3026 *Inorg. Chem.* **1991**, *30*, 3026–3032

Contribution from the Département de Chimie,
Université de Montréal, Montréal, Québec, H3C 3J7 Canada

Multidentate Lewis Acids. Adducts of Monodentate and Bidentate Vanadyl Dichloride Alkoxides with Ketones

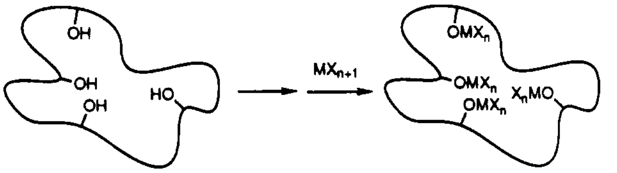
Minh Tan Phan Viet,[1] Vijay Sharma, and James D. Wuest*

Received October 12, 1990

Combined use of ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy shows that the interaction of $VOCl_3$ with 2 equiv of a ketone in solution at low temperatures produces complex mixtures of neutral and ionic adducts. In contrast, vanadium dichloride isopropoxide (**4**) forms neutral 1:2 adducts under similar conditions. These adducts are presumably octahedral, with ketones trans to the oxo and alkoxy oxygens. Bound and free ketones exchange by dissociation with free energies of activation near 7 kcal/mol. Analysis of the temperature dependence of the ^{51}V chemical shift of mixtures of compound **4** and excess pinacolone gives $\Delta H = -10.9$ kcal/mol and $\Delta S = -51$ eu for the formation of the 1:2 adduct. At low temperatures, solutions of compound **4** containing 1 equiv of a ketone consist primarily of a 1:1 mixture of free compound **4** and the neutral 1:2 adduct. Vanadyl dichloride alkoxide **6**, a bidentate Lewis acid, behaves similarly, and solutions containing 1 equiv of a ketone consist largely of free compound **6** and its unsymmetric 1:2 adduct **8**. Significant amounts of symmetric 1:1 adduct **9** with a cooperatively bound carbonyl ligand are not formed, and no other unusual chemical effects can be attributed to the special juxtaposition of electrophilic sites in bidentate Lewis acid **6**.

Introduction

Well-designed multidentate Lewis acids have unique and potentially useful properties, including the ability to recognize, bind, transport, and chemically activate complementary basic guests.[2,3] These features have prompted chemists to design and synthesize a broad range of multidentate Lewis acids with electrophilic sites differing in number, orientation, and nature. In principle, such reagents can be generated with particular ease by the reaction of metal salts MX_{n+1} with compounds containing hydroxyl groups or similar sites suitably juxtaposed by an organic framework (eq 1).[3] We have used this simple strategy to make multidentate metal halide alkoxides with high affinities for basic guests. In particular, we have made a determined effort to devise chiral bidentate derivatives able to achieve one of the most elusive goals in the chemistry of Lewis acids, the double electrophilic activation of carbonyl compounds (eq 2).[3b,4,5] Any attempt to exploit the special reactivity of adducts **1** containing cooperatively bound carbonyl ligands must confront two major obstacles: one is the ability of multidentate metal halide alkoxides to undergo redistribution reactions or conformational changes that destroy the carefully arranged juxtaposition of electrophilic sites; the other is a preference for unsymmetric alternative complexes **2** and **3**, in which adjacent electrophilic sites are bridged not by a carbonyl oxygen but by an alkoxy oxygen or halide. In this paper, we describe our efforts to detect symmetric ketone adducts **1** of a potentially bidentate vanadyl dichloride alkoxide.



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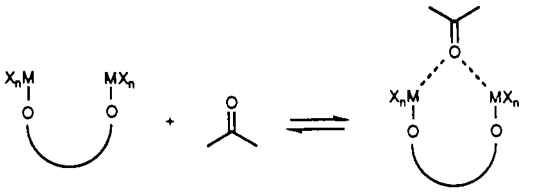

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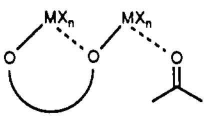

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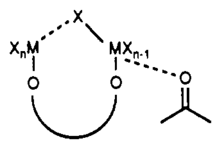

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Results and Discussion

Ketone Adducts of Vanadyl Chloride ($VOCl_3$). Vanadyl chloride ($VOCl_3$) is known to form isolable 1:1 and 1:2 adducts with a variety of monodentate Lewis bases,[6] but few of these complexes have been characterized in detail. X-ray crystallographic studies have established that 1:1 complexes with nitriles are square pyramidal with an apical oxo oxygen and that 1:2 complexes with nitriles are *mer* octahedral with one ligand trans to the oxo oxygen.[7] Well-defined coordination compounds therefore exist in the solid state, but the interaction of $VOCl_3$ with Lewis bases in solution appears to be more complex, and a confusing variety of weak solvates, charge-transfer complexes, and neutral and charged adducts of various stoichiometries have been proposed.[6,8,9c] For

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(1) Regional High-Field NMR Laboratory, Département de Chimie, Université de Montréal.

(2) For references to recent work on multidentate Lewis acids, see: Nadeau, F.; Simard, M.; Wuest, J. D. *Organometallics* **1990**, *9*, 1311–1314. Narasaka, K.; Sakurai, H.; Kato, T.; Iwasawa, N. *Chem. Lett.* **1990**, 1271–1274. Dohmeier, C.; Mattes, R.; Schnöckel, H. *J. Chem. Soc., Chem. Commun.* **1990**, 358–359. Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545–546. Chujo, Y.; Tomita, I.; Saegusa, T. *Macromolecules* **1990**, *23*, 687–689. Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277–282. Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53–C56. Kelly, T. R.; Meghani, P. *J. Org. Chem.* **1990**, *55*, 3684–3688. Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422–2424. Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *Ibid.* **1989**, *111*, 6294–6301. Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755–2759. Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179–2183. Schmidbaur, H.; Öller, H.-J.; Wilkinson, D. L.; Huber, B.; Müller, G. *Chem. Ber.* **1989**, *122*, 31–36. Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297–300. Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901–905. Khan, M. A.; Peppe, C.; Tuck, D. G. *Organometallics* **1986**, *5*, 525–530.

(3) (a) Bachand, B.; Wuest, J. D. *Organometallics*, in press. (b) Bachand, B.; Bélanger-Gariépy, F.; Wuest, J. D. *Ibid.* **1990**, *9*, 2860–2862. (c) Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Inorg. Chem.*, in press. (d) Sharma, V.; Simard, M.; Wuest, J. D. *Ibid.* **1991**, *30*, 579–581. (e) Galeffi, B.; Simard, M.; Wuest, J. D. *Ibid.* **1990**, *29*, 955–958.

(4) For examples of complexes in which a carbonyl oxygen bridges two metals, see: Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153–156. Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360–1361. Rao, C. P.; Rao, A. M.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 2080–2085. Verbist, J.; Meulemans, R.; Piret, P.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 391–395. Palm, J. H.; MacGillavry, C. H. *Acta Crystallogr.* **1963**, *16*, 963–968.

(5) For references to related studies of doubly hydrogen-bonded complexes of carbonyl compounds, see: Kelly, T. R.; Meghani, P.; Ekkundi, V. S. *Tetrahedron Lett.* **1990**, *31*, 3381–3384. Hine, J.; Ahn, K. *J. Org. Chem.* **1987**, *52*, 2089–2091, 2083–2086.

(6) (a) Brunette, J.-P.; Heimburger, R.; Leroy, M. J. F. *C. R. Acad. Sci., Ser. C* **1971**, *272*, 2147–2150. (b) Nicholls, D. *Coord. Chem. Rev.* **1966**, *1*, 379–414. (c) Krauss, H.-L.; Gnatz, G. *Chem. Ber.* **1962**, *95*, 1023–1030. (d) Funk, H.; Weiss, W.; Zeising, M. *Z. Anorg. Allg. Chem.* **1958**, *296*, 36–45.

(7) Daran, J.-C.; Gourdon, A.; Jeannin, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 309–312. Gourdon, A.; Jeannin, Y. *Ibid.* **1980**, *B36*, 304–309. Daran, J. C.; Jeannin, Y.; Constant, G.; Morancho, R. *Ibid.* **1975**, *B31*, 1833–1837.

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confirmation we decided to reexamine the interaction of $VOCl_3$ with ketones in solution by variable-temperature nuclear magnetic resonance (NMR) spectroscopy.

Although vanadyl chlorides are considered to be Lewis acids capable of oxidative transformations of carbonyl compounds and other Lewis bases,[9a,10] we saw no evidence of significant redox chemistry in complexation experiments with simple acyclic ketones. Nevertheless, we were careful to mix potential ligands with $VOCl_3$ and related compounds at low temperatures and to protect the resulting solutions from light.[8c,9c] This protocol limited the formation of oxovanadium(IV) species and minimized paramagnetic broadening of NMR signals. At 25 °C in $CDCl_3$, the ^1H NMR spectrum of a 0.11 M solution of $VOCl_3$ containing 2 equiv of acetone consisted of a single peak at δ 2.23, only slightly downfield of the signal of free acetone itself. In similar ^1H NMR spectra, peaks derived from 3,3-dimethyl-2-butanone (pinacolone) also appeared near their normal positions. At −40 °C in CH_2Cl_2 containing 20% CD_2Cl_2, the ^{51}V NMR spectrum of a 0.61 M solution of $VOCl_3$ containing 2 equiv of pinacolone consisted of a single peak at δ −3 ($w_{1/2}$ = 1600 Hz), close to that of $VOCl_3$ itself.[9] We conclude that $VOCl_3$ is a relatively weak Lewis acid and that at these concentrations and temperatures its ketone complexes are almost fully dissociated.[6c]

In contrast, spectra recorded at significantly lower temperatures provided clear evidence for the quantitative formation of adducts. At −140 °C in a 4:1 mixture of CHF_2Cl and CD_2Cl_2, the ^1H NMR spectrum of a 0.11 M solution of $VOCl_3$ containing an equimolar amount of pinacolone showed two sharp methyl singlets at δ 2.75 and 2.64 in an approximately 1:1 ratio and no peak near δ 2.20 corresponding to free pinacolone. At −120 °C, the proton-decoupled ^{13}C NMR spectrum of a similar 0.91 M solution contained two signals at δ 242 and 234 corresponding to the carbonyl carbons of two different bound pinacolones. The low-temperature ^1H and ^{13}C NMR spectra of equimolar solutions of $VOCl_3$ and acetone showed similar features, but the two bound ketones no longer produced signals of nearly equal intensity. Spectra of solutions containing excess ketone were even more complex. For example, at −135 °C in a 4:1 mixture of CHF_2Cl and CD_2Cl_2, the ^{13}C NMR spectrum of a 0.91 M solution of $VOCl_3$ containing 3 equiv of pinacolone showed distinct signals at δ 232, 226, and 221 corresponding to the carbonyl carbons of at least three different bound pinacolones. Furthermore, the ^{51}V NMR spectrum of a similar 0.61 M solution of $VOCl_3$ at −80 °C consisted of a broad peak at δ −46 ($w_{1/2}$ = 1900 Hz) and a narrower peak of similar intensity at δ +37 ($w_{1/2}$ = 300 Hz). The chemical shift of the broader signal is characteristic of neutral adducts of $VOCl_3$,[9] while the narrower signal presumably corresponds to $VOCl_4^-$ or related anionic derivatives of $VOCl_3$.[9] The complexity of all of these spectra confirms earlier reports that the interaction of $VOCl_3$ and ketones in solution at low temperature produces a mixture of neutral and ionic adducts.

Ketone Adducts of Monodentate Vanadyl Dichloride Alkoxides. Like $VOCl_3$, vanadyl dichloride alkoxides form solid 1:1 and 1:2 adducts with a variety of monodentate Lewis bases.[8d] The structures of these solids are unknown, and studies of the interaction of vanadyl dichloride alkoxides with Lewis bases have reached divergent conclusions about the major species present in solution.[8d,11] To obtain further information, we used variable-temperature NMR spectroscopy to study the interaction of vanadyl dichloride isopropoxide (4)[8d,12] with ketones. Compound **4** was

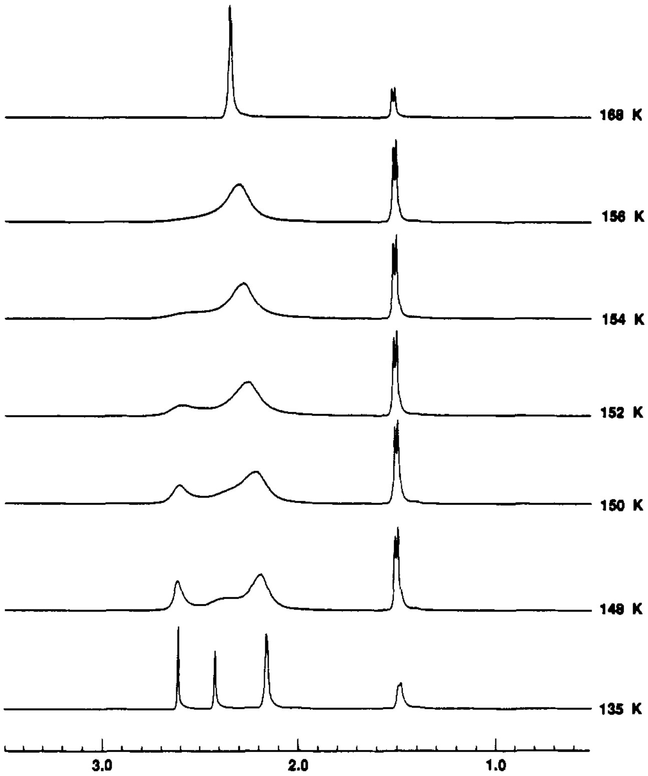
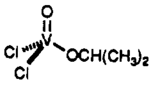


Figure 1. Variable-temperature ^1H NMR spectra of a 0.14 M solution of vanadyl dichloride isopropoxide (**4**) in 4:1 CHF_2Cl/CD_2Cl_2 containing 3 equiv of acetone.



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prepared by the direct reaction of 2-propanol with $VOCl_3$[8d,12] and was purified by distillation in vacuo. The volatility of this material, its high solubility in organic solvents, and the invariance of its ^{51}V NMR chemical shift with changes in temperature[9c] corroborate earlier work indicating that isopropyl vanadates are largely monomeric in solution.[9a] At −140 °C in CHF_2Cl containing 20% CD_2Cl_2, the ^{51}V NMR spectrum of a 1.0 M solution of compound **4** consisted of a single sharp peak at δ −317 ($w_{1/2}$ = 400 Hz).[9d] At −120 °C, the ^1H NMR spectrum of a similar 0.21 M solution showed a single sharp isopropyl doublet at δ 1.61 (6 H) and a characteristically broadened multiplet at δ 6.30 (1 H).[13] The simplicity of these spectra demonstrates that pure vanadyl dichloride isopropoxide (**4**) resists redistribution in solution, unlike similar compounds of aluminum,[3c] titanium,[3a] and zirconium.[3e] This is a prerequisite for the construction of well-defined multidentate Lewis acids containing electrophilic sites derived from $VOCl_3$.

At 25 °C in $CDCl_3$, the ^1H NMR spectrum of a 0.14 M solution of vanadyl dichloride isopropoxide (**4**) containing 1 equiv of pinacolone consisted of singlets at δ 1.11 and 2.12, essentially identical with those of free pinacolone itself. We conclude that compound **4**, like $VOCl_3$, is a relatively weak Lewis acid and that

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(8) (a) Howarth, O. W.; Trainor, J. R. *Inorg. Chim. Acta* **1987**, *127*, L27–L28. (b) Hibbert, R. C.; Logan, N.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1986**, 369–372. (c) Konovalova, A. A.; Bainova, S. V.; Kopanev, V. D.; Buslaev, Yu. A. *Koord. Khim.* **1982**, *8*, 1364–1367. (d) Miles, S. J.; Wilkins, J. D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2271–2276.

(9) (a) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013–3019. (b) Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Ibid.* **1988**, *27*, 584–587. (c) Weidemann, C.; Rehder, D. *Inorg. Chim. Acta* **1986**, *120*, 15–20. (d) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–3062. (e) Paulsen, K.; Rehder, D. *Z. Naturforsch.* **1982**, *37A*, 139–149. (f) Rehder, D. *Ibid.* **1977**, *32B*, 771–775.

(10) Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1990**, *31*, 3917–3918. Meier, I. K.; Schwartz, J. *J. Org. Chem.* **1990**, *55*, 5619–5624. Hirao, T.; Mori, M.; Ohshiro, Y. *Ibid.* **1990**, *55*, 358–360. Baker, K. L.; Edwards, D. A.; Fowles, G. W. A.; Williams, R. G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1881–1885.

(11) Konovalova, A. A.; Bainova, S. V.; Kopanev, V. D.; Buslaev, Yu. A. *Koord. Khim.* **1982**, *8*, 1211–1216.

(12) Mittal, R. K.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* **1964**, *332*, 189–196.

(13) Since similar broadening persists even at 25 °C, it cannot be due to association or to rotational isomerization.[14] Instead, we attribute it primarily to a nonzero $^3J(^1H, ^{51}V)$.

(14) Witke, K.; Lachowicz, A.; Brüser, W.; Zeigan, D. *Z. Anorg. Allg. Chem.* **1980**, *465*, 193–203.

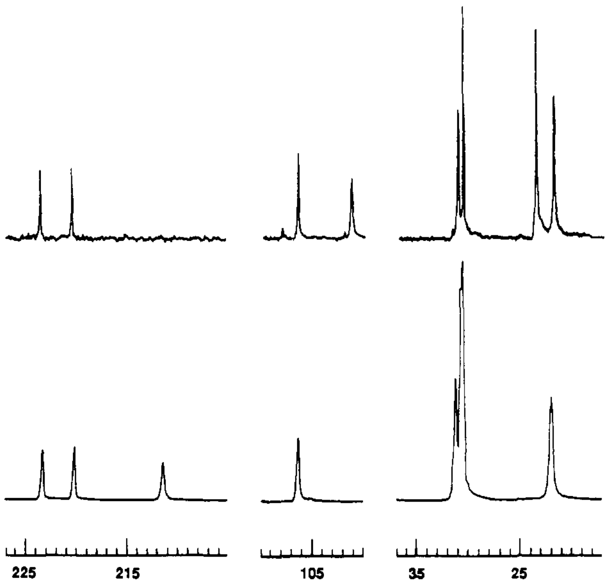
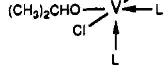
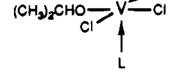


Figure 2. Proton-decoupled ^{13}C NMR spectra of mixtures of vanadyl dichloride isopropoxide (**4**) and acetone in 4:1 CHF_2Cl/CD_2Cl_2 at −134 °C: (a) 0.67 M solution of compound **4** containing 1 equiv of acetone; (b) 0.62 M solution of compound **4** containing 3 equiv of acetone.

at these concentrations and temperatures its ketone complexes are almost completely dissociated.[8d] We then recorded an extremely informative series of low-temperature ^1H NMR spectra of a 0.10 M solution of compound **4** with 3 equiv of acetone in CHF_2Cl containing 20% CD_2Cl_2 (Figure 1). At −146 °C, three sharp singlets appeared at δ 2.61, 2.42, and 2.16 in a 1:1:1 ratio. The first two correspond to bound acetone, and the third corresponds to free acetone. In addition, the spectrum showed one isopropyl doublet at δ 1.49. These observations suggest that a single 1:2 adduct with nonequivalent molecules of acetone is formed at low temperature. We propose that this is a neutral octahedral complex **5a** (L = acetone) with acetones trans to the strongly π-donating oxo and alkoxy oxygens.[15] This structure maximizes oxygen-p vanadium-d π-bonding and geometrically resembles the known *mer* octahedral 1:2 adducts of $VOCl_3$,[7] so we prefer it to alternatives **5b–f**. Moreover, structures **5c,d,f** cannot explain our results, since they contain acetones that are equivalent by symmetry. Spectra of 1:3 mixtures of vanadyl dichloride isopropoxide (**4**) and pinacolone recorded under similar conditions showed the same principal features, so we conclude that a neutral 1:2 adduct **5a** (L = pinacolone) is again the major species present in solution.



5a



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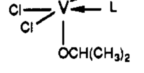

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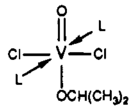
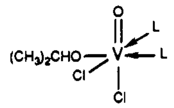
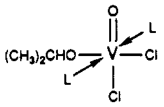


5d



5e



5f

This conclusion is supported by further studies using low-temperature ^{13}C and ^{51}V NMR spectroscopy. At −134 °C in a 4:1 mixture of CHF_2Cl and CD_2Cl_2, the proton-decoupled ^{13}C NMR spectrum of a 0.62 M solution of compound **4** containing 3 equiv of acetone revealed peaks at δ 223.9, 220.8, 31.7, and 31.2 for two nonequivalent bound acetones, as well as peaks at δ 211.9 and 31.2 for free acetone (Figure 2b). Single peaks at δ 107.1 and 22.5 confirmed that only one isopropyl group was present. Again, spectra of 1:3 mixtures of vanadyl dichloride isopropoxide (**4**) and pinacolone recorded under these conditions showed similar features, suggesting that the formation of 1:2 ketone adducts **5a** is a general preference. At −80 °C in a 4:1 mixture of CH_2Cl_2 and CD_2Cl_2, the ^{51}V NMR spectrum of a 0.80 M solution of compound **4** containing 2 equiv of pinacolone consisted of a single major peak at δ −371 ($w_{1/2}$ = 1000 Hz), shifted 64 ppm upfield from the signal of pure compound **4**. In a spectrum recorded at −115 °C, this signal was further broadened but did not split. Since similar upfield shifts of ^{51}V NMR signals are characteristic of complexation,[9] this supports our conclusion that vanadyl dichloride isopropoxide (**4**) forms neutral 1:2 adducts with ketones in solution. The ^{51}V NMR spectrum at −80 °C also contained two very minor peaks at δ −508 and +40, which can be attributed to the presence of small amounts of vanadyl chloride diisopropoxide[9d] and anionic derivatives of $VOCl_3$ produced by redistribution of compound **4** (eq 3). Signals corresponding to the products of redistribution do not appear in low-temperature ^{51}V NMR spectra of pure vanadyl dichloride isopropoxide (**4**), so redistribution must be more significant when ligands are present, presumably because $VOCl_3$ is a somewhat stronger Lewis acid than vanadyl chloride alkoxides.

$$\underset{\mathbf{4}}{2\ \mathrm{VOCl_2OCH(CH_3)_2}} \rightleftharpoons \mathrm{VOCl[OCH(CH_3)_2]_2} + \mathrm{VOCl_3} \qquad (3)$$

Detailed analysis of the low-temperature ^1H NMR spectra of 1:3 mixtures of vanadyl dichloride isopropoxide (**4**) and acetone (Figure 1) has shown that the peaks for bound acetone at δ 2.61 and 2.42 coalesce with the peak for free acetone at −119 and −125 °C, respectively. This indicates that ΔG_{154}^{*} for the exchange of free acetone and the bound acetone responsible for the downfield singlet is approximately 7.1 ± 0.1 kcal/mol, while ΔG_{148}^{*} for the other exchange is 6.8 ± 0.1 kcal/mol.[16] A similar analysis of the low-temperature ^1H NMR spectra of 1:3 mixtures of vanadyl dichloride isopropoxide (**4**) and pinacolone shows that ΔG_{145}^{*} for the exchange of free pinacolone and the bound pinacolone responsible for the downfield singlet is 6.6 ± 0.1 kcal/mol, while ΔG_{135}^{*} for the other exchange is 6.2 ± 0.1 kcal/mol. These low values confirm that both acetone and pinacolone are weakly bound and suggest that the mechanism of exchange with free ketone is dissociative. Pinacolone exchanges more rapidly than acetone, presumably because it is more bulky and therefore slightly more weakly bound. As expected, the more deshielded ketone exchanges more slowly in both complexes. We propose that this ketone is the one bound trans to the alkoxy oxygen, and we suggest that the ketone trans to the oxo oxygen is more weakly bound. This hypothesis is consistent with the results of crystallographic studies of the 1:1 and 1:2 complexes of $VOCl_3$ with nitriles,[7] which indicate that the second ligand is added trans to the oxo oxygen.

In ^1H NMR spectra of 1:3 mixtures of vanadyl dichloride isopropoxide (**4**) and acetone recorded at temperatures as low as −146 °C (Figure 1), the two methyl groups of each bound acetone cannot be distinguished. Like similar compounds of titanium[3a,3b] and zirconium,[3c] vanadyl dichloride isopropoxide therefore appears to form nonlinear σ-bonded complexes of ketones in which syn–anti isomerization is extremely rapid (eq 4). The transition state for this process is presumably a linear σ complex stabilized by significant oxygen-p vanadium-d π-bonding or by an important

(4)

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(15) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 15.3.

(16) ΔG^{*} (kcal/mol) at the coalescence temperature was estimated by using the equation $\Delta G^{*} = aT_c(9.97 + \log T_c/\delta\nu)$, where T_c is the coalescence temperature (K), $a = 4.575 \times 10^{-3}$, and $\delta\nu$ is the shift difference (Hz) between the two exchanging sites in the limiting low-temperature spectrum. See: Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1973; p 243.

electrostatic contribution to the energy of complexation.

We were surprised to find that solutions prepared by mixing vanadyl dichloride isopropoxide (**4**) with equimolar amounts of ketones do not contain significant amounts of neutral 1:1 adducts at low temperatures. Our observations indicate that 1:2 adducts are favored instead and that the equilibrium of eq 5 (L = ketone)

$$2\ \mathrm{VOCl_2OCH(CH_3)_2 \cdot L} \rightleftharpoons \underset{\mathbf{4}}{\mathrm{VOCl_2OCH(CH_3)_2}} + \mathrm{VOCl_2OCH(CH_3)_2 \cdot 2L} \qquad (5)$$

lies far to the right. At −146 °C in a 4:1 mixture of CHF_2Cl and CD_2Cl_2, the ^1H NMR spectrum of a 0.14 M solution of compound **4** containing an equimolar amount of acetone consisted of two sharp methyl singlets at δ 2.61 and 2.42 characteristic of the 1:2 adduct. Moreover, the spectrum showed the isopropyl doublet at δ 1.49 previously assigned to the 1:2 adduct, as well as a second doublet of equal intensity at δ 1.61 derived from free vanadyl dichloride isopropoxide (**4**). At −134 °C, the proton-decoupled ^{13}C NMR spectrum of a similar 0.67 M solution revealed the characteristic signals of the 1:2 adduct at δ 223.9, 220.8, 107.1, 31.7, 31.2, and 22.5, as well as the expected signals of free vanadyl dichloride isopropoxide (**4**) at δ 101.8 and 24.2 (Figure 2a). Low-temperature ^1H and ^{13}C NMR spectra of solutions containing equimolar amounts of compound **4** and pinacolone showed similar features, confirming that 1:1 ketone adducts are generally disfavored in solution. Additional evidence that equimolar mixtures of vanadyl dichloride isopropoxide (**4**) and pinacolone consist primarily of equal amounts of free compound **4** and 1:2 adduct was provided by low-temperature ^{51}V NMR spectra. At −80 °C in 3:1 CH_2Cl_2/CD_2Cl_2, the spectrum of a 0.88 M solution showed a single averaged peak at δ −346, but at −145 °C in 4:1 CHF_2Cl/CD_2Cl_2, the spectrum of a 0.90 M solution consisted of two distinct signals of nearly equal intensity at δ −317 ($w_{1/2}$ = 1700 Hz) and −409 ($w_{1/2}$ = 1900 Hz). The downfield signal corresponds to free compound **4**, while the upfield signal corresponds to its 1:2 pinacolone adduct. We conclude that solutions of vanadyl dichloride isopropoxide (**4**) containing 2 equiv of ketone consist almost exclusively of the neutral 1:2 complex **5a** (L = ketone) at low temperatures, while equimolar mixtures contain equal concentrations of complex **5a** and free compound **4**. Since the coalescence temperatures for exchange of the two nonequivalent bound ketones under both conditions are identical to within 2 °C, exchange cannot occur by an associative mechanism involving the direct reaction of complex **5a** with free vanadyl dichloride isopropoxide (**4**).

Thermodynamic parameters for the equilibrium of eq 6 (L = pinacolone) could be derived from the temperature dependence of the ^{51}V chemical shift of a 0.90 M solution of vanadyl dichloride

$$\underset{\mathbf{4}}{\mathrm{VOCl_2OCH(CH_3)_2}} + 2\mathrm{L} \rightleftharpoons \mathrm{VOCl_2OCH(CH_3)_2 \cdot 2L} \qquad (6)$$

isopropoxide (**4**) in 4:1 CHF_2Cl/CD_2Cl_2 containing 5 equiv of pinacolone. As the temperature decreased from 0 to −100 °C, $\delta(^{51}V)$ moved sharply upfield (Figure 3). Since the chemical shift of free compound **4** does not vary significantly with temperature,[9e] and since significant amounts of the 1:1 pinacolone adduct are never present, the upfield shift can only be attributed to the formation of increasing amounts of the 1:2 pinacolone adduct. Limiting chemical shifts of δ −317 and −383 for free vanadyl dichloride isopropoxide (**4**) and its 1:2 adduct were used to calculate the association constants at each temperature. A van't Hoff plot (Figure 4) then showed that $\Delta H = -10.9$ kcal/mol and $\Delta S = -51$ eu for the equilibrium of eq 6 (L = pinacolone). The small negative ΔH and large negative ΔS are fully consistent with our hypothesis that a relatively weak ternary adduct is formed.

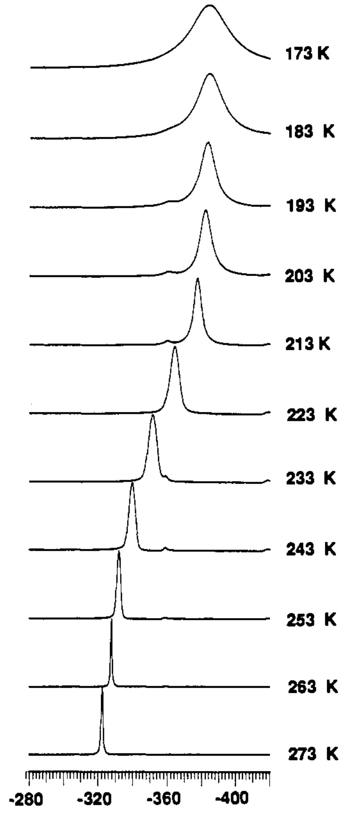


Figure 3. Temperature dependence of the ^{51}V chemical shift of a 0.90 M solution of vanadyl dichloride isopropoxide (**4**) in 4:1 CHF_2Cl/CD_2Cl_2 containing 5 equiv of pinacolone.

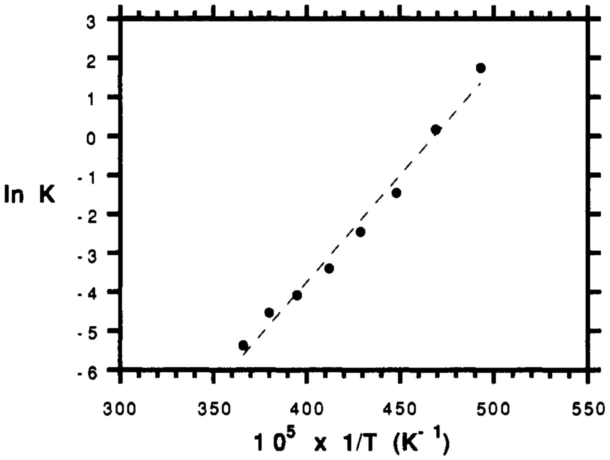
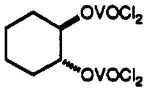


Figure 4. Standard van't Hoff plot for the formation of the 1:2 pinacolone adduct of vanadyl dichloride isopropoxide (**4**).

Ketone Adducts of Bidentate Vanadyl Dichloride Alkoxides. Our observations demonstrate that simple monodentate vanadyl dichloride alkoxides are sufficiently Lewis acidic to bind ketones at low temperatures, that they favor 1:2 adducts in solution at the expense of 1:1 adducts, that they exchange ketones dissociatively, and that they normally resist redistribution, aggregation, and the formation of ionic adducts. Their well-defined coordination chemistry therefore provided a solid and promising foundation for studies of more complex multidentate analogues. Bidentate vanadyl dichloride alkoxide **6** could be prepared in 99% yield by treating the bis(trimethylsilyl) ether[17] of racemic *trans*-1,2-cyclohexanediol with 2 equiv of $VOCl_3$. Although the product decomposed when heated and could not be purified by distillation even at 10^{-5} Torr, it could be crystallized with difficulty from a cold mixture of CHF_2Cl and CH_2Cl_2. In general, however, the initial product was pure enough to be used directly in com-



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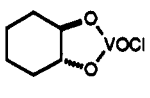

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[17] (a) Lasocki, Z. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 29–35. (b) For related work, see: Hwu, J. R.; Anderson, D. A.; Wang, N.; Buchner, M. M.; Gani, P.; Tsay, S.-C. *Chem. Ber.* **1990**, *123*, 1667–1671.

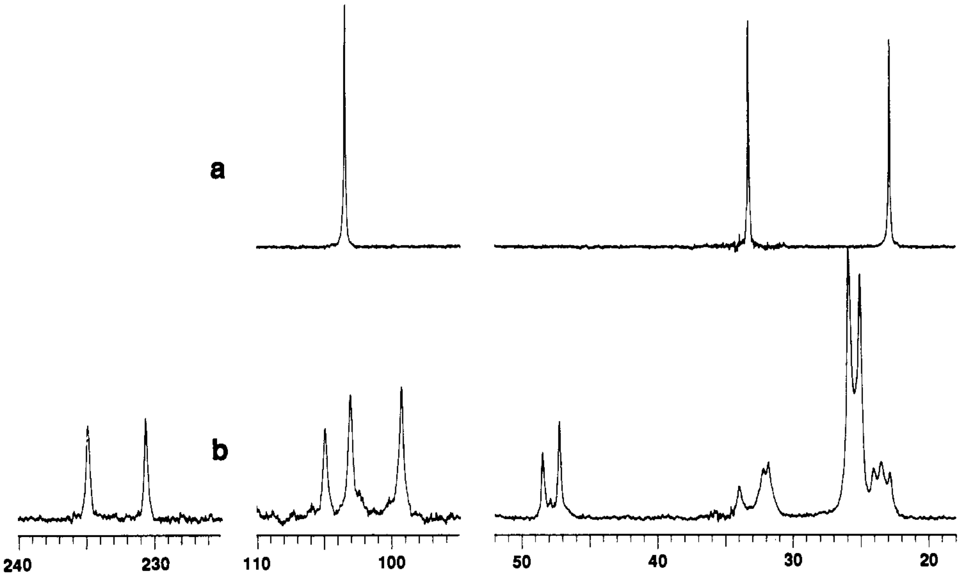
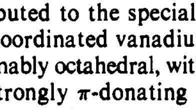


Figure 5. (a) Proton-decoupled ^{13}C NMR spectrum of a 0.24 M solution of bidentate vanadyl dichloride alkoxide **6** in CD_2Cl_2 at −100 °C. (b) Spectrum of a 0.21 M solution of compound **6** in 4:1 CHF_2Cl/CD_2Cl_2 at −135 °C in the presence of 1 equiv of pinacolone.

plexation experiments with ketones. At 25 °C in $CDCl_3$, the ^{1}H NMR spectrum of compound **6** contained a somewhat broadened multiplet at δ 5.81 (2 H, $w_{1/2} \sim 20$ Hz)[13] characteristic of axial carbinolic hydrogens, and the proton-decoupled ^{13}C NMR spectrum consisted of three peaks at δ 102.1, 33.9, and 23.4. No important changes occurred when the ^{1}H NMR spectrum was recorded at −120 °C in 4:1 CHF_2Cl/CD_2Cl_2 or at −78 °C in pure CD_2Cl_2, or when the ^{13}C NMR spectrum was recorded at −100 °C in CD_2Cl_2 (Figure 5a), so compound **6** does not appear to undergo significant redistribution or aggregation, nor does it contain important amounts of the conformer with diaxial $OVOCl_2$ groups. In addition, the ^{51}V NMR spectrum of a 0.23 M solution in 4:1 CH_2Cl_2/CD_2Cl_2 at −118 °C showed a sharp peak at δ −293 ($w_{1/2}$ = 250 Hz) characteristic of a normal, unassociated vanadyl dichloride alkoxide,[9] as well as a very minor signal at δ −330 that could not be assigned. The absence of a peak for $VOCl_3$ at δ 0 is noteworthy, since it confirms that compound **6** resists redistribution in solution. Its infrared spectrum (Nujol mull) revealed strong bands for V═O and V—Cl stretching near 1000 and 480 cm^{-1}, respectively, which are closely similar to those of simple monodentate vanadyl dichloride isopropoxide (**4**) itself.[9a,14] We conclude that bidentate Lewis acid **6** is a stable molecule with two equatorial $OVOCl_2$ groups that do not interact intramolecularly or intermolecularly by oxygen or chloride bridging. These groups are therefore in close proximity and freely available for the cooperative binding of complementary Lewis bases.

Treatment of the bis(trimethylsilyl) ether[17] of *trans*-1,2-cyclohexanediol with a single equivalent of $VOCl_3$ provided a 92% yield of a less soluble substance, presumably cyclic vanadyl chloride dialkoxide **7**, an aggregate, or an oligomeric derivative.[9a,18] At −100 °C, the ^{51}V NMR spectrum of a saturated solution of this product in 4:1 CH_2Cl_2/CD_2Cl_2 consisted of a narrow peak at δ −474 ($w_{1/2}$ = 900 Hz), which is close to the chemical shifts of other vanadyl chloride dialkoxides.[9]

At 25 °C in $CDCl_3$, the ^{1}H NMR spectrum of a 0.056 M solution containing equimolar amounts of bidentate vanadyl dichloride alkoxide **6** and pinacolone showed no significant shifts, so simple ketone adducts of compound **6** are almost fully dissociated under these conditions. Despite the presence of two adjacent electrophilic sites, bidentate Lewis acid **6** therefore appears to resemble its monodentate analogues $VOCl_3$ and vanadyl dichloride isopropoxide (**4**). In a series of pivotal experiments, we then recorded spectra of equimolar mixtures of bidentate vanadyl dichloride alkoxide **6** and pinacolone at low temperatures. At −135 °C in 4:1 CHF_2Cl/CD_2Cl_2, the proton-decoupled ^{13}C NMR spectrum of a 0.21 M solution showed a pair of carbonyl carbons of nearly equal intensity at δ 235 and 231 (Figure 5b), as well as a related pair of methyl carbons at δ 49 and 47, indicating that pinacolone is bound in two similar but different environments. In addition, three distinct peaks derived from the equivalent carbinolic carbons of compound **6** appeared at δ 105, 103, and 99. The peak at δ 103 corresponds to uncomplexed compound **6**, and we assign the pair of remaining peaks to a nearly equal amount of unsymmetric 1:2 adduct **8** (L = pinacolone). Like its simple monodentate analogue **4**, bidentate vanadyl dichloride alkoxide **6** therefore appears to favor 1:2 pinacolone complexes at the expense of 1:1 complexes, including symmetric structure **9** (L = pinacolone) with a cooperatively bound carbonyl ligand. This suggests immediately that no unusual chemical effects can be attributed to the special juxtaposition of electrophilic sites.



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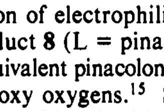
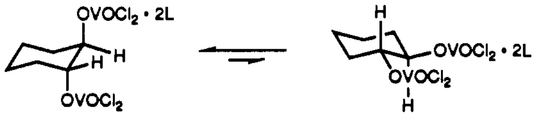


9

The coordinated vanadium in 1:2 adduct **8** (L = pinacolone) is presumably octahedral, with two nonequivalent pinacolones trans to the strongly π-donating oxo and alkoxy oxygens.[15] Similar complexation of vanadyl dichloride isopropoxide (**4**) with ketones causes the carbinolic carbon at δ 101.8 to shift downfield to δ 107.1, so the carbon in adduct **8** responsible for the signal at δ 105 must be the one bearing the $OVOCl_2{\cdot}2L$ group. The other carbinolic carbon, which appears at δ 99 and bears the free $OVOCl_2$ group, is anomalously shielded. Since similar upfield shifts are highly characteristic of carbinolic carbons in axial derivatives of cyclohexanol,[19] we propose that 1:2 adduct **8** (L = pinacolone) exists primarily as diaxial conformer **8a**, not diequatorial conformer **8b**. Diaxial structure **8a** is presumably favored because it separates the electrophilic sites and allows one



8a **8b**

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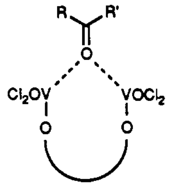
(18) Related cyclic vanadates are discussed by: Crans, D. C.; Felty, R. A.; Miller, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 265–269. Bottomley, F.; Magill, C. P.; White, P. S. *Ibid.* **1989**, *111*, 3070–3071. Tracey, A. S.; Gresser, M. J. *Inorg. Chem.* **1988**, *27*, 2695–2702.

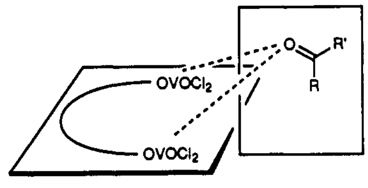
(19) Schneider, H.-J.; Freitag, W.; Weigand, E. *Chem. Ber.* **1978**, *111*, 2656–2664.

or both to accept the normal complement of two ligands, even when they are as bulky as pinacolone. In effect, the flexibility of bidentate vanadyl dichloride alkoxide **6** and its stubborn preference for 1:2 ketone adducts join forces to oppose the formation of symmetric 1:1 adduct **9** with a bridging pinacolone.

The bridging ketone in the elusive adduct **9** (L = ketone) can be bound in two distinct ways. In structure **10a**, both vanadiums lie near the carbonyl plane and interact formally with the two sp^2 lone pairs of the carbonyl oxygen, creating a purely σ-bonded adduct. In alternative **10b**, the vanadiums lie well above and below the carbonyl plane and interact with a single lone pair. In this case, the bonding can be described as a σ–π hybrid or as a three-center, two-electron bond formed by the interaction of one sp^2 lone pair with two empty orbitals contributed by vanadium. Carbonyl bridging of either type is rare,[4] presumably because carbonyl compounds are only weakly basic and because a suitable juxtaposition of strongly electrophilic sites is hard to achieve. We reasoned that motif **10b** would be able to accommodate a highly unsymmetric ketone such as pinacolone without difficulty, since both OVOCl$_2$ groups can be placed syn to the smaller substituent R. In contrast, formation of σ-adduct **10a** would be problematic for pinacolone but perhaps feasible for small, symmetric ketones. We therefore recorded low-temperature ^{13}C NMR spectra of solutions containing equimolar amounts of bidentate vanadyl dichloride alkoxide **6** and acetone. At −125 °C in 4:1 CHF$_2$Cl/CD$_2$Cl$_2$, the spectrum of a 0.23 M solution showed four carbonyl carbons at δ 228, 225, 224, and 220, as well as five distinct signals for carbinolic carbons at δ 108, 105, 104, 103, and 99. The conspicuously deshielded and shielded carbinolic carbons at δ 108 and 99 are particularly informative, since they suggest that a bound equatorial OVOCl$_2$·2L group is present, as well as a free axial OVOCl$_2$ group. We conclude that significant amounts of diaxial 1:2 adduct **8a** (L = acetone) and diequatorial adduct **8b** (L = acetone) are present simultaneously, in addition to corresponding amounts of free vanadyl dichloride alkoxide **6**.

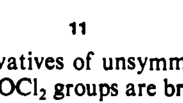


10a



10b

Formation of detectible amounts of diequatorial 1:2 adduct **8b** is plausible, since acetone may be small enough to be bound without forcing the electrophilic sites to become exclusively diaxial. The detection of unsymmetric diequatorial adduct **8b** is noteworthy, because it demonstrates that a ketone can be bound in close proximity to a free electrophilic site without necessarily promoting carbonyl bridging. Our evidence is fully consistent with the hypothesis that adduct **8b** is formed, but we cannot rigorously eliminate alternative structures, including unsymmetric diequatorial 1:2 adduct **11** (L = acetone) with a single bridging carbonyl or closely related derivatives of unsymmetric 1:2 adduct **8b** in which diequatorial OVOCl$_2$ groups are bridged by chloride or by oxo or alkoxy oxygens. We doubt that carbonyl bridging is involved, however, since our ^{13}C NMR spectra do not reveal the abnormally deshielded carbonyl carbon expected for the bridging ketone of structure **11**. Moreover, structure **11** would presumably provide an unusually rapid, intramolecular, associative mechanism for exchange of the nonequivalent ketones and vanadiums and for the resulting symmetrization of the complex. In fact, variable-temperature ^{13}C NMR studies indicate that the symmetrizations of diaxial adduct **8a** (L = acetone) and diequatorial conformer **8b** are nearly equally rapid and are slightly slower than intermolecular exchange of acetone between vanadyl dichloride isopropoxide (**4**) and its 1:2 adduct.[20] These observations provide strong evidence that adducts **8a** and **8b** both exchange dissociatively and that bridged complex **11** (L = acetone) is disfavored, either as a stable entity or as an intermediate or transition state involved in an intramolecular exchange of ketones.



11

Attempts to use ^{1}H NMR spectroscopy to study the interaction of bidentate vanadyl dichloride alkoxide **6** with equimolar amounts of ketones were inconclusive. At −137 °C in 4:1 CHF$_2$Cl/CD$_2$Cl$_2$, the spectrum of a 0.14 M solution containing acetone showed broad, overlapping signals near δ 2.7 attributable to bound acetone and equatorial cyclohexyl hydrogens adjacent to the OVOCl$_2$ groups. As a result, these spectra could not be analyzed in great detail. In contrast, low-temperature ^{51}V NMR spectra provided clear evidence for the formation of unsymmetric 1:2 adduct **8** (L = ketone). At −110 °C in 4:1 CH$_2$Cl$_2$/CD$_2$Cl$_2$, the ^{51}V NMR spectrum of a 0.30 M solution containing equimolar amounts of compound **6** and acetone consisted primarily of a single broad peak at δ −298 ($w_{1/2}$ = 1500 Hz), in addition to minor signals at δ −474 and +40 presumably derived from the products of redistribution. Analogous mixtures of compound **6** and pinacolone produced a similar ^{51}V NMR spectrum with a principal signal at δ −295 ($w_{1/2}$ = 1300 Hz). At still lower temperatures the major signal broadened and then split, and at −135 °C in 4:1 CHF$_2$Cl/CD$_2$Cl$_2$ the spectrum of an equimolar mixture of compound **6** and pinacolone consisted of two signals at δ −293 ($w_{1/2}$ = 1100 Hz) and −383 ($w_{1/2}$ = 1200 Hz) in a 3:1 ratio. The downfield signal corresponds to three unbound OVOCl$_2$ groups and the upfield to a single bound OVOCl$_2$ group, so this observation is perfectly consistent with our hypothesis that equimolar mixtures of bidentate vanadyl dichloride alkoxide **6** and ketones consist primarily of equal amounts of free compound **6** and unsymmetric 1:2 adduct **8** (L = ketone) at low temperatures.

Despite persistent efforts, we have not been able to isolate crystalline ketone adducts of bidentate vanadyl dichloride alkoxide **6**, so we cannot confirm that the preferences manifested in solution are retained in the solid state. We attribute our failure to obtain solid adducts to the characteristically low formation constants, and attempts to compensate by working with concentrated solutions at low temperatures were unsuccessful. In addition, attempts to prepare more stable adducts by using particularly basic carbonyl compounds were thwarted by redox and redistribution reactions in which V(V) is reduced to V(IV).[10] For example, treatment of compound **6** with *N*,*N*,*N'*,*N'*-tetramethylurea provided magnificent blue crystals of bis(tetramethylurea)dichlorooxovanadium(IV)[21] in 64% yield.

Conclusions

Our results demonstrate that potentially bidentate vanadyl dichloride alkoxide **6** does not form significant amounts of symmetric 1:1 ketone adducts **10a** or **10b** in which the ligand experiences double electrophilic activation. This is true even though compound **6** can form diequatorial adducts **8b** in which a bound ketone is held close to a free electrophilic site. Failure to detect symmetric adducts does not rule out the possibility that small amounts may nevertheless play a kinetically important role in reactions of the bound ligand. However, it raises urgent questions about what specific structural features in bidentate Lewis acids promote or oppose the formation of complexes in which a bound carbonyl compound experiences double electrophilic activation. The principal defects of bidentate vanadyl dichloride alkoxide **6** appear to include its low intrinsic Lewis acidity and its fundamental preference for 1:2 adducts. In addition, bridging by chloride or by oxo or alkoxy oxygens may compete favorably with bridging by a carbonyl oxygen. Furthermore, the C–O–V angles in compound **6** may adopt values near 180° to maximize oxygen-p vanadium-d π-bonding,[15] thereby causing the electrophilic sites

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(20) Inductive effects presumably make bidentate vanadyl dichloride alkoxide **6** an intrinsically stronger Lewis acid than simple monodentate analogues.

(21) Coetzer, J. *Acta Crystallogr., Sect. B* **1970**, *B26*, 872–874.

to diverge and become unavailable for the cooperative binding of a carbonyl compound. By eliminating these flaws systematically, we hope to create bidentate Lewis acids that can accomplish the double electrophilic activation of carbonyl compounds and can therefore provide powerful new capabilities in organic synthesis.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. A Varian VXR-300 spectrometer was used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra at 300 MHz, ^{13}C NMR spectra at 75.4 MHz, and ^{51}V NMR spectra at 78.9 MHz. In addition, a Bruker WH-400 instrument was used to record ^{1}H NMR spectra at low temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ), and ^{51}V chemical shifts are relative to external neat $VOCl_3$. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. CH_2Cl_2 and CD_2Cl_2 were dried by distillation from CaH_2, $CDCl_3$ was dried by distillation from P_2O_5, CHF_2Cl was dried by passage over 3-Å molecular sieves and then P_2O_5, acetone was dried over 3-Å molecular sieves and distilled, and pinacolone was dried over anhydrous $MgSO_4$ and 3-Å molecular sieves and was then distilled. $VOCl_2OCH(CH_3)_2$ (**4**) was prepared from 2-propanol by the standard method[8d,12] and purified by distillation in vacuo. Vanadyl chloro alkoxides were handled under dry Ar in Schlenk tubes or in a Vacuum Atmospheres HE-43-2 glovebox. All vanadyl chlorides were mixed with potential ligands at low temperature, and the resulting solutions were protected from light.[8c,9c]

Reaction of the Bis(trimethylsilyl) Ether of *trans*-1,2-Cyclohexanediol with $VOCl_3$ (2 equiv). A solution of the bis(trimethylsilyl) ether[17a] of racemic *trans*-1,2-cyclohexanediol (1.39 g, 5.34 mmol) in CH_2Cl_2 (5 mL) was stirred at −78 °C in the dark under dry Ar and was treated dropwise with $VOCl_3$ (1.85 g, 10.7 mmol). The resulting mixture was then brought to 25 °C. After 24 h, volatiles were removed by evaporation in vacuo. This yielded bidentate vanadyl dichloride alkoxide **6** as a yellow solid of analytical purity (2.06 g, 5.28 mmol, 99%): IR (Nujol mull, CsI) 1000–1050, 450–500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.59 (t, 2 H), 1.90 (d, 2 H), 1.98 (m, 2 H), 2.63 (d, 2 H), 5.81 (bs, 2 H); ^{13}C NMR (75.4 MHz, CD_2Cl_2, −100 °C) δ 22.9, 33.3, 103.5; ^{51}V NMR (78.9 MHz, 4:1 CH_2Cl_2/CD_2Cl_2, −118 °C) δ −293 ($w_{1/2}$ = 250 Hz). Anal. Calcd for $C_6H_{10}Cl_4O_4V_2$: C, 18.49; H, 2.59. Found: C, 19.25; H, 3.06.

Reaction of the Bis(trimethysilyl) Ether of *trans*-1,2-Cyclohexanediol with $VOCl_3$ (1 equiv). A solution of the bis(trimethylsilyl) ether[17a] of racemic *trans*-1,2-cyclohexanediol (0.847 g, 3.25 mmol) in CH_2Cl_2 (6 mL) was stirred at −78 °C in the dark under dry Ar and was treated dropwise with $VOCl_3$ (0.564 g, 3.25 mmol). The resulting mixture was then brought to 25 °C. After 24 h, volatiles were removed by evaporation in vacuo. This yielded the vanadyl chloride dialkoxide assigned structure **7** as a beige solid of analytical purity (0.649 g, 3.00 mmol, 92%): IR (Nujol mull, CsI) 1055, 1035, 1005, 475, 425, 390 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.4–1.6 (m, 4 H), 1.85 (d, 2 H), 2.33 (d, 2 H), 5.78 (m, 2 H); ^{51}V NMR (78.9 MHz, 4:1 CH_2Cl_2/CD_2Cl_2, −100 °C) δ −474 ($w_{1/2}$ = 900 Hz). Anal. Calcd for $C_6H_{10}ClO_3V$: C, 33.28; H, 4.66. Found: C, 33.55; H, 4.84.

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, and Merck Frosst.

Contribution from the Department of Chemistry,
Waseda University, Tokyo 169, Japan

A Tetranuclear Tervalent Platinum Complex with α-Pyrrolidonate and Deprotonated Ammine Bridging Ligands, $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$

Kazuko Matsumoto* and Kazuo Harashima

Received February 5, 1991

From the reaction of α-pyrrolidonate-bridged $[Pt^{II}{}_2Pt^{III}{}_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$ with excess pyrazine in water were obtained dark green, almost black block crystals of $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$. The crystal is monoclinic ($P2_1/c$) with cell dimensions of a = 10.652 (5) Å, b = 18.512 (7) Å, c = 10.430 (4) Å, β = 102.42 (3)°, Z = 2, and V = 2008 (1) Å^3. The complex consists of two α-pyrrolidonate-bridged Pt(III) dimeric units. The two dimers are bridged by two NH_2^- ligands to form tetranuclear $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}$. The Pt–Pt distance in the dimeric unit is 2.608 (1) Å, whereas that of the interdimer separation is 3.160 (2) Å.

We have synthesized a series of α-pyrrolidonate-bridged tetranuclear mixed-valent platinum complexes with various platinum oxidation states, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ (n = 5, 6, 8).[1-6] In the course of the study on the solution behavior of the tetranuclear complexes, we recently isolated a very unusual tetranuclear Pt(III) complex from an aqueous solution of $[Pt^{III}{}_2Pt^{II}{}_2(NH_3)_8(C_4H_6NO)_4]^{6+}$ with pyrazine. The tetranuclear Pt(III) complex is composed of two α-pyrrolidonate-bridged Pt(III) dimers, which are bridged by two NH_2^- ligands to form a tetranuclear complex with a formula of $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}$. The complex is the first example of a structurally elucidated NH_2^--bridged tetranuclear Pt(III) complex.

Experimental Section

The complex was synthesized by adding 8 mg (0.1 mmol) of pyrazine to a solution of 100 mg (0.06 mmol) of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$ (**1**)[1] in 4 mL of H_2O. After the solution was left at 5 °C for a few days, dark green, almost black block crystals appeared. The yield was 8%. The formula of the complex is $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$ (**2**).[7]

Table I. Crystallographic Data for $[(NO_3)(NH_3)_2Pt(C_4H_6NO)_2Pt(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$ (**2**)

formula	$Pt_4C_{16}H_{46}N_{18}O_{22}$	Z	2
fw	1623.12	T, °C	25
space group	$P2_1/c$ (No. 14)	radiation (λ, Å)	Mo Kα (0.71068)
a, Å	10.652 (5)	ρ_{calcd}, g cm^{-3}	2.68
b, Å	18.512 (7)	μ(Mo Kα), cm^{-1}	147.2
c, Å	10.430 (4)	transm coeff	1.00–0.70
β, deg	102.42 (3)	R^a	0.058
V, Å^3	2008 (1)	$R_w{}^b$	0.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

The X-ray analysis of **2** was carried out with a Rigaku AFC-5R automated diffractometer and the programs UNICS-III[8] and ORTEP.[9] Accurate unit cell dimensions were calculated from the setting angles of 20 reflections with 20° < 2θ < 25°. The structure was solved by a standard heavy-atom method. The crystallographic data for **2** are shown in Table I. Three standard reflections were measured every 200 measurements during the data collection. Lorentz and polarization corrections were applied to the data. All the non-hydrogen atoms were located in succeeding Fourier syntheses. An empirical absorption correction was

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(1) Matsumoto, K.; Takahashi, H.; Fuwa, K. *Inorg. Chem.* **1983**, *22*, 4086.
(2) Matsumoto, K.; Takahashi, H.; Fuwa, K. *J. Am. Chem. Soc.* **1984**, *106*, 2049.
(3) Matsumoto, K.; Watanabe, T. *J. Am. Chem. Soc.* **1986**, *108*, 1308.
(4) Matsumoto, K.; Matoba, N. *Inorg. Chim. Acta* **1986**, *120*, L1.
(5) Matsumoto, K.; Miyamae, H.; Moriyama, H. *Inorg. Chem.* **1989**, *28*, 2959.
(6) Matsumoto, K. *Chem. Lett.* **1984**, 2061.
(7) Anal. Calcd for $Pt_4C_{16}H_{46}N_{18}O_{22}$: C, 11.84; H, 2.86; N, 15.53. Found: C, 12.07; H, 3.07; N, 15.79.
(8) Sakurai, T.; Kobayashi, K. *Rigaku Kenkyusho Hokoku* **1979**, *55*, 69.
(9) Johnson, C. K. Report ORNL-3794 (revised); Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

0020-1669/91/1330-3032$02.50/0 © 1991 American Chemical Society