$_3$, as expected for dioxovanadium(V) complexes.[2b,15,21b,25]

The FAB$^+$ or ESI$^+$-mass spectra of complexes **1**–**5** show the molecular ion [M]$^+$. In FAB-MS, the fragmentation pathways occur upon cleavage of metal-ligand bonds and/or rupture of pyrazolyl rings. Coupling of pyrazolyl (or pyrazole in **1**) with metal fragments and their oxygenation (by the NBA matrix) are also observed.

Solid State Structure of Complex 5

[VO{HB(pz)$_3$}{H$_2$B(pz)$_2$}] (**5**) displays a neutral mononuclear molecular structure that is depicted in Figure 2, while the crystallographic details are given in Table 1, and selected bond distances and angles in Table 2. This mononuclear V(IV) complex bears a tridentate tris(pyrazolyl)borate and a bidentate bis(pyrazolyl)borate, apart from the oxo ligand. The coordination geometry around the vanadium atom is best

Table 1. Crystallographic data for $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**).

Empirical formula	$VO(C_{15}H_{18}N_{10}B_2)]$
Formula weight	426.95
Crystal system	Orthorhombic
Space group	*Pca*21
a (Å)	15.534(12)
b (Å)	8.484(6)
c (Å)	15.042(12)
V (Å^3)	1982(3)
Z	4
Density (calculated) (Mg/m^3)	1.431
Absorption coefficient (mm^{-1})	0.530
F(000)	876
Reflections collected/unique	11037/3566 [R(int) = 0.1154]
Goodness-of-fit on F^2	0.9810
Final R indices [$I > 2\,\sigma(I)$]	$R_1 = 0.0578$, $wR_2 = 0.1073$
R indices (all data)	$R_1 = 0.1058$, $wR_2 = 0.1264$
GOF	0.981

Table 2. Selected bond lengths (Å) and angles (°) for $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**).

V1–O1	1.607(4)
V1–N11	2.120(5)
V1–N21	2.098(5)
V1–N31	2.268(6)
V1–N41	2.097(5)
V1–N51	2.118(5)
N11–V1–N21	86.49(17)
N11–V1–N31	80.30(17)
N11–V1–N41	162.96(18)
N11–V1–N51	90.64(17)
N21–V1–N31	80.87(18)
N21–V1–N41	91.82(18)
N21–V1–N51	164.03(18)
N31–V1–N41	82.69(17)
N31–V1-N51	83.15(18)
N41–V1–N51	86.34(17)
O1–V1–N11	95.8(2)
O1–V1–N21	96.41(19)
O1–V1–N31	175.45(19)
O1–V1–N41	101.2(2)
O1–V1–N51	99.49(18)

described as a distorted octahedron. The ligand N–V–N angles are restrained by the chelate rings to 80.4–91.8°.

Two nitrogen atoms from the tridentate $HB(pz)_3^-$ ligand (N11 and N21) and two nitrogem atoms from the bidentate $H_2B(pz)_2^-$ ligand (N41 and N51) form the equatorial plane, while the axial positions are occupied by the remaining nitrogen (N31) from the tridentate $HB(pz)_3^-$ ligand and the oxygen atom (O1). The N11, N21, N41 and N51 atoms are on a plane and V1, O1 and N31 lay 0.302(3), 1.908(5) and −1.965(6) Å out of this plane. The V1–O1 bond length of 1.607(4) Å is similar to that reported for other six-coordinate vanadyl complexes (1.62 Å),[26,27] although smaller than that found in a similar structure reported previously[28] [average 1.591(1) Å]. The V–N distances for both chelating ligands in **2** vary from 2.097(5) to 2.120(5) Å (average 2.108 Å); however, the bond length involving the N31 atom in *trans* position to the oxo ligand is considerably longer [2.268(6) Å]. This lengthening can be attributed to a significant *trans* influence of the latter ligand. The V–N bond lengths in **5** are comparable to those observed for other V-pyrazolyl(borate) complexes, such as $[VOCl\{HB(3,5\text{-}Me_2pz)_3\}(DMF)]$,[29] $[VOCl_2\{HB(3,5\text{-}Me_2pz)_3\}]$ and $[V\{HB(pz)_3\}_2][BPh_4]$.[30]

Electrochemical Studies

Complexes **1**, **2**, **4** and **5** exhibit by cyclic voltammetry (as illustrated by Figure 3 for compound **1**), at a platinum disc electrode, 25 °C, in a 0.2 M $[n\text{-}Bu_4N][BF_4]$ solution in dichloromethane or DMSO, a first irreversible single-electron reduction (confirmed by controlled potential electrolysis), assigned to the V(V)→V(IV) reduction (complexes **1**, **2** and **4**, $^{I}E_p^{red}$ in the −0.17 to −0.48 V *vs.* SCE range) or to the V(IV)→V(III) reduction (complex **5**, as expected at the much lower $^{I}E_p^{red}$ value of −1.19 V *vs.* SCE) (Table 3).

For the V(V) complexes **1**, **2** and **4** a second irreversible reduction wave is also observed at $^{II}E_p^{red}$ *ca.* −1.25 to −1.82 V *vs.* SCE, conceivably involving the V(IV)→V(III) reduction. Accordingly, the reduction of the V(IV) complex **5** occurs at a comparable reduction potential ($^{I}E_p^{red} = -1.19$ V *vs.* SCE).

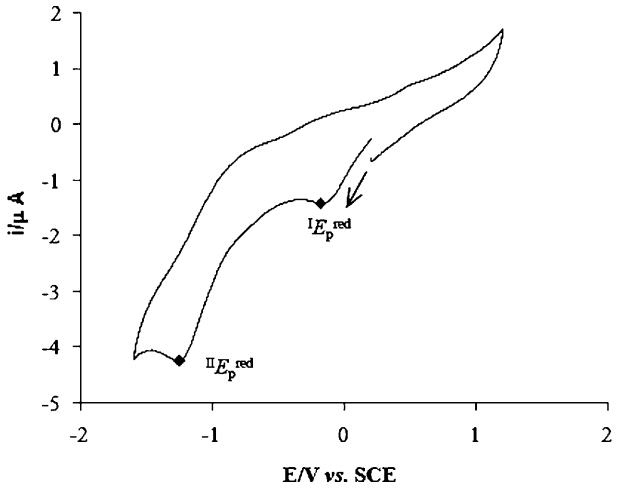


Figure 3. Cyclic voltammogram of $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**), initiated by the cathodic sweep, at a Pt disc electrode, in a 0.20 M $[n\text{-}Bu_4N][BF_4]/CH_2Cl_2$ solution ($v = 200$ mV/s). Complex concentration: 1.5 mM.

Table 3. Cyclic voltammetric data[a] for $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**), $[VO_2\{SO_3C(pz)_3\}]$ (**2**), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) and $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**).

Complex	$^{I}E_p^{red}$	$^{II}E_p^{red}$	E_p^{ox}
$[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**)[b]	−0.17	−1.25	–
$[VO_2\{SO_3C(pz)_3\}]$ (**2**)[c]	−0.46	−1.82	–
$[VO_2\{HC(pz)_3\}][BF_4]$ (**4**)[c]	−0.48	−1.70	–
$[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**)[b]	−1.19	–	1.76

[a] Values in V ± 0.02 relative to SCE; scan rate of 200 $mV\,s^{-1}$.
[b] In CH_2Cl_2.
[c] In DMSO.

Although comparisons of the redox potentials have to be taken rather cautiously in view of the irreversibility of the waves and the different solvents used, the measured $^{I}E_p^{red}$ values suggest[31] that $HC(pz)_3$ and $SO_3C(pz)_3^-$ seem to display comparable electron-donor characters (in **4** and **2**, respectively), while 3,5-Me_2Hpz (in **1**) appears to behave as a weaker electron-donor than each coordinating arm of the former ligands.

Complex **5** displays one oxidation wave at E_p^{ox} = 1.76 V *vs.* SCE, assigned to V(IV)→V(V). This oxidation potential is markedly higher than that reported for the hydrotris(1-pyrazolyl)borate oxovanadium(IV) $[VO\{HB(pz)_3\}(acac)]$ (1.21 V *vs.* SCE),[30] suggesting that the η^2-$BH_2(pz)_2^-$ ligand in **5** seems to behave as a weaker electron donor than η^2-acetylacetonate (acac) in the latter complex. However, the above conclusions have to be confirmed by comparative studies of other complexes with those ligands which should exhibit reversible redox waves.

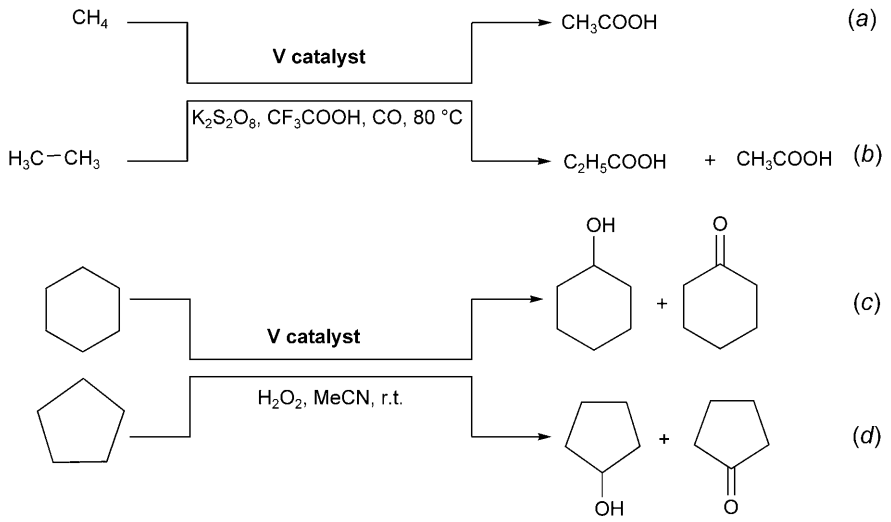
Catalytic Studies

Carboxylation of Gaseous Alkanes

The carboxylation reactions of methane and ethane (reactions *a* and *b*, Scheme 2) were typically performed under CO, in trifluoroacetic acid (TFA), at 80 °C for 20 h, by using a $K_2S_2O_8$ as the oxidizing agent, in the presence of a V-catalyst (0.020 mmol): compounds **1**–**5** or the related chloro-complexes $[VCl_3\{HC(pz)_3\}]$ (**6**) and $[VCl_3\{SO_3C(pz)_3\}]$ (**7**) prepared elsewhere.[13b] The experimental conditions (i.e., temperature, time and molar ratios of reactants) were those found by some of us[32–37] and others[38] to be optimal for the carboxylation reactions of alkanes in TFA catalyzed by various transition metal coordination compounds.

To the best of our knowledge, compounds **1**–**7** are the first scorpionate and related pyrazole vanadium complexes to be used as catalysts for the carboxylation of alkanes.

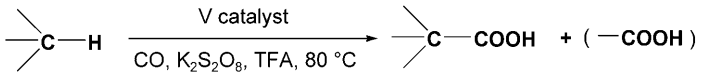
The complexes bearing the tris(1-pyrazolyl)methanesulfonate ligand $[VO_2\{SO_3C(pz)_3\}]$ (**2**) and $[VCl_3\{SO_3C(pz)_3\}]$ (**7**) are the most active ones towards methane carboxylation (yields up to *ca.* 40%), whereas the activity decreases on replacement of that scorpionate by the analogous neutral hydrotris(1-pyrazolyl)methane (**4** and **6**, respectively) (Table 4 and Table S1, Supporting Information). The carboxylation of methane by our systems can proceed even without CO gas as the TFA solvent can behave as a carbonylating agent[32a,b,33] (Table S1, entry 2, Supporting Information). However, in this case the yield of acetic acid is much lower. The effect of the pressure of CO on the yield of the acetic acid product has been studied, showing an optimal value of 5 atm. Higher CO pressures lead to an acetic acid yield drop (Figure 4,



Scheme 2.

Table 4. Carboxylation of alkanes catalysed by V complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**), $[VO_2\{SO_3C(pz)_3\}]$ (**2**), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**), $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**), $[VCl_3\{HC(pz)_3\}]$ (**6**) and $[VCl_3\{SO_3C(pz)_3\}]$ (**7**).[a]

Carboxylation Reaction:



Substrate: CH_4 Substrate: C_2H_6

Catalyst \ Product	MeCOOH TON (Yield)	EtCOOH TON (Yield)	MeCOOH TON (Yield)	Total TON (Total Yield)
1	14 (25)	5 (6)	9 (11)	14 (17)
2	22 (39)	11 (13)	8 (10)	19 (23)
3	9 (16)	12 (14)	9 (11)	21 (25)
3[b]	traces	157 (0.5)	–	157 (0.5)
4	9 (16)	10 (12)	9 (11)	19 (23)
5	17 (31)	3 (4)	3 (3)	6 (7)
6	11 (20)	2 (2)	2 (3)	4 (5)
7	21 (37)	5 (6)	2 (2)	7 (8)

[a] Selected results (for the full results see Supporting Information, Table S1); turnover numbers (TON, moles of product/mol of catalyst) determined by GC; values of product yields (moles of product/100 moles of alkane) are given in brackets. Typical reaction conditions for carboxylation: p(alkane) = 5 atm (1.02 and 1.53 mmol for CH_4 and C_2H_6, respectively), p(CO) = 5 atm, n(catalyst) = 0.020 mmol, 80 °C, 20 h, $K_2S_2O_8$ (4.00 mmol), CF_3COOH (7.5 mL for CH_4 and 5.5 mL for C_2H_6).

[b] Conditions for carboxylation of CH_4: p(alkane) = 5 atm, p(CO) = 7.5 atm, n(catalyst) = 0.05 μmol (used as a fine mixture with $K_2S_2O_8$ (4.00 mmol)), 80 °C, 20 h, CF_3COOH (5.0 mL). Conditions for carboxylation of C_2H_6: p(alkane) = 10 atm, p(CO) = 25 atm, n(catalyst) = 0.1 μmol (used as a fine mixture with $K_2S_2O_8$ (4.00 mmol)), 80 °C, 20 h, CF_3COOH (5.0 mL).

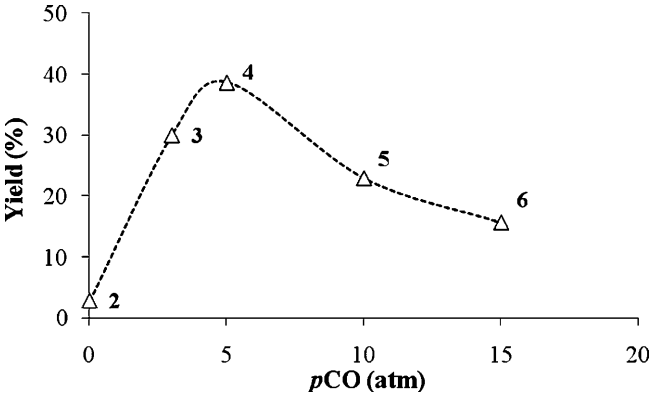


Figure 4. Effect of CO pressure on the yield of acetic acid derived from methane (at 5 atm) by using catalyst $[VO_2\{SO_3C(pz)_3\}]$ (**2**) and $K_2S_2O_8$ in CF_3COOH. Reaction conditions and point numbers are those of Table S1 (Supporting Information).

Table S1, entries 5 and 6, Supporting Information), CO conceivably acting as a ligand with a resulting loss of the catalyst activity. The mechanism of carboxylation of methane possibly involves the formation of the methyl radical (upon hydrogen abstraction from CH_4) by the $HSO_4^{\bullet}$ radical (derived from thermolysis of $S_2O_8^{2-}$ in acid medium), followed by carbonylation.[33]

The conversion of ethane into propionic (as a result of carboxylation) and acetic (as a result of oxidation) acids (reaction *b*, Scheme 2) proceeds under the above mentioned conditions, in the presence of **1**–**7** (Table 4 and Table S2, Supporting Information). The maximum activity was observed for complex **3** (overall turnover number TON of 157, although under conditions that lead to a low yield), which, however, does not reach the high levels we have observed for Amavadin models.[34]

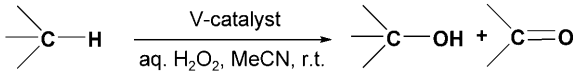
We found that our V complexes show some selectivity in the ethane carboxylation: acetic acid is the main product when using **1**, whereas for **7** propionic acid is produced in a higher amount than that of acetic acid (Table 4 and Table S2, Supporting Information).

Hydroxylation/Oxygenation of Liquid Alkanes

All our vanadium complexes act as catalysts or catalyst precursors for the oxidation, with aqueous H_2O_2 (30% aqueous solution), of cyclohexane and cyclopentane to the corresponding alcohols and ketones, in CH_3CN and in the presence of HNO_3, at room temperature, according to Scheme 2 (reactions *c* and *d*). The reactions were typically performed under dinitrogen and the final reactions solutions were analyzed by GC.

Table 5. Peroxidative oxidation of cycloalkanes catalyzed by V complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**), $[VO_2\{SO_3C(pz)_3\}]$ (**2**), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**), $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**), $[VCl_3\{HC(pz)_3\}]$ (**6**) and $[VCl_3\{SO_3C(pz)_3\}]$ (**7**).[a]

Hydroxylation/Oxygenation Reaction:



Substrate: C_5H_{10} Substrate: C_6H_{12}

Catalyst \ Product	C_5H_9OH TON	C_5H_8O TON	Total TON	$C_6H_{11}OH$ TON	$C_6H_{10}O$ TON	Total TON
1	12[c]	0[c]	12[c]	46	67	113
2	25[b]	16[b]	41[b]	47	70	117
3	7[c]	4[c]	11[c]	33	53	86
4	3[c]	2[c]	5[c]	38	61	99
5	15[c]	14[c]	29[c]	32	43	75
6	4[c]	3[c]	7[c]	74[d]	93[d]	167[d]
7	18[b]	0[b]	18[b]	35[d]	86[d]	121[d]

[a] Selected results (for the full results see Supporting Information, Table S3 and Table S7): turnover numbers (TON, moles of product/mol of catalyst) determined by GC; yields (%) can be estimed as: TON × [n(catalyst)/n(cycloalkane)] × 100. Typical (unless otherwise stated) reaction conditions: NCMe (3.0 mL), $H_2O_2 = 10$ mmol; $n(HNO_3)/n(catalyst) = 100$; 20 °C; 6 h. For cyclohexane oxidation: $n(H_2O_2)/n(catalyst) = 40000$, $n(catalyst)/n(C_6H_{12}) = 5 \times 10^{-5}$.

[b] $n(H_2O_2)/n(catalyst) = 500$; catalyst (0.010 mmol); $n(catalyst)/n(C_5H_{10}) = 2 \times 10^{-3}$.

[c] $n(H_2O_2)/n(catalyst) = 1500$; catalyst (0.010 mmol); $n(catalyst)/n(C_5H_{10}) = 2 \times 10^{-3}$.

[d] Included for comparative purposes.[13b]

Cyclohexane Oxidation

As for carboxylation reactions, the dioxovanadium complex $[VO_2\{SO_3C(pz)_3\}]$ (**2**) displays the highest catalytic activity towards oxidation of cyclohexane, within this work, leading to a maximum TON of 117 (Table 5) upon 6 h reaction time, in the presence of HNO_3. This TON is higher than those of some other vanadium catalysts with N,O-ligands, such as Amavadin (TONs of *ca.* 50),[39c] and of commercially available V oxides (TONs of 47).[33a] However, the activity is slightly lower than those recently reported for the half-sandwich vanadium compounds **6** and **7** (TONs of 167 and 121, respectively).[13b]

Effect of the Catalyst Amount

The effect of catalyst amount was studied for complexes **1**–**5**. The obtained TON values are given in Table S3 (Supporting Information), with typical curves shown in Figure 5. In all cases the catalyst amount has a relevant effect, since an increase of the $n(H_2O_2)/n(catalyst)$ molar ratio results in the rise of the catalyst TON, e.g., the overall TON for complex **2** increases from *ca.* 10 to 117, upon changing that ratio from 100 to 40,000 (entries 6 and 10, Table S3, Supporting Information).

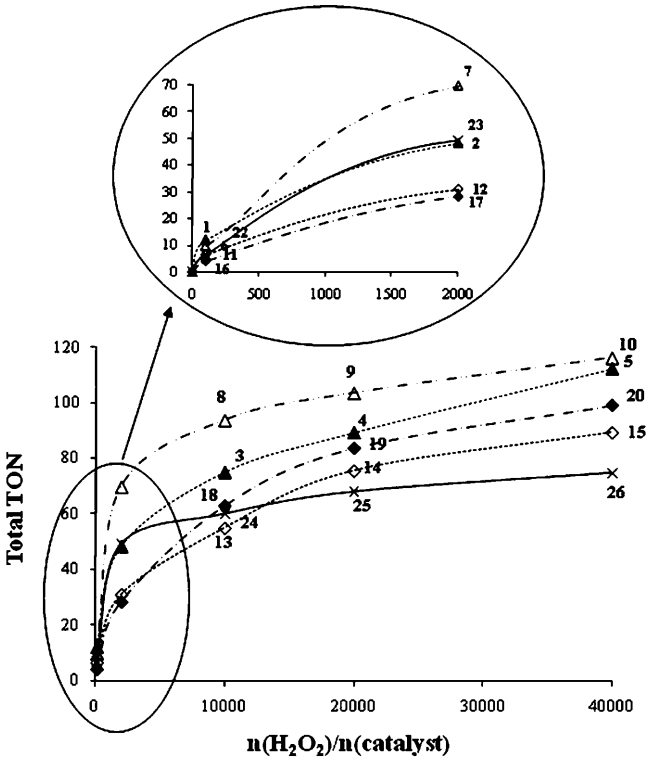


Figure 5. Effect of the catalyst amount on the total (cyclohexanone and cyclohexanol) TON, in the peroxidative oxidation of cyclohexane catalysed by vanadium complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (▲), $[VO_2\{SO_3C(pz)_3\}]$ (**2**) (△), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) (◇), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) (◆) or $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**) (x). $H_2O_2 = 10$ mmol. Reaction conditions and point numbers are those of Table S3 (Supporting Information).

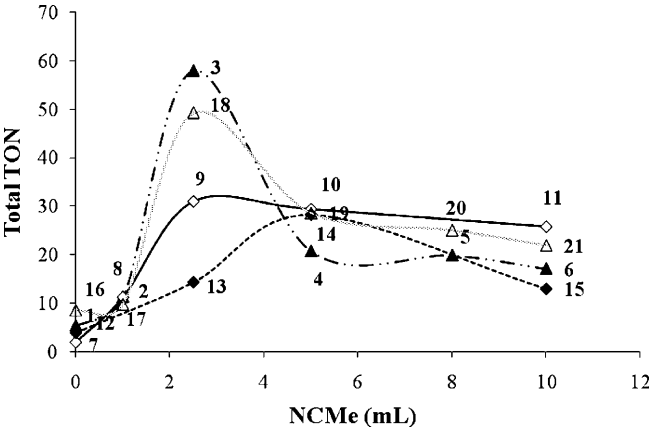


Figure 6. Effect of the solvent amount on the total (cyclohexanone and cyclohexanol) TON in the reaction of peroxidative oxidation of cyclohexane catalysed by vanadium complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (▲),$[VO_2\{SO_3C(pz)_3\}]$ (**2**) (△), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) (◇) or $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) (◆). Reaction conditions and point numbers are those of Table S4 (Supporting Information).

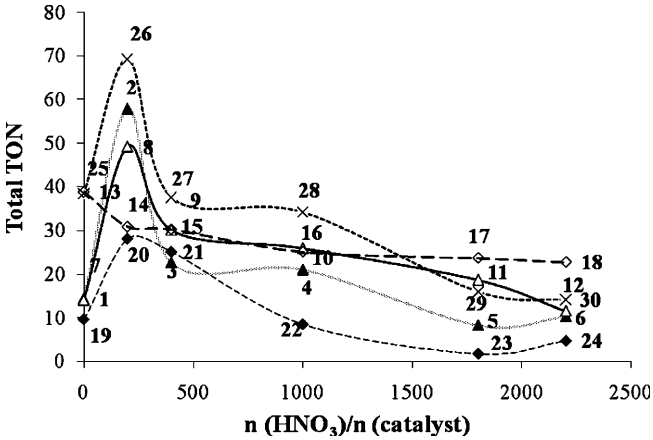


Figure 7. Effect of nitric acid on the total (cyclohexanone and cyclohexanol) TON in the peroxidative oxidation of cyclohexane catalysed by vanadium complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (▲), $[VO_2\{SO_3C(pz)_3\}]$ (**2**) (△), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) (◇), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) (◆) or $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**) (x). n(catalyst) = 5×10^{-3} mmol. Reaction conditions and point numbers are those of Table S5 (Supporting Information).

Effect of the Solvent Amount

The activity of the studied systems also depends on the solvent, which determines the polarity of the medium.[13] The choice of acetonitrile, as the typical solvent for our system, is due to its high resistance to oxidising agents and also in view of the higher solubility of the alkane and organic products in this solvent in contrast with other ones, e.g., methanol, ethanol or acetone. Besides, it has also been used in many other cases as the most appropriate solvent for such a type of alkane oxidations.[33a,36,37,39–41]

The formation of the products is observed even in the absence of acetonitrile (Table S4, entries, 1, 7, 13 and 18, Supporting Information), what could be of significance towards the establishment of an effective "green" process. The increase of the acetonitrile amount results in the rise of activity (Figure 6). The maximum TON value was obtained for *ca.* 3.0 mL of acetonitrile, for catalysts **1**–**3** (with 1 mL of 30% aqueous H_2O_2). Further increases of the CH_3CN amount lead to lower TONs, most likely due to the dilution effect of reagents and/or intermediates.

Effect of the Amount of Nitric Acid

It has been shown that the presence of a small amount of nitric acid increases the TONs in catalytic oxidation systems containing vanadium,[39] iron,[40] copper[41a–f] or rhenium[33a,37,41g] complexes with N,O ligands as the catalysts.

The effects of the addition of nitric acid in the systems catalyzed by complexes **1**–**5** are shown in Figure 7 and Table S5 (Supporting Information). A promoting effect of a slight amount of nitric acid up to n(HNO_3/n(catalyst) of *ca.* 200 was observed for complexes **1**, **2**, **4** and **5**. This fact can be related to a decreased decomposition of hydrogen peroxide to water and oxygen,[42] resulting in a faster formation of possible intermediate peroxo complexes.[43,44] In contrast, for **3**, a slight inhibiting effect is observed upon nitric acid addition.

However, interestingly, some of our catalytic systems operate even in the absence of acid (e.g., TONs of 39 for catalysts **3** and **5**), which is of significance for the design of a "green process".

Effect of the Reaction Time, Radical Initiator and Radical Traps

The effect of the reaction time on the activity of the complexes **1**, **2** and **4** was studied and an increase of TON with time up to 6 h (Figure 8) was observed. A further increase of the reaction time results in a TON drop, most likely due to subsequent reactions.

For complex **2**, the effect of the presence of 3-chloroperoxybenzoic acid, $3\text{-}ClC_6H_4COOOH$ (a possible radical initiator)[45] was studied and is shown in Figure 9. An accelerating effect is observed for the first 3 h, whereafter inhibition occurs. A similar behaviour was reported[37] for some of our Re scorpionate or pyrazole complexes, e.g., $[ReClF\{N_2C(O)Ph\}(Hpz)_2(PPh_3)]$ or $[ReO_3\{SO_3C(pz)_3\}]$.

No alkane oxidation products were detected when the reaction was performed in the presence of either a carbon or an oxygen radical trap ($CBrCl_3$ or

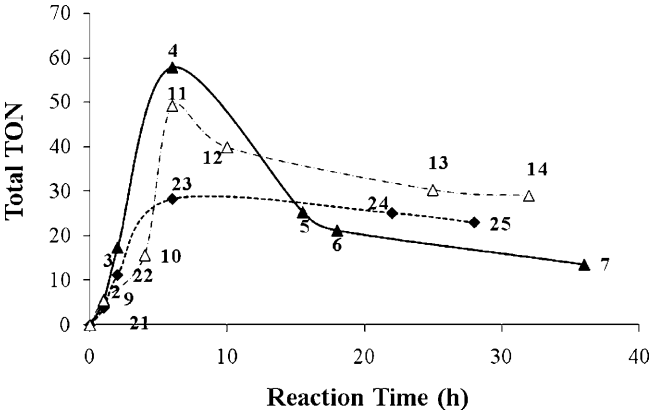


Figure 8. Effect of reaction time on the total (cyclohexanone and cyclohexanol) TON, in the peroxidative oxidation of cyclohexane catalysed by vanadium complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (▲), $[VO_2\{SO_3C(pz)_3\}]$ (**2**) (△) and $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) (◇). Reaction conditions and point numbers are those of Table S6 (Supporting Information).

Ph_2NH, respectively), thus supporting a radical mechanism for the peroxidative oxidation of the alkane.

Effect of the Addition of PPh_3

An increase in the amount of alcohol, *ca.* 10% for complex **4**, with a concomitant decrease in the amount of ketone is observed (Table S3, entry 21, Supporting Information) when the final reaction solution is treated with an excess of PPh_3, prior to the GC analysis, according to a method reported by Shul'pin.[46,47] This shows that at the end of the reaction there is a significant amount of cyclohexyl hydroperoxide (CyOOH) which is reduced to the alcohol by PPh_3. However, in the case of **2**, no appreciable change in the relative amounts of products was observed upon addition of PPh_3, indicating that either CyOOH had already decomposed (further reacted) in the presence of this catalyst or the reaction did not proceed *via* that hydroperoxide.

Regioselectivity

In order to gain a further mechanistic insight[46,47c,48] into the cycloalkane oxidation, we have also studied the oxidation of methylcyclohexane with hydrogen peroxide, catalysed by **2**. The reaction was run for 6 h, and the sample was analysed by GC after treatment with PPh_3 (in order to reduce the alkyl hydroperoxides to the corresponding alcohols). The reaction products show the following 1°:2°:3° selectivity: 1:7:17.5, respectively. The molar ratios of the obtained alcohols were normalised taking into account the equivalent hydrogen atoms at each position. This limited selectivity is indicative of the involvement of the highly reactive hydroxyl ($HO^{\bullet}$) radical, as reported[33a,39b,40b,41e,43,46,49,54] for other systems, e.g., H_2O_2-$Fe(ClO_4)_3$[47c] and H_2O_2-$[NBu_4][VO_3]$-PCA (PCA = pyrazine-2-carboxylic acid).[46,47c]

Cyclopentane Oxidation

Effect of the Oxidant Amount

Complexes **1**–**7** also catalyse the peroxidative oxidation of cyclopentane to the corresponding cyclopentanone and cyclopentanol, but their catalytic activity (Table 5) is lower than that for the oxidation of cyclohexane (e.g., overall TONs of 41 and 117, respectively, for **2**). In contrast, a higher selectivity is observed for the formation of the alcohol, i.e., cyclopentanol, which can be the only oxidation product detected in the presence of **1** or **7**. The total TONs increase

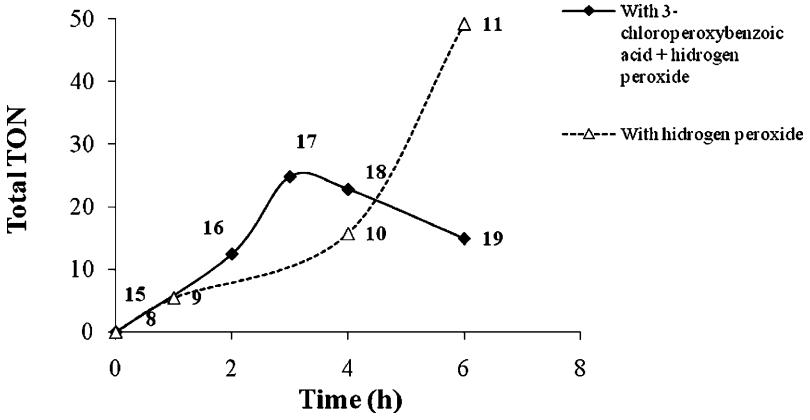


Figure 9. Effect of radical initiator ($3\text{-}ClC_6H_4COOOH$) on the total (cyclohexanone and cyclohexanol) TON, in the peroxidative oxidation of cyclohexane catalysed by $[VO_2\{SO_3C(pz)_3\}]$ (2). Reaction conditions and point numbers are those of Table S6 (Supporting Information).

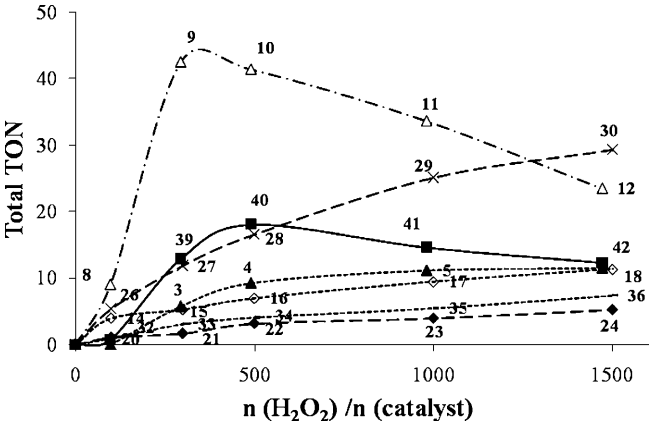


Figure 10. Effect of the catalyst amount on the total (cyclopentanone and cyclopentanol) TON, in the peroxidative oxidation of cyclopentane catalysed by vanadium complexes: $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$ (**1**) (▲), $[VO_2\{SO_3C(pz)_3\}]$ (**2**) (△), $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**) (◇), $[VO_2\{HC(pz)_3\}][BF_4]$ (**4**) (◆), $[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (**5**) (x), $[VCl_3\{HC(pz)_3\}]$ (**6**) (–) and $[VCl_3\{SO_3C(pz)_3\}]$ (**7**) (■). $H_2O_2 = 10$ mmol. Reaction conditions and point numbers are those of Table S7 (Supporting Information).

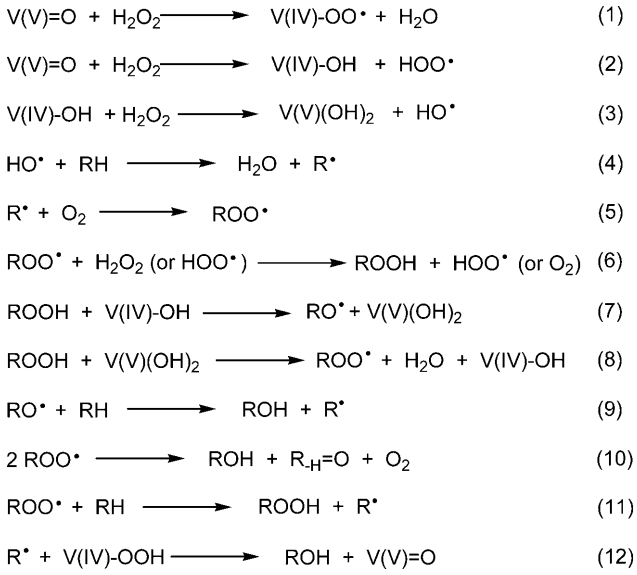
(Figure 10) with the H_2O_2/catalyst molar ratio (i.e., with an increase of the H_2O_2 amount or a decrease of that of the catalyst), but up to maximum values for **2** and **7**. The further TON decrease for the high $n(H_2O_2)/n(catalyst)$ ratios conceivably results from overoxidation.

Mechanistic Considerations

The *carboxylations* of methane and ethane (RH) are expected to proceed via free radical mechanisms,[33,34,50] and theoretical calculations[33b,34] performed for other oxo-vanadium systems with TFA/$K_2S_2O_8$ disclose a particularly favourable process involving the sequential formation of R•, RCO• and RCOO• which, upon H-abstraction (from TFA or RH),[33b,34] form the RCOOH acid.

R• can be formed by H-atom abstraction from the alkane by the sulfate radical $SO_4^{-\bullet}$ (or its protonated $HSO_4^{\bullet}$ form)[33b,34,51a] derived from thermolytic decomposition of $K_2S_2O_8$.[50,51b] Carbonylation of R• would form the acyl radical RCO• that upon oxygenation by a peroxo-metal complex would lead to RCOO• from which RCOOH would be formed (see above).[33b] Alternatively, RCO• could be oxidized to RCO^+ which, on reaction with TFA, would lead to the mixed anhydride $CF_3COOCOR$. Further reaction of the latter with TFA would yield the acid RCOOH and $CF_3COOCOCF_3$ (trifluoroacetic anhydride), as proposed[33b,50] in other cases.

The mechanisms of the *peroxidative oxidations* possibly involve both C-centred and O-centred radicals,



Scheme 3.

since the reactions are essentially suppressed when they are carried out in the presence of either a C- or an O-centred radical trap (such as $CBrCl_3$ and Ph_2NH).[14b,33a,34,37,41b]

Peroxo-metal V-OO• and hydroxyl HO• radicals can be derived from oxo-metal-promoted decomposition reactions of H_2O_2,[7,33a,43,46,47] followed by H-abstraction from the alkane (RH) to form the alkyl radical R• (Scheme 3, reactions 1–4). The process could then proceed *via* formation of the organo-peroxyl radical ROO• (upon reaction of R• with O_2) and the organo-hydroperoxide ROOH[55] (reactions 5 and 6) which could undergo metal-assisted homolytic decomposition to the organooxyl RO• and organoperoxyl ROO• radicals,[56] the latter thus being regenerated (reactions 7 and 8). H-abstraction from the alkane by RO• would form the alcohol ROH and R• (reaction 9), whereas ROO• could either decompose to the alcohol and the ketone (reaction 10) or regenerate ROOH and R• upon H-abstraction from RH (reaction 11), as proposed[42,47] for some metal-catalysed alkane oxidations with O_2. The alcohol can also be formed from R• and a metal hydroperoxide (reaction 12),[33b] the latter being derived, e.g., upon H-abstraction from RH by V(IV)-OO•.

The involvement of the highly reactive HO• radical is suggested by the restricted regioselectivity of the oxidation of methylcyclohexane, whereas the participation of the hydroperoxide ROOH is corroborated for the catalyst **4** by the increase of the alcohol amount with a concomitant decrease of that of the ketone when the final reaction solution, prior to GC analysis, is treated with an excess of PPh_3 (method reported by Shul'pin.[46]). For the metal catalyst **2**, no ROOH was detected at the end of the experiments

probably due to its possible[41a,b,48] metal-promoted decomposition to the alcohol and ketone.

Conclusions

We have found a simple and convenient route for the formation of dioxovanadium complexes with scorpionate or pyrazole ligands based on the use of the easily generated *in situ* $[VO(OEt)_3]$ as the VO_2^+ moiety source, thus contributing to expand the still relatively little explored coordination chemistry of $HC(pz)_3$ and $SO_3C(pz)_3^-$ types of scorpionate ligands. That route has allowed the synthesis of the first dioxovanadium complexes bearing tris(1-pyrazolyl)-methanesulfonate or borate, or pyrazole ligands. The work also shows that the oxovanadium centre can promote the rupture of a C(sp^3)–N(pyrazolyl) bond in $HC(3,5\text{-}Me_2pz)_3$ and of a B–N bond in $HB(pz)_3^-$ to afford pyrazole and $H_2B(pz)_2^-$ complexes, what has be taken into account when studying coordination reactions of those scorpionates.

The vanadium(V and IV) complexes are redox active, what allows us to gain an insight into the relative electron-donor abilities of the scorpionate and pyrazole ligands, based on the redox potential values, although a firm comparison is precluded by the irreversibility of the redox waves.

The work also shows that oxovanadium complexes with scorpionate ligands, such as those reported herein, can act as catalysts or catalyst precursors for alkane functionalisation reactions under mild conditions, including their one-pot carboxylation and peroxidative hydroxylation or oxygenation. Complex $[VO_2\{SO_3C(pz)_3\}]$ (**2**) exhibits the highest catalytic activity for the carboxylation of methane to acetic acid and for the cycloalkane oxidations, whereas, for ethane carboxylation, the most active catalyst is $[VO_2\{HB(3,5\text{-}Me_2pz)_3\}]$ (**3**). The dioxo-scorpionate-V(V) complexes **1–4** are usually more active than the monooxo-discorpionate-V(IV) **5** and than the trichloro-V(IV) compounds **6** and **7**. However, for the oxidation of cyclohexane, their activities are comparable or lower than those of the latter compounds. Nervertheless, the generality of these observations should be taken cautiously and tested further for other types of alkane reactions and vanadium catalysts. The search for greener systems should proceed, and the favourable features of the oxo-scorpionato-vanadium catalysts reported here (including their operation under mild conditions and, in some cases, even in acid-free systems) should encourage further investigation within this challenging field of research.

Experimental Section

Materials and Instrumentation

Pyrazole, 3,5-dimethylpyrazole and V_2O_5 were used as received from the supplier (Aldrich). Triethyl vanadate, $[VO(OEt)_3]$ was synthesized *in situ via* a known[15a] procedure immediately before use, and employed as a solution in ethanol (1.00 mmol of $[VO(OEt)_3]$ corresponds to *ca.* 20 mL of ethanol solution) without further isolation. Potassium hydrotris(l-pyrazolyl)borate,[57] potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate,[57] hydrotris(l-pyrazolyl)methane,[10] hydrotris(3,5-dimethyl-1-pyrazolyl)methane[10] and lithium tris(l-pyrazolyl)methanesulfonate[12a] were prepared in accord with the published procedures. Complexes $[VCl_3\{HC(pz)_3\}]$[13b] (**6**) and $[VCl_3\{SO_3C(pz)_3\}]$[13b] (**7**) were prepared from VCl_3, also according to procedures described earlier.

Solvents were purified by standard procedures and freshly distilled immediately prior to use. All manipulations and reactions were performed under an atmosphere of dinitrogen using standard vacuum and inert-gas flow techniques. Cyclohexane (Merck), methylcyclohexane (Merck), cyclopentane (Merck), acetonitrile (Riedel-de-Haën), hydrogen peroxide (30%) (Fluka), nitric acid (65%) (Riedel-de-Haën), 3-chloroperoxybenzoic acid (Aldrich), triphenylphosphine (Merck), potassium and ammonium peroxodisulfates (Fluka), trifluoroacetic acid (Aldrich), bromotrichloromethane (Fluka), diphenylamine (Fluka), *n*-butyric acid (Aldrich), cycloheptanone (Aldrich), cyclopentanone (Aldrich), diethyl ether (Riedel-de-Haën), ethane (AlphaGaz), carbon monoxide (Air Products), dioxygen (Air Liquid Portugal) and dinitrogen (Air Liquid Portugal) were used as purchased.

Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet Impact 400D or a BIO-RAD FTS 3000 MX spectrophotometer instrument in KBr pellets; wavenumbers are in cm^{-1}; abbreviations: vs, very strong; s, strong; m, medium. ^1H, ^{13}C, $^{13}C\{^1H\}$, ^{19}F and ^{51}V NMR spectra were recorded on Bruker Avance II+ 300 and 400 MHz (UltraShield™ Magnet) or a Varian Unity 300 spectrometer at ambient temperature. δ values are in ppm relative to Me_4Si (^1H and ^{13}C), CCl_3F (^{19}F) or $[VOCl_3]$ (^{51}V). Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; t, triplet; m, complex multiplet; br, broad. In the ^{13}C NMR data, assignments and coupling constants common to the $^{13}C\{^1H\}$ NMR spectra are not repeated. Atom labelling for the Hpz ligand: HN(1)N(2)C(3)HC(4)HC(5)H; the numbering of the coordinated pyrazolyl ring is VN(1)N(2)C(3)HC(4)HC(5)H. EPR spectra were recorded on a Bruker ESP 300E X-band spectrophotometer equipped with an ER 4111 VT variable-temperature unit.

FAB^+ and FAB^- mass spectra were obtained on a Trio 2000 spectrometer by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. ESI^+/ESI^- mass spectra were obtained on a Varian 500-MS LC ion trap mass spectrometer [solvent: dimethyl sulfoxide; flow: 20 $\mu L\,min^{-1}$; needle spray voltage: ±5 kV, capillarity voltage: ±100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature (N_2): 350 °C]. For the mass spectra description, M de-

notes the complex part of compounds **1**–**5**. The C, H, N, S elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

The electrochemical experiments were performed on an EG&G PAR 273 A potentiostat/galvanostat connected to personal computer through a GPIB interface. Cyclic voltammograms (CV) were obtained in 0.2 M [*n*-Bu_4N][BF_4]/CH_2Cl_2 or DMSO, at a platinum disc working electrode (d = 1 mm). Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capil1ary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring that no significant potential drift occurred along the electrolyses. Ferrocene was used as an internal standard for the measurement of the oxidation potentials of the complexes; the redox potential values are quoted relative to the SCE by using as internal reference[58] the ferrocene/ferricinium couple ($E_{1/2}^{ox}$ = 0.525 V *vs.* SCE in CH_2Cl_2 or 0.44 V *vs.* SCE in DMSO).

Gas chromatographic (GC) measurements were carried out using a Fisons Instruments GC 8000 series gas chromatograph with an FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. Helium was used as the carrier gas.

X-Ray Structure Determinations

Intensity data were collected on a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation. Data were collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. The structure was solved by direct methods by using the SHELXS-97 package[59] and refined with SHELXL-97[60] with the WinGX graphical user interface.[61] All hydrogens were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave R_1 = 0. 0578 [I > 2σ(I); R_1 = 0. 1058 (all data)]. The maximum and minimum peaks in the final difference electron density map are of 0.32 and −0.43 e Å^{-3}.

CCDC 697173 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and Characterization of the Complexes

[VO_2(3,5-Me_2Hpz)$_3$][BF_4] (1): A mixture of hydrotris(3,5-dimethyl-1-pyrazolyl)methane (298 mg, 1.00 mmol) and [VO($OEt)_3$] (202 mg, 1.00 mmol) in ethanol (20 mL) was refluxed for *ca.* 24 h, resulting in a brown solution. Na[BF_4] (329 mg, 3.00 mmol) in THF (5 mL) was then added, and the mixture was refluxed for further 2 h. The reaction mixture was filtered, and the brown-yellow filtrate was concentred under vacuum,, followed by slow addition of Et_2O (5 mL), resulting in the precipitation of **1** as a dark brown solid. This was filtered off, washed with Et_2O and dried under vacuum; yield: 206 mg (45% yield).

Complex **1** can also be obtained by an alternative way: a mixture of 3,5-dimethylpyrazole (288 mg, 3.00 mmol) and [$VO(OEt)_3$] (1.00 mmol) in ethanol (20 mL) was refluxed during *ca.* 24 h, resulting in the formation of an orange solution. Then Na[BF_4] (326 mg, 3.00 mmol) in THF (5 mL) was added, and the solution was refluxed for further ca. 2 h. The filtered yellow solution was concentred under vacuum to *ca.* one half followed by slow addition of Et_2O, resulting in the precipitation of the brown compound **1**; yield: 308 mg (50%).IR (KBr pellet): ν = 3206 [s, ν(N−H)], 2022, 1638 and 1298 [s, ν(N=N), ν(C=N), ν(C−N), 3,5-Me_2pz)$_3$], 1057 [vs, ν(B−F), BF_4], 951, 888 [s (sym. and antisym. VO_2)] and 443 [m, ν(V−N)]; ^{1}H NMR: (DMSO-d_6), δ = 5.75 [s, br, 3H, H(4) 3,5-Me_2Hpz], 2.12 [s, br, 18H, CH_3, 3,5-Me_2Hpz]; ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 143.2 [s, C(3) and C(5), 3,5-Me_2Hpz], 103.9 [s, C(4), 3,5-Me_2Hpz], 12.3 [s, CH_3, 3,5-Me_2Hpz];^{13}C NMR (DMSO-d_6): δ = 103.3 [d, J_{CH} = 132 Hz, C(4), 3,5-Me_2Hpz], 11.8 [q, J_{CH} = 92.3 Hz, CH_3, 3,5-Me_2Hpz]; ^{51}V NMR (DMSO-d_6): δ = −472; ^{19}F NMR (DMSO-d_6): δ = −148.3; FAB$^+$-MS: m/z = 553 [M + (3,5-Me_2Hpz)]$^+$, 387 [M + O]$^+$, 371 [M]$^+$, 276 [M−(3,5-Me_2Hpz)]$^+$(MI); ESI$^+$-MS: m/z = 371 [M]$^+$; FAB$^-$-MS: m/z = 87 [BF_4]$^-$; anal. calcd. for $C_{15}H_{24}N_6BF_4O_2V$: C 39.3, H 5.3, N 18.3%; found: C 39.7, H 5.9, N 18.4%.

This complex is soluble in DMSO, dichloromethane and chloroform, but insoluble in diethyl ether, acetone, acetonitrile, toluene, hexane and methanol.

[VO_2{$SO_3C(pz)_3$}] (2): A solution of lithium tris(pyrazolyl)methanesulfonate (300 mg, 1.00 mmol) in ethanol (5 mL) was added to an ethanolic solution (50 mL) of [$VO(OEt)_3$] (202 mg, 1.00 mmol) at 20–25 °C. The reaction mixture was then refluxed for *ca.* 24 h, resulting in a green solution. Concentration under vacuum of the filtered green solution followed by slow addition of Et_2O (*ca.* 5 mL) resulted in the precipitation of **2** as a green solid. This was filtered off, washed with Et_2O (two portions of 10 mL) and dried under vacuum; yield: 188 mg (50%); IR (KBr pellet): ν = 1639 and 1524 [s, ν(N=C) and ν(C=C), $SO_3C(pz)_3^-$], 1046 [m, ν(S=O)], 986 [m, ν(V=O)], 921, 860 [s (sym. and antisym. VO_2)], 647 [m, ν(S−C)] and 424 [m, ν(V−N)]; ^{1}H NMR (DMSO-d_6): δ = 8.11 [s, br, 3H, H(3), $SO_3C(pz)_3^-$], 7.39 [s, br, 3H, H(5), $SO_3C(pz)_3^-$], 6.30 [s, br, 3H, H(4), $SO_3C(pz)_3^-$]; ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 138.3 [s, C(3), $SO_3C(pz)_3^-$], 132.2 [s, C(5), $SO_3C(pz)_3^-$], 105.8 [s, C(4), $SO_3C(pz)_3^-$], 80.1 [s, $SO_3C(pz)_3$]; ^{13}C NMR (DMSO-d_6): δ = 138.2 [d, J_{CH} = 187.9 Hz, C(3), $SO_3C(pz)_3^-$], 132.1 [d, J_{CH} = 192.8 Hz, C(5), $SO_3C(pz)_3^-$], 105.7 [d, J_{CH} = 168.1 Hz, C(4), $SO_3C(pz)_3^-$]; ^{51}V NMR (DMSO-d_6): δ = −556; FAB$^+$-MS: m/z = 376 [M]$^+$, 309 [M−pz]$^+$; ESI$^+$-MS: m/z = 376 [M]$^+$; anal. calcd. for $C_{10}H_9N_6O_5SV$: C 31.9, H 2.4, N 22.3, S 8.5%; found: C 31.5, H 2.5, N 22.4, S 8.5%.

This complex is soluble in DMSO, but insoluble in diethyl ether, acetone, acetonitrile, toluene, hexane, dichloromethane, chloroform and methanol and water.

[VO_2{HB(3,5-Me_2pz)$_3$}] (3): A mixture of potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (336 mg, 1.00 mmol) with [$VO(OEt)_3$] (202 mg, 1.00 mmol) in ethanol (20 mL)

was refluxed for *ca.* 24 h, resulting in a yellow solution. The solution was filtered and concentred under vacuum to *ca.* one half, followed by slow addition of Et_2O (*ca.* 5 mL), resulting in the precipitation of a brown solid of **3**. The latter was filtered off, washed with Et_2O (two portions of 10 mL) and dried under vacuum; yield: 198 mg (52%); IR (KBr pellet): ν = 2450, 2365, 1638, 1421, 1296 [s, ν(H−B), ν(N=C), ν(B–N), ν(C–N), $HB(3,5\text{-}Me_2pz)_3^-$], 947, 886 [s (sym. and antisym. VO_2)] and 442 [m, ν(V−N)]; ^{1}H NMR (DMSO-d_6): δ = 5.75 [s, br, 3 H, H(4), $HB(3,5\text{-}Me_2pz)_3^-$], 2.08 [s, br, 18 H, CH_3, $HB(3,5\text{-}Me_2pz)_3^-$]; ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 142.1 [s, C(3) and C(5), $HB(3,5\text{-}Me_2pz)_3^-$], 103.2 [s, C(4), $HB(3,5\text{-}Me_2pz)_3^-$], 11.8 [s, CH_3, $HB(3,5\text{-}Me_2pz)_3^-$]; ^{13}C NMR (DMSO-$d_6$): δ = 103.5 [d, J_{CH} = 128.9 Hz, C(4), $HB(3,5\text{-}Me_2pz)_3^-$], 11.8 [q, J_{CH} = 92.9 Hz, CH_3, $HB(3,5\text{-}Me_2pz)_3^-$]; ^{51}V NMR (DMSO-$d_6$): δ = −501; FAB$^+$-MS: *m/z* = 381 [M]$^+$, 286 [M−(3,5-$Me_2pz$)]$^+$; ESI$^+$-MS: *m/z* = 381 [M]$^+$; anal. calcd. for $C_{15}H_{23}N_6BO_2V$: C 47.3, H 6.1, N 22.1%; found: C 47.1, H 6.2, N 22.5%.

This complex is soluble in DMSO, dichloromethane, chloroform, acetone and acetonitrile, but insoluble in diethyl ether and methanol.

$[VO_2\{HC(pz)_3\}][BF_4]$ (4): A mixture of hydrotris(1-pyrazolyl)methane (204 mg, 1.00 mmol) with an ethanolic solution (50 mL) of $[VO(OEt)_3]$ (202 mg, 1.00 mmol) was refluxed for *ca.* 24 h, forming a green solution. A suspension of $Na[BF_4]$ (329 mg, 3.00 mmol) in THF (5 mL) was then added, and the solution was further refluxed for 2 h. The resulting yellow-green solution was concentred under vacuum to *ca.* one half, followed by slow addition of Et_2O (*ca.* 5 mL) to yield a green solid of **4** which was filtered off, washed with Et_2O (two portions of 10 mL) and dried under vacuum; yield: 161 mg (42%); IR (KBr pellet): ν = 3127 [m, ν(C−H)], 1618, 1524, 1295 [s, ν(N=C), ν(C=C), ν(C−N), $HC(pz)_3$], 1068 [vs, ν(B−F), BF_4], 912, 839 [s (sym. and antisym. VO_2)], 431 [m, ν(V−N)]; ^{1}H NMR (DMSO-d_6): δ = 8.96 [s, 1 H, $HC(pz)_3$], 7.88 [m, br, 3 H, $^3J_{HH}$ = 2.4 Hz, H(3) or H(5), $HC(pz)_3$], 7.66 [m, br, 3 H, $^3J_{HH}$ = 2.2 Hz, H(5) or H(3), $HC(pz)_3$], 6.42 [m, br, $^3J_{HH}$ = 2.0 Hz, H(4), $HC(pz)_3$]; ^{13}C{^{1}H NMR} (DMSO-d_6): δ = 140.9 [s, C(3), $HC(pz)_3$], 130.1 [s, C(5), $HC(pz)_3$], 106.8 [s, C(4), $HC(pz)_3$], 82.3 [s, $HC(pz)_3$]; ^{13}C NMR (DMSO-d_6): δ = 140.9 [d, J_{CH} = 139.1 Hz, C(3), $HC(pz)_3$], 130.1 [d, J_{CH} = 144.3 Hz, C(5), $HC(pz)_3$], 106.9 [d, J_{CH} = 137.5 Hz, C(4), $HC(pz)_3$]; ^{51}V NMR (DMSO-d_6): δ = −538; ^{19}F NMR (DMSO-d_6): δ = −148.3; FAB$^+$-MS: *m/z* = 297 [M]$^+$, 230 [M−pz]$^+$; FAB$^-$-MS, *m/z* = 87 $[BF_4]^-$; ESI$^+$-MS: *m/z* = 297 [M]$^+$; anal. calcd. for $C_{10}H_{10}N_6BF_4O_2V$: C 31.3, H 2.6, N 21.9; found: C 31.5, H 2.3, N 21.5.

This complex is soluble in DMSO, but insoluble in diethyl ether, dichloromethane, chloroform, acetone, acetonitrile, toluene, hexane and methanol.

$[VO\{HB(pz)_3\}\{H_2B(pz)_2\}]$ (5): A mixture of potassium hydrotris(1-pyrazolyl)borate (504 mg, 2.00 mmol) and $[VO(OEt)_3]$ (202 mg, 1.00 mmol) in ethanol (20 mL) was refluxed for *ca.* 24 h, yielding a blue solution. The latter was concentrated under vacuum, followed by slow addition of Et_2O (5 mL), resulting in the precipitation of blue crystals of **2**, which were separated by filtration and dried in air; yield: 158 mg (37%); IR (KBr pellet): ν = 2412, 2384 [s, ν(B−H), $HB(pz)_3^-$], 2410, 2346, 2284, 2246 [s, ν(B−H), $H_2B(pz)_2^-$], 1740, 1637, 1407, 1153 [s, ν(N=N), ν(C=N), ν(B−N), ν(C−N), $HB(pz)_3^-$], 973 [s, ν(V=O)], 839 [m, ν(V−O)], 460 [m, ν(V−N)]. EPR (r.t., CH_2Cl_2): *A* = 101.9 G, *g* = 1.9989; FAB$^+$-MS: *m/z* = 510 [M + O + pz]$^+$, 443 [M + O]$^+$, 427 [M]$^+$, 414 [M−$H_2B(pz)_2$ + 2pz]$^+$, 360 [M−pz]$^+$, 347 [M−$H_2B(pz)_2$ + pz]$^+$, 280 [M−$HB(pz)_2$]$^+$, 229 [M−$H_2B(pz)_2$ + O−pz]$^+$, 213 [M−$H_2B(pz)_2$−pz]$^+$; anal. calcd. for $C_{15}H_{18}N_{10}B_2OV$: C 42.2, H 4.3, N 32.8%; found: C 42.3, H 4.3, N 32.8%.

This complex is soluble in dichloromethane, chloroform, DMSO and water.

Catalytic Activity Studies

Carboxylation of gaseous alkanes: In a typical experiment the reaction mixtures were prepared as follows. To a mixture of 20.0 μmol of the vanadium catalyst with 4.00 mmol (1.08 g) of $K_2S_2O_8$, contained in a 13.0-mL stainless steel autoclave, were added 7.5 mL or 5.0 mL of CF_3COOH (TFA) for methane or ethane carboxylation, respectively. Then the autoclave was closed and flushed with dinitrogen three times for replacing the air inside and finally pressurized with CH_4 (5 atm, 1.02 mmol) or C_2H_6 (5 atm, 1.53 mmol) and CO (0–15 atm, 0.00–4.59 mmol). The reaction mixture was vigorously stirred for 20 h at 80 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed and opened. The product analysis was undertaken as follows. To 1.0 mL of the reaction mixture were added 5.0 mL of diethyl ether and 90 μL of internal standard *n*-butyric acid. The obtained mixture was stirred, then filtered and analysed by gas chromatography (GC). Blank experiments were performed for all tested alkanes in the presence of CO and $K_2S_2O_8$, and confirmed that no carboxylic acid formation was detected unless the catalyst was used.

Hydroxylation/oxygenation of liquid alkanes: In typical conditions, the reaction mixtures were prepared as follows: 0.010 mmol of V catalyst were dissolved in 2.50 mL of MeCN. The required amount of this solution for the desired catalyst amount was transferred to a second flask, whereafter MeCN was added until a total acetonitrile volume of 3.00 mL, 5.00 mmol of H_2O_2 (30% H_2O solution, 0.50 mL) and 5.00 mmol of cycloalkane were then added (in this order) and the reaction solution was stirred for 6 h, at room temperature and under N_2 atmosphere. In the experiments with HNO_3, this acid (0–11 mmol) was added before the addition of the substrate. For the products analysis, 90 μL of cyclopentanone or cycloheptanone (internal standards) for cyclohexane or cyclopentane oxidations, respectively, and 6.5 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC by the internal standard method. Blank experiments were performed for both cycloalkanes with H_2O_2 and confirmed that no product of alkane oxidation was obtained unless the vanadium catalyst was used. The amount of alkyl hydroperoxide (if formed) was estimated from the variations in the alcohol and ketone yields, determined by GC analyses, upon addition of PPh_3 to the final reaction solution, according to a method reported by Shul'pin[46,47,62] The carbon radical trap[63] $CBrCl_3$ was used in a stoichiometric amount relative to substract (cyclohexane) and the oxygen radical trap Ph_2NH was added in a stoichiometric amount relative

to H_2O_2. The radical initiator ($3\text{-}ClC_6H_4COOOH$)[45] was used in a stoichiometric amount relative to the substrate. For studying the selectivity with methylcyclohexane, the reaction was run for 6 h, whereafter 90 μL of cyclopentanone (internal standard) and 6.5 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added, and the sample was then analysed by GC.

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