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Vanadium(I) Chloride and Lithium Vanadium(I) Dihydride as Epimetallating Reagents for Unsaturated Organic Substrates: Constitution and Mode of Reaction[‡]

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Dedicated to Professor Dr. Dr. h. c. mult. Wolfgang A. Herrmann on the occasion of his 60th birthday

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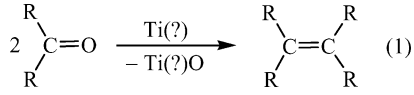
Subvalent vanadium(I) salts, of empirical formulas, VCl, vanadium(I) chloride and $LiVH_2$, lithium vanadium(I) dihydride, can be conveniently prepared in THF solution, starting at –78 °C, by treating either VCl_3 or VCl_4 with an appropriate number of equivalents of *n*BuLi. As judged by the stability of solutions or solid samples of $LiVH_2$, the preparation of $LiVH_2$ from VCl_4 is the preferred method. Individual physical characterization of solid samples of VCl or of $LiVH_2$, admixed with their LiCl by-product, was carried out after removal of all volatiles in vacuo and by the following measurements: 1) gasometric protolysis with glacial acetic acid and measurement of the H_2 evolved in the oxidation of V^I to V^{II}; 2) infrared spectroscopic search for V–H bands; and 3) examination for unpaired electrons by EPR activity. Such measurements applied to VCl lend strong support for a V^I oxidation state but only probable evidence for paramagnetism and for the association of VCl units. Similar measurements applied to $LiVH_2$ give unambiguous gasometric and IR evidence favoring the $LiVH_2$ stoichiometry and the biradical nature of the VH_2 anion with a linear array of H–V–H atoms. Chemical characterization of both VCl and $LiVH_2$ toward individual organic substrates, such as olefins, ketones, epoxides and organic halides, yielded convincing evidence that organic radical mechanisms are involved, both for the proven biradical, $LiVH_2$, as well as for the diamagnetic VCl. Finally, the question of why $LiVH_2$ prepared from VCl_4 is more stable than the $LiVH_2$ obtained from VCl_3 is addressed in terms of the actual coordination sphere of the VH_2 anion in THF solution and in the solid state. Preliminary studies comparing the reactivities of $LiVH_2$ and $LiCrH_2$ toward organic substrates indicate that $LiVH_2$ is the distinctly more moderate and usefully selective reductant.

Introduction

Subvalent Early Transition Metal Reductants in Organic Synthesis

The great utility and versatility of subvalent early transition metal salts as reductants in organic chemistry became evident in 1973, when the research groups of Mukaiyama,[2] Tyrlik[3] and McMurry[4] reported independently on the novel reductive dimerization of organic carbonyl derivatives by various combinations of titanium(III) or titanium(IV) salts with a main-group metal reductant, such as $LiAlH_4$, Mg, Al or Zn, cf. Equation (1). This transformation, which has been explored by the McMurry group[5] and a host of other researchers,[6] is a most valuable method for the assembly of a great variety of open-chain and ring-carbon skeletons. Unfortunately, the great number of recipes offered for generating the active subvalent titanium reagent have provided little insight into the actual oxidation state involved, Ti^0 and/or Ti^{II}, nor into the role that any ligands on Ti or an excess of main-group metal reductant might play in the reaction mechanism of C–C bond formation.[7]



(1)

Therefore, over the last 15 years our group has endeavored to develop preparative routes to defined oxidation states of subvalent titanium and other early transition metals, which reagents would be soluble and sufficiently stable in various ethers and would be free of any residual main-group reductant. Our first target was $TiCl_2$,[7–9] where we

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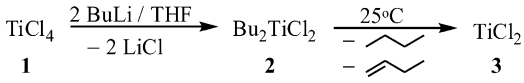
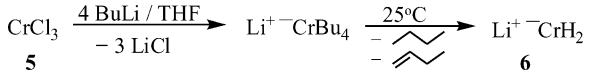
were pleased to discover that it could be prepared essentially quantitatively by the process given in Scheme 1. The $TiCl_4$ (**1**), dissolved in THF at –78 °C, was treated at –78 °C with two equivalents of BuLi in hexane to generate the tan-colored compound **2**. By raising the temperature thereafter to 25 °C, the butyl groups were lost, as butane and 1-butene, and titanium(II) chloride (**3**) was isolated as a black solid. Although **3** can be isolated free of LiCl as the complex, $TiCl_2$·2THF (**3a**), there is evidence that in the original solution **3** may also form complexes with 1-butene or with LiCl (cf. infra). Thus $TiCl_2$ should be considered as the empirical formula of **3** and not representative of the molecular formula, the state of solvation or the actual coordinated number of ligands.



Scheme 1.

The two-step process depicted in Scheme 1, known as alkylative reduction, has subsequently been applied to preparing subvalent reductants having empirical formulas of $Ti(OiPr)_2$ from $Ti(OiPr)_4$,[7,10] $ZrCl_2$ from $ZrCl_4$,[7,11] $HfCl_2$ from $HfCl_4$,[7,11] and CrCl (**4**) from $CrCl_3$.[12]

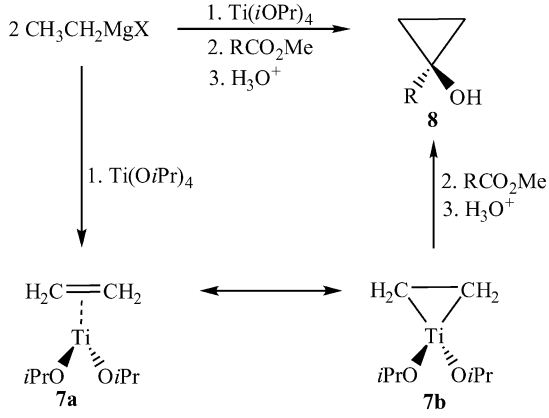
Adding significantly to potential reductants obtainable through alkylative reduction was the surprising finding that anionic hydride complexes could be generated by an excess of BuLi over the replaceable chlorides on the transition metal (Scheme 2). Chromium(III) chloride (**5**), for example, can give rise in high yield to lithium chromium(I) dihydride (**6**).[13] Here again, as with the empirical formula of the foregoing neutral subvalent complexes, it can be assumed that the coordination sphere of **6** could be expanded by solvation with THF molecules at the Li and Cr centers and/or by coordination of chloride anions or of η^2-bonded 1-butene units at the chromium atom.



Scheme 2.

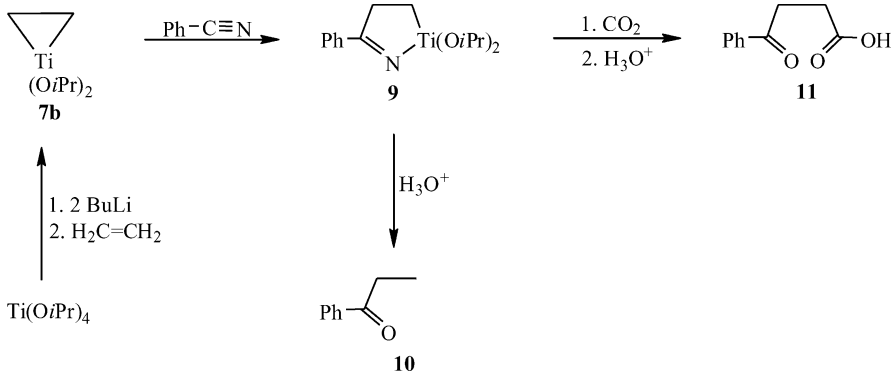
Oxidative Additions of Neutral and Anionic Transition-Metal Complexes to Unsaturated Covalent Bonds

The great potential of such transition reductants in organic synthesis is their oxidative addition to π-bonded C=C, C≡C, C=O or C=N functional groups. The first recognition of the vital role of such an addition was the discovery of the high-yielding synthesis of cyclopropanols (**8**) by Kulinkovich and co-workers from the interaction of esters with ethyl Grignard reagents and titanium(IV) isopropoxide.[14] In rationalizing this surprising result it was suggested that the three-membered intermediate **7** was involved.[15] Intermediate **7** can be described by two extreme resonance structures: **7a** as an η^2-π complex with little electron-transfer to the organic ligand and **7b** as a metallacyclopropane with much electron-transfer from the metal (Scheme 3). Strong support for the intermediacy of **7** in the Kulinkovich reaction was brought forward from our group by preparing **7** separately and then showing that the two apparent Ti–C bonds of **7b** can be detected by stepwise insertions of benzonitrile and then of CO_2 (Scheme 4).[16] Products **10** and **11** could only arise via intermediates **7b** and **9**.



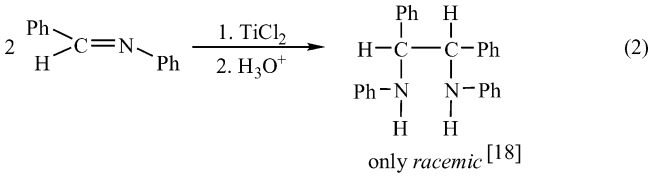
Scheme 3.

Such oxidative additions to π-bonds of C=C, C≡C, C=O and C=N linkages, leading to three-membered metallocyclic intermediates, as are involved in the reactions depicted in Equations (2)–(4), and the oxidative additions to



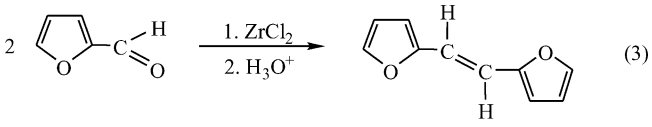
Scheme 4.

sigma-covalent bonds leading to bond cleavage and C–C bond coupling, as illustrated in Equations (5)–(7), have been termed by our group as *epimetallations* (Greek: literally *metallations* upon a bond, by analogy with *epoxidation* of an olefin).[17]



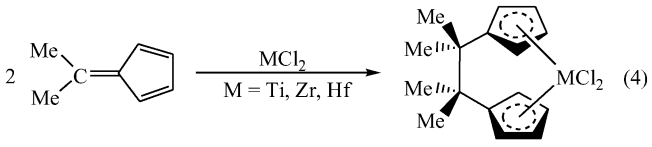
(2)

only *racemic* [18]



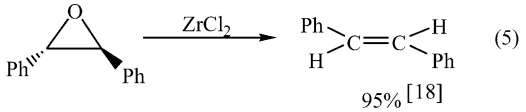
(3)

95% [8]



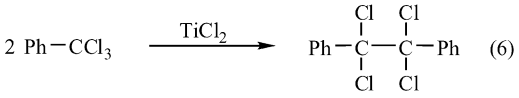
(4)

85-90% [19, 20]



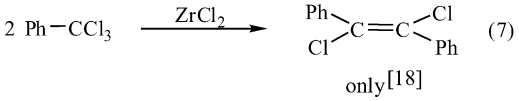
(5)

95% [18]



(6)

90% [8]



(7)

only [18]

The selective conversion to specific reduction products by these Group 4 reductants has spurred our interest in studying the reactivity of Groups 5 and 6 neutral and anionic reducing agents.

Goal of the Present Investigation

In our aforementioned studies of CrCl (**4**)[12] and $LiCrH_2$ (**6**),[13] we found that these reagents have proved to be the most powerful and chemically versatile of the early transition metal reductants thus far examined. Chromium(I) chloride (**4**) is capable of the efficient reductive coupling of carbonyls to pinacols, of α-bromo ketones to 1,4-diketones and of benzylic halides variously to bibenzyls or, with dehalogenation, to diarylethenes or to diarylethynes.[12] Lithium chromium(I) dihydride (**13**) shows a high reactivity in cleaving C–O, C–S, C–N and C–X *sigma*-bonds and in oligomerizing acetylenes and olefins.[13]

The remarkable properties of these chromium reagents have therefore motivated us to attempt the preparation of the analogous derivatives of vanadium, namely VCl (**12**) and $LiVH_2$ (**13**). Such reagents would lack one proton and one electron in the metal atom, compared with their chromium counterparts. There have been several reports of treating vanadium salts with RLi or RMgX reagents and utilizing the unexamined reagent solution for applications in organic synthesis but no systematic study of such vanadium reactants has yet appeared.[21] Therefore, it was of great interest to learn what differences in properties such vanadium reagents would exhibit in their changed electronic environment.

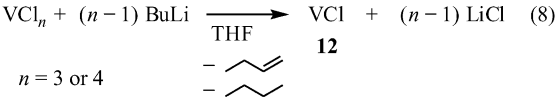
Results and Discussion

Preparation and Gasometric Analysis of Vanadium(I) Chloride (12)

General Observation

A most reliable and convenient assay for the subvalent oxidation state of an early transition metal, *when the amount of metal is already known to be present from the initial weight of salt introduced*, and for the presence of M–H bonds, is the protolysis of the solid metal salt under an inert atmosphere. Vanadium compounds of lower than V^{II} oxidation state are known to release one equivalent of H for each unit of oxidation and of course each M–H bond would release one equivalent of H_2. Thus V^0 would release two H and V^I one H. This type of gasometric analysis has been applied to Ti^{II},[8] Zr^{II}[19] and Cr^{I}[12,13] complexes.

Samples of VCl (**12**), admixed with LiCl by-product, were prepared and isolated from THF solution as a black solid, either by treating purple VCl_3 with two equivalents of *n*-butyllithium or by reacting red-brown VCl_4 with three equivalents of *n*-butyllithium at –78 °C and then warming to room temp., cf. Equation (8).



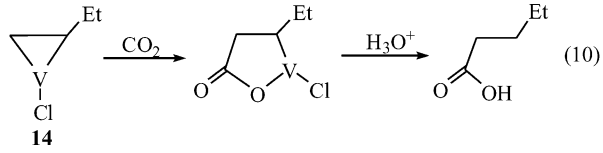
(8)

After prolonged pumping under high vacuum to remove volatiles, each sample was subjected to gasometric analysis of gas liberated by treatment with acetic acid. Three typical samples gave gas volumes of 0.67, 0.63 and 0.55 mol at STP, which gas by mass spectral analysis consisted of ca. 90% of H_2 and various small amounts of THF, butane and a butene, as judged by minor mass peaks, cf. Equation (9). Such an amount of H_2 (0.56 mol of H_2 as an average) is in reasonable agreement with the 0.50 mol of H_2 at STP expected from Equation (9).[22]

$$2\ VCl + 2\ HOAc \rightarrow 2\ VCl(OAc) + H_2\uparrow \quad (9)$$

That the butane or butene in the gas evolved could well have arisen from 1-butene remaining in the solid VCl as epimetallated product **14** was demonstrated as follows.

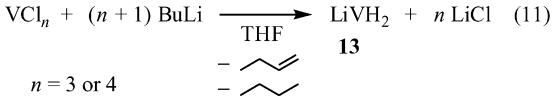
When a solution of **12** in THF was treated with CO_2 at –78 °C and then hydrolyzed, an 11% yield of pentanoic acid was obtained. This supports the existence of **14** in solution and its trapping by carbonation[10], cf. Equation (10).



(10)

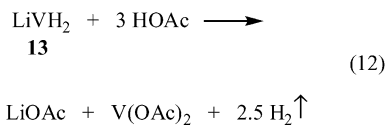
Preparation and Gasometric Analysis of Lithium Vanadium(I) Dihydride (13)

Samples of $LiVH_2$ (**13**), admixed with LiCl by-product, were prepared from THF solution as a black solid, either by treating purple VCl_3 (97%) with four equivalents of *n*-butyllithium or by allowing red-brown VCl_4 (99% minimum) to react with five equivalents of *n*-butyllithium at –78 °C and warming to room temp., cf. Equation (11). The $LiVH_2$ reagents of a given formal concentration prepared from either source had comparable reducing actions towards ketones as to kinds and proportions of reduction products but there are noteworthy differences. For example, $LiVH_2$ prepared from VCl_4 yielded 75% of the principal reduction products, 9-fluorenol and fluorene, in a ratio of 50:50, while $LiVH_2$ from VCl_3 gave a total yield of these two products of 70% but in a ratio of 81:19. Thus the $LiVH_2$ reagent from VCl_4 is somewhat a more potent reductant.



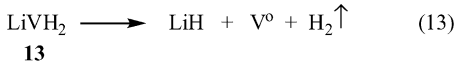
(11)

The measured differences in the properties of $LiVH_2$ samples generated from VCl_3 or from VCl_4 became much more pronounced when the $LiVH_2$ samples were allowed to stand in THF at room temp. or especially when the solvent was completely removed to produce a solid mixture of supposedly $LiVH_2$ and LiCl. Acetolysis of such samples of $LiVH_2$ should theoretically evolve 2.5 mol of H_2 per vanadium atom at STP per mol of **13**, cf. Equation (12).[22]



(12)

In fact, samples of $LiVH_2$ (**13**) prepared from VCl_4 did generate 2.5 ± 0.4 mol of H_2 at STP. In sharp contrast, however, acetolysis of the $LiVH_2$ generated from VCl_3 provided between 1.0–2.0 mol of H_2 per vanadium atom at STP, values consistent with extensive decomposition of **13** into LiH, cf. Equations (13) and (14).



(13)

(14)

The source of the greater instability of the $LiVH_2$ obtained from the VCl_3 starting material may stem from its impurities (3%) or from the smaller proportion of the LiCl by-product ($LiVH_2$/4LiCl), which LiCl may help to stabilize the $LiVH_2$ by chloride coordination. Therefore, for the more sensitive reactions of $LiVH_2$, its preparation from VCl_4 is to be preferred.[23]

Infrared Examination of Vanadium(I) Chloride (12) and Lithium Vanadium(I) Dihydride(13)

Examination of a solid sample of the VCl/LiCl mixture (**12**) as a mineral oil mull by infrared spectroscopy showed the absence of any sharp absorptions, other than those of the mineral oil, in the 1500–1650 cm^{-1} region and thus confirmed the absence of any V–H bonds. On the other hand, solid samples of the $LiVH_2$/LiCl mixture (**13**) generated from VCl_4 showed an absorption of medium intensity at 1625 cm^{-1} [24] and one of weak intensity at 1511 cm^{-1}. By comparison, the paramagnetic Cp_2V–H exhibits a medium band at 1625 cm^{-1} [25] and the paramagnetic [CpV(μ-H)-dmp]$_2$ a band at 1570 cm^{-1}.[24] Absorptions of this $LiVH_2$ at these two wavenumbers indicates the presence of a terminal V–H bond and a bridging V–H bond.

The foregoing gasometric and infrared spectroscopic data, therefore, support the conclusion that the solid $LiVH_2$/LiCl mixture obtained from VCl_4 has chemical, protolytic and infrared spectral properties consistent with the empirical formula of $LiVH_2$.

Electron Paramagnetic Resonance Spectroscopy of Vanadium(I) Chloride (12) and Lithium Vanadium(I) Dihydride (13)

General Observations

Solutions of the VCl/LiCl mixture in THF at 30 K gave a broad but undefined absorption, indicating the presence of some unknown paramagnetic component. Possibly this may be monomeric VCl, formed from the dissociation of a diamagnetic oligomer, $(VCl)_n$ but further studies will be required to clarify this possibility.[26]

The CW-EPR spectrum of the flash-frozen solution of lithium vanadium(I) dihydride (**13**) prepared from VCl_3 in a 1:1 heptane/toluene solution at 30 K, is the most revealing of the biradical paramagnetism and bonding in the dihydridovanadium(I) anion in **13**. The CW-EPR spectrum of the flash-frozen 0.09 M sample in 1:1 toluene/heptane solvent at 30 K is shown in Figure 1. At temperatures of 140 K and above, the spectrum collapses into a single central line with little or no hyperfine structure. A weak, but prominent, central peak is also evident in Figure 1 and is present in all but

the least concentrated (0.0108 M) sample. The intensity of this peak was much weaker in samples of **13** prepared from VCl_4. The spectrum with the hyperfine structure in Figure 1, which will be shown to belong to the VH_2^-, persists in the least concentrated sample. This central peak observed at low temperatures is an impurity evidently associated with a side reaction.

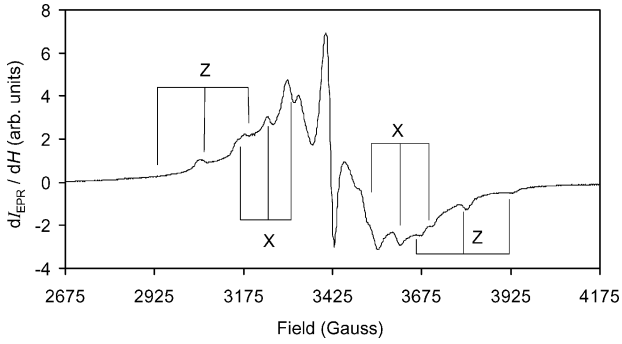


Figure 1. The CW-EPR spectrum of the flash-frozen 0.09 M sample of **13** in 1:1 toluene/heptane solvent at 30 K The 1:2:1 proton hyperfine multiplets and principal axis assignments are indicated with lines.

In order to estimate the proportion of this paramagnetic impurity, the aforementioned sample of **13** was compared with an EPR intensity standard to make a "spin count". The double integral of the triplet portion of the spectrum corresponded to about 0.20 M in the triplet species. These concentrations we believe to be equal within the precision of the EPR experiment. The narrow central peak near the center of the triplet spectrum is clearly an impurity, which was most evident in EPR spectra of $LiVH_2$ samples prepared from VCl_3 (cf. supra). Double integration of its intensity shows it to be present at a concentration of no more than 10% of the concentration of the triplet species.

It is interesting to note the absence of any resolvable vanadium hyperfine structure. It is possible, however, that vanadium hyperfine interactions from this anion are distorted by the solvent molecules and thus contribute to the surprisingly intense, featureless background underlying the relatively narrow hyperfine features. Alternatively, the broad background may be due to a paramagnetic impurity.

Analysis of the EPR Data for Lithium Vanadium(I) Dihydride (13)

The 30 K pulsed EPR spectrum, which had somewhat lesser resolution than the 30 K CW-EPR spectrum, confirmed the presence of peaks at the inflections indicated in Figure 1. What appeared to be 1:2:1 hyperfine multiplets at the low field *z* (2897.4 G, 3063.5 G, and 3188.2 G), low field *x* (3182.2 G, 3249.4 G, and 3307.5 G), high field *x* (3540.1 G, 3604.7 G, and 3698.6 G), and high field *z* (3663.8 G, 3793.0 G, and 3944.9 G) transitions, were carefully measured from the digital records of the spectra. The *y* axis features could not be distinguished.

The recorded fields of the transitions were fitted by least-squares with the parameters in the following spin Hamiltonian, cf. Equation (15).

$$H = H\cdot\mathbf{g}\cdot S + D\,[S_{z^2} - (1/3)S(S+1)] + E(S_{x^2-y^2}) + \Sigma_{i=1,2}\, S\cdot\mathbf{A}_i^{\mathbf{H}}\cdot I_i, \quad (15)$$

In Equation (15) $g_\parallel$ is the *zz* principal value of **g**, $g_\perp$ is the *xx* and *yy* principal value, and likewise $A_\parallel^H$ and $A_\perp^H$ are the corresponding, identical, principal values of $\mathbf{A}_i^{\mathbf{H}}$.[27,28] A satisfactory fit to the data was obtained by assuming that the two proton hyperfine coupling constants for the two protons, $i = 1,2$, are the same, as was indicated by the evident 1:2:1 patterns in the spectrum. The electron spin multiplicity is triplet, $S = 1$, and the proton spins have $I_i = 1/2$. The results of the fit, together with the results of the uncertainty analysis, are given in Table 1. The fact that the value of $E = 0$ within experimental error confirms the assumption of axial symmetry for the **g** and **A** matrixes.

Table 1. Spin Hamiltonian parameters for the ground triplet state of VH_2^-, determined from the EPR spectrum of a 0.14 M preparation at 30 K.

Parameter	Value	Uncertainty
$g_\parallel$	2.011	0.003
$g_\perp$	2.005	0.003
$D/g_e\beta_e$ (Gauss)	±377	5
$E/g_e\beta_e$ (Gauss)	±3	3
$A_\parallel^H/g_e\beta_e$ (Gauss)	±144	6
$A_\perp^H/g_e\beta_e$ (Gauss)	±71	6

One can break the A values down into an isotropic part, $A_{iso}^H/g_e\beta_e = \pm 95.3$ Gauss, and an anisotropic part whose $A_{aniso}^H{}_\parallel/g_e\beta_e = \pm 48.7$ Gauss and whose $A_{aniso}^H{}_\perp/g_e\beta_e =$ –/+ 34.3 Gauss. (We reject the unlikely result, $A_{iso}^H/g_e\beta_e = \pm 0.7$ Gauss, from $A_\parallel^H$ and $A_\perp^H$ being of opposite sign.) These values will be discussed in the next section in terms of the shape of VH_2^- and its electron spin distribution and electronic structure.

The triplet ground electronic state of the paramagnetic system being observed by EPR is of axial symmetry, based on the parameters given in Table 1. Principal *g* values and principal A values of parallel axial symmetry fit the spectrum well. The fact that the spectrum is also fit well with $E = 0$ within experimental error also points, as do the axial *g* values, to an unpaired electron spin distribution of axial symmetry. The Hamiltonian, based on the presence of two I = 1/2 nuclei in parallel axial environments is consistent with *a linear molecular system with two equivalent H atoms*, as depicted in **15**. It remains probable but unknown that THF is coordinated both with the cationic Li and anionic VH_2.[29]

Let us next consider further the implications of the values of the parameters in Table 1 under the hypothesis that the spectrum is from the symmetric, linear VH_2 anion.

$$[H–V–H]^-$$
15

The isotropic part of the $\mathbf{A}_i^{\mathbf{H}}$ for the two protons was found to be $A_{iso}^H/g_e\beta_e = \pm 95.3$ Gauss. On the basis on the

known A_{iso}^{H} = 508 Gauss of the H atom the value of the VH_2^- A_{iso}^{H} implies that 19% of the triplet electron spin resides in each H 1s orbital of VH_2^-.[27,28]

The value of the observed D parameter is too small for the electron spin dipolar interaction in a triplet molecule in which the molecular orbitals of the two unpaired electrons involve different atomic orbitals of the same atom.[30] The relatively small *g* shifts from the free electron *g* value, 2.0023, preclude large spin-orbital contributions. Therefore, in the small VH_2^- molecular ion this implies that one unpaired electron is situated around the H atoms and the other resides near the V atom, nearly exclusively.

Let us assume that the bonding of the H atoms with the V atom is of the σ type between the H 1s orbitals and the $3d_{z^2}$ orbital of the V atom. Simple molecular orbital considerations would predict a bonding σ orbital with no nodes perpendicular to the molecular axis, an essentially nonbonding sigma type orbital (n) with a node through the V nucleus, and an antibonding σ* orbital with two nodes cutting the V–H bonds. Two of the eight electrons of this system fill the bonding σ orbital, leaving six electrons to fill the remaining orbitals of the molecular ion. One would expect the d_{xz}, d_{yz}, $d_{x^2-y^2}$, and n orbitals, all of essentially nonbonding character, to be moderately close in energy.

We suggest that the only configuration that satisfies the need for one unpaired electron essentially entirely on the H atoms and that maintains axial symmetry is $\sigma^2\ d_{xz}\ d_{yz}\ d^1_{x^2-y^2}\ n^1$. This idealization places 50% of the unpaired electron density in the V $d_{x^2-y^2}$ orbital and 50% in the mainly H atom n σ-type orbital. Thus, were there no contribution to the n orbital and were there only 1s H character in the n orbital, then 25% of the unpaired electron density would reside in each H atom 1s orbital. Given that these absolutes will not fully obtain, the observed 19% unpaired spin density in the H 1s orbitals is further evidence for the essential truth of this simple description of the VH_2^- molecular anion. Clearly the small, symmetric VH_2^- molecular anion would be an attractive candidate in which to test these hypotheses with quantum mechanical calculations and to compare calculated values of $A_{aniso}^{H}{}_{\parallel}$ and $A_{aniso}^{H}{}_{\perp}$ with the corresponding experimental values.

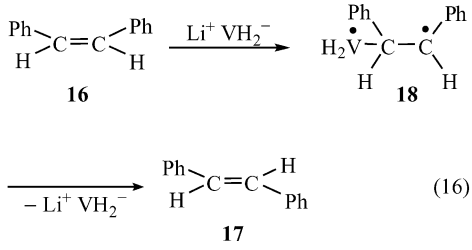
Chemical Characterization of Vanadium(I) Chloride (12) and Lithium Vanadium(I) Dihydride (13)

With reliable methods for the preparation and analysis of THF solutions of VCl (**12**) and $LiVH_2$ (**13**) reagents now in hand, we have launched a study of their applications in organic synthesis. The need for such a study becomes apparent when one notes that a review of vanadium in modern organic synthesis published in 1997 has only 18 citations out of 139 references possibly involving subvalent vanadium.[21] We hope to publish our complete results in the near future.[31]

However, our studies thus far with certain σ- and π-bonded organic substrates give insight into the scope and mode of reaction of **12** and **13**, especially when compared with the corresponding chromium reagents **4** and **6**. The reactions with olefins, ketones, epoxides and halides have proved to be especially revealing and are given here.

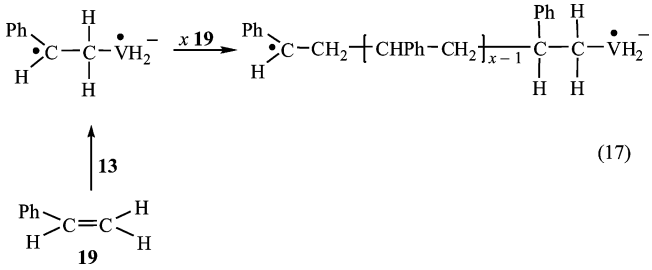
Olefins

Neither olefins nor acetylenes undergo epimetallation readily but do undergo *cis-trans* isomerization efficiently. *cis*-Stilbene (**16**) is isomerized by catalytic amounts of either **12** or **13** to more stable *trans*-stilbene (**17**). For the reaction with **13** one could propose a radical addition-elimination (via **18**) as the operative pathway, cf. Equation (16). As a reasonable extension, it is likely that with VCl (**12**), the proposed diamagnetic oligomer $(VCl)_n$ could produce VCl radicals by dissociation. The alternative suggestion by a referee that such isomerization could be due to the Lewis acidity of VCl is most unlikely: in THF any monomeric VCl would be completely complexed with THF solvent and thus be rendered only weakly electrophilic.



(16)

Another reaction consistent with the operation of free radicals is the observed polymerization of styrene (**19**) into atactic polymer at 25 °C, again by catalytic amounts of **12** or **13**. Here initiation by **12** or **13** to form a biradical intermediate similar to **18** would be a reasonable pathway, cf. Equation (17).

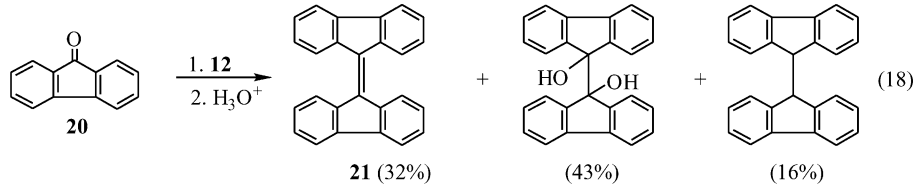


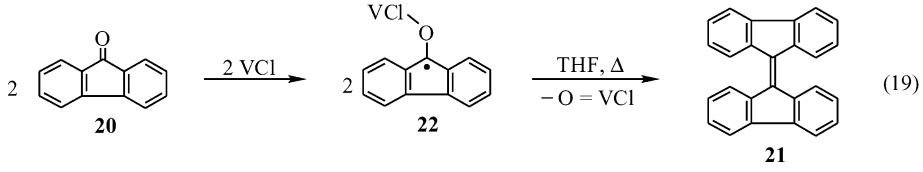
(17)

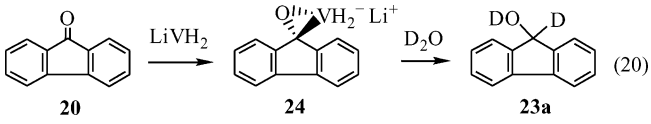
Ketones

The behavior of the hindered ketone, 9-fluorenone (**20**) toward **12** and toward **13** offers an instructive comparison: two equivalents of VCl causes a 91% conversion of **20** into reduced dimers at 25 °C, cf. Equation (18). When conducted at reflux, 1.25 equivalents of **12** produces **21** in 99% yield. This dimerization could readily be ascribed to dimerization via the radical **22**, cf. Equation (19).

By contrast, two equivalents of $LiVH_2$ converts **20** at 25 °C into an 84% yield of 9-fluorenol (**23**). When such a reaction mixture was treated with D_2O, the resulting **23a** was completely deuteriated at C^9 and at O. This permits the







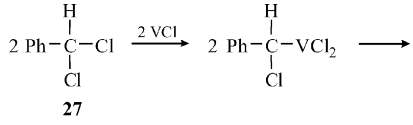
conclusion that the precursor to **23a** was the epimetallated adduct **24**, cf. Equation (20). This is an astonishing finding: *despite the presence of V–H bonds, $LiVH_2$ epimetallates, rather than hydrometallates, 9-fluorenone.*

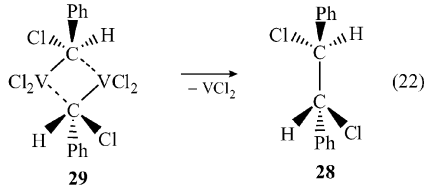
Epoxides

The interaction of **12** or **13** with epoxides, such as styrene oxide (**25**) and *cis*-stilbene oxide (**26**), again indicate the operation of radical processes, both in the non-stereoselective deoxygenation of **26** into the thermodynamic 93:7 mixture of **17** and **16**, cf. Equation (21) and in the subsequent polymerization of the resultant styrene, cf. Equation (17).

Halides

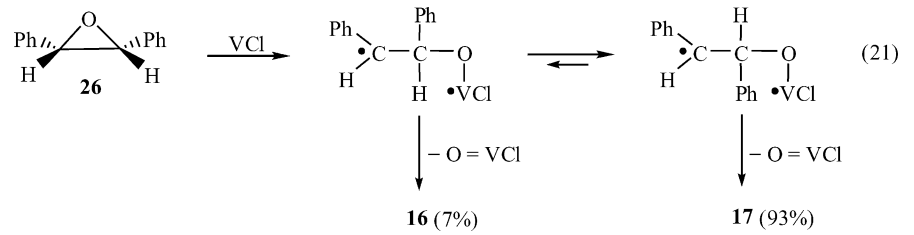
Here the interest has been in the reactions of VCl, in order to note signs of radical involvement. Vanadium(I) chloride has a low reactivity toward most C–X bonds but can readily insert into benzylic halogen bonds. Thus 2 equivalents of VCl convert benzyl chloride into toluene (24%) and bibenzyl (76%). Similarly, benzal chloride (**27**) yields 77% of benzyl chloride and 23% of *meso*-1,2-dichloro-1,2-diphenylethane (**28**). The formation of only the *meso*-isomer may indicate the steric ordering of the chlorobenzyl groups on the vanadium intermediate (possibly **29**) before concerted reductive elimination of the coupled **28** takes place, cf. Equation (22). In summary, the superior reactivity of benzylic halides toward **12** and **13** and their pattern of reactions can be readily identified with the intermediacy of radical intermediates. It is not yet clear whether such radicals are completely "free" of a metal center.





Prospects for the Relative Reducing Actions of VCl and $LiVH_2$ Compared with those of the Analogous Chromium Reagents

At this stage it can be noted that reducing actions of VCl and $LiVH_2$ appear generally to involve radical intermediates and are distinctly more moderate and usefully selective than those of the chromium reagents. As a telling example, the reductive cleavage of σ-C–O, C–S and C–N bonds, often facile in $LiCrH_2$ reductions, is seldom encountered or is much slower with $LiVH_2$. This greater selectivity of reduction with $LiVH_2$ therefore permits the epivanadation of C=C, C=O and C=N bonds with less undesired σ-bond cleavages.



Experimental Section

General Experimental Procedures and Starting Materials: All procedures involving the purification of reaction solvents, distillation of reagents, the preparations of vanadium(I) chloride (**12**), lithium vanadium(I) dihydride (**13**) and their subsequent measurements or reactions with organic substrates were conducted under a positive atmospheric pressure of anhydrous, deoxygenated argon employing vacuum techniques and with standard Schlenk apparatus. The Schlenk apparatus typically involved a two- or three-necked Pyrex flask, with the one neck for the introduction of reaction substrates, the second for connection with the argon while the third neck could be coupled to a condenser for heating of reaction mixtures at reflux. The drying and deoxygenation of argon, as well as the solvents, such as tetrahydrofuran, toluene and hexane, used in the reactions were carried out according to established procedures. Glassware and needles used to transfer liquid samples were dried in an oven at 140 °C overnight to ensure complete absence of moisture.[32] Moreover, each needle-equipped syringe was repeatedly flushed with argon before every use.

The *n*-butyllithium in hexane was purchased from Sigma–Aldrich in Sure Seal™ bottles and was used at the stated concentration as received, uniformly 2.5 M. Any punctures made in the rubber septum for removal of the reagent by gastight syringe were resealed with wax after each withdrawal. The anhydrous vanadium(III) chloride was purchased from Sigma–Aldrich at 97% purity and the vanadium(IV) chloride in at least 99% purity.

Gasometric analysis of samples of VCl/LiCl and $LiVH_2$/LiCl solid residues were carried out in a Schlenk flask and the evolved gases were collected in a calibrated gas buret over mercury. The individual analysis was carried out as follows: Black solutions of either **12** or **13** in THF at room temperature were freed of all volatiles and THF under an argon atmosphere at reduced pressure until a black solid remained. Prior to this step, 8 mL of degassed acetic acid was introduced into the 10-mL Schlenk flask used for protolysis. Flask A containing solid **12** or **13** and flask B containing degassed acetic acid were then connected and one outlet joined to the calibrated gas buret filled with mercury while the other was closed. The pressure in the flask was then balanced against atmospheric pressure and the initial volume read off to the nearest one-fifth of a milliliter [mL]. The solid **12** or **13** and acetic acid were allowed to mix, after which a mildly exothermic gas reaction occurred and the color of the mixture gradually changed over time from black through olive-green and finally to green with a white deposit [note: vanadium(II) chloride is green]. The resulting pressure in the gas buret was then balanced against the atmospheric pressure, the final volume read to the nearest one-fifth of a milliliter [mL] and the ambient temperature and atmospheric pressure recorded. Because the concentration of the *n*-butyllithium was known to two significant figures, namely 2.5 M, the equivalents of dihydrogen evolved upon protolysis could be known only to two significant figures.

The standard hydrolytic workup procedure employed for the usual reactions of **12** or **13** is as follows. The reaction mixture is treated with deoxygenated distilled water, 1 N or 3 N HCl aqueous solutions or deuterium oxide at room temperature or with methanol at –78 °C. The organic layer containing the desired products is then extracted four times with 15 mL of anhydrous diethyl ether. The combined ether extracts were washed with three 20-mL portions of saturated, aqueous $NaHCO_3$ or 10% aqueous NaOH solution and finally with saturated NaCl solution. The combined organic extract is washed with 20 mL water, dried with solid anhydrous Na_2SO_4 and then filtered, after which the solvent was removed at the rotary film evaporator. Carboxylic acids produced in reactions were isolated from the neutral combined ether extracts (see above) by extracting with three 20-mL portions of saturated, aqueous $NaHCO_3$ or 10% aqueous NaOH solution. These extracts were then combined, neutralized with dilute hydrochloric acid, extracted several times with ether and the combined ether extracts dried with anhydrous Na_2SO_4. The resulting ether extract was then filtered and freed of solvent to obtain the crude acid product. Product identification of known compounds was achieved principally by comparison of ^1H and ^{13}C NMR spectra of such reaction products with those spectra of authentic compounds given in the literature.[33,34] Similarly, product yields from such reactions were calculated based on integration of the respective NMR proton peaks, except for carboxylic acids, where the yields were based on the weight of product obtained.

Instrumentation and Analysis: All melting points were measured with a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded with the Perkin–Elmer spectrophotometers, Model 457 and 283B, which were equipped with sodium chloride optics. The nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were measured in deuteriated solvents with a Bruker spectrometer, Model AM-360. The ^1H NMR spectroscopic data are reported on the δ scale in parts per million with reference to an internal standard of tetramethylsilane (TMS) for solutions in deuteriated chloroform ($CDCl_3$) or deuteriated dimethyl sulfoxide ([D_6]DMSO) solvent. The ^{13}C NMR spectroscopic data are reported on δ scale in parts per million with reference to deuteriated solvents.

Gas chromatographic analyses were performed with a Hewlett–Packard chromatograph, Model HP5890A, equipped with programmed temperature rise and with an electronic peak-area integrator and a flame ionization detector (FID).

Electron paramagnetic resonance measurements (EPR) were made in this department with the use of a CW Varian Spectrometer, Model V4500, having the X-band set at about 9.2 GHz and fitted with a Varian Klystron microwave source, model VA297V and a Varian TE^{102} cavity.

Mass spectral analyses of the hydrogen gas from the acetolysis of samples of VCl and $LiCrH_2$ were performed by injecting gas samples directly into the mass spectrometer of a Hewlett–Packard gas chromatograph-mass spectrometer, model 5890, series II.

Preparation of Vanadium(I) Chloride (12)

(1) From Vanadium(III) Chloride: In a typical procedure, a purple suspension of anhydrous VCl_3 (330 mg, 2.1 mmol) in 30 mL of anhydrous, deoxygenated THF at –78 °C (dry ice/acetone bath) was treated dropwise with 2.0 equivalents of *n*-butyllithium in hexane (2.6 mL of 1.6 M solution, 4.2 mmol). The resulting purple mixture was stirred for 30 min at –78 °C and then brought to room temp. after which the mixture turned black. After 2 h the VCl (**12**) in solution was ready for reaction with individual organic substrates or the solution could be subjected to high vacuum, in order to obtain solid **12**, admixed with LiCl, which could be subjected to acetolysis in a gasometric analysis.

(2) From Vanadium(IV) Chloride: In an analogous manner, a reddish brown solution of VCl_4 (330 mg, 1.7 mmol) in 30 mL of THF was treated with 3.0 equivalents of *n*-butyllithium (3.2 mL of 1.6 M hexane solution, 5.1 mmol) at –78 °C, during time the solution turned from reddish orange to purple. Again, upon warming to room temp. the solution turned black, consistent with formation of **12**.

Characterization of Vanadium(I) Chloride(12)

(1) Gasometric Analysis: Treatment of 2.0 to 3.0 mmol samples of solvent-free solid samples of VCl/LiCl mixtures, prepared either from VCl_3 or VCl_4 in the aforementioned manner, with an excess of glacial acetic acid in a gasometric apparatus (cf. supra) led, from three samples to the evolution of 0.67, 0.63 and 0.55 mol or an average 120% of the H_2 expected, 0.5 molar equivalent of H_2 at STP according to Equation (9). A typical analysis: VCl prepared from 2.0 mmol of VCl_3 yielded upon acetolysis 34.8 mL of H_2 at 297 K and 728 Torr or 0.67 mmol. The mass spectrum of the H_2 showed traces of 1-butene (*m*/*z* 56), butane (*m*/*z* 58) and THF (*m*/*z* 72) and indicated the presence of about 90% of H_2.

(2) Attempted ^{51}V NMR and EPR Spectra: A solid sample of the residual mixture of VCl and LiCl was suspended in C_6D_6. Attempts to record the ^{51}V NMR spectrum of this sample gave only very broad absorptions. A similar outcome resulted from attempts to obtain an EPR spectrum at room temp. However, the presence of some paramagnetic vanadium component is indicated by such broad signals.

(3) Carbonation of Reagent 12: A solution of 6.5 mmol of reagent VCl (**12**) in 60 mL of THF at –78 °C was treated with a stream of dry CO_2. Subsequent warming to room temp. and hydrolysis with 5% aqueous NaOH, separation of the aqueous layer, acidifying with 5% aqueous HCl, and extracting the aqueous layer with ether gave an ether extract containing 11% of pentanoic acid. This product indicates that in the original THF solution VCl has undergone partial epivanadation with the 1-butene formed by the alkylative reduction of VCl_3, cf. Equation (10).

Preparation of Lithium Vanadium(I) Dihydride (13)

(1) From Vanadium(III) Chloride: In a typical procedure, a purple suspension of VCl_3 (760 mg, 4.8 mmol) in 30 mL of anhydrous, deoxygenated THF at –78 °C was treated dropwise with 4.0 equivalents of *n*-butyllithium in hexane (7.7 mL of 1.6 M solution, 19.3 mmol). The resulting purple mixture was stirred for 30 min at –78 °C and then brought to room temp. after which the mixture turned black. After 2 h the **13** in solution was ready for the recording of its EPR spectrum, for reaction with individual organic substrates or for the preparation of solid samples of $LiVH_2$, admixed with LiCl, which could be subjected to acetolysis in a gasometric analysis.

(2) From Vanadium(IV) (Chloride): In an analogous manner, a reddish brown solution of VCl_4, (920 mg, 4.8 mmol) in 30 mL of THF at –78 °C was treated dropwise with 5.0 equivalents of *n*-butyllithium in hexane (14.9 mL of 1.6 M solution, 23.8 mmol). The resulting mixture was stirred for 30 min at –78 °C and then rapidly brought to room temp. during which warming the mixture promptly turned black. After a further stirring of 2 h the reagent **13** was ready for reactions or measurements.

Characterization of Lithium Vanadium(I) Dihydride (13)

(1) Gasometric Analysis: The acetolysis of a solid sample of **13**, prepared from 0.88 mmol of VCl_4 and freed from all THF and other volatiles under reduced pressure, yielded 84.2 mL of H_2 at 298 K and under 728 mm mercury. This corresponds to 73.9 mL or 2.9 mol of H_2 at STP. According to Equation (18) the acetolysis of **13** should afford 2.5 mol of H_2. Similar acetolysis provided 2.4, 2.1 and 2.6 mol of H_2. (The resulting acetolysis solutions were pale green.) Mass spectrometric analysis of this H_2 showed that it contained traces of THF, butane and 1-butene. The averaged equivalents of H_2 from these four runs is 2.5 ± 0.4 equivalents, in reasonable agreement with the value expected of the empirical formula of $LiVH_2$ and in light of the aforementioned impurities.

By contrast, when gasometric analyses were carried out on solid samples of **13** prepared from VCl_3, the equivalents of H_2 gas evolved ranged between 1.0 and 2.0 of the expected amount of H_2. This results would be consistent with the conclusion that the reagent **13**, which has been prepared from VCl_3, is much less stable than the reagent **13** prepared from VCl_4. Especially upon solvent removal the reagent **13** from VCl_3 appears to decompose with loss of H_2 to yield lithium hydride, cf. Equations (19) and (20), whose hydrolysis would provide one equivalent of H_2. Any particles of vanadium metal would react only slowly with glacial acetic acid.

(2) Infrared Spectroscopic Analysis: The FT-IR spectrum of solid **13** obtained from VCl_4, examined in mineral mull under argon, displayed the following principal peaks (cm^{-1}): $\tilde{\nu}$ = 3376 (m), 2921 (m), 2850 (m), 1650 (m), 1511, 1457 (w), 1251 (w), 1000 (m) and 990 (w).

(3) NMR Spectroscopic Analysis: The attempted ^{51}FT-NMR analysis of **13** in C_6D_6 solution with a $VOCl_3$ reference, generated from either VCl_4 or VCl_3, displayed no useful absorption peaks.

(4) EPR Spectroscopy: The reaction product of the butyllithium reaction with either VCl_3 or VCl_4, namely $LiVH_2$ (**13**), was examined with CW EPR, in tetrahydrofuran and 1:1 toluene-heptane solutions at room temperature (0.14 M) and with a 1:1 toluene-heptane frozen solution at 140–170 K. Subsequent CW-EPR experiments were done on products in flash frozen: 1:1 toluene/heptane solvent at 0.14 M at 30 K. In addition to the CW-EPR experiments, a Hahn-echo detected pulsed EPR spectrum was acquired at 30 K. The experiments were performed with a Bruker ESP 580 X-band EPR spectrometer equipped with a split-ring ER4AA9 resonator and were detected with 100 kHz field modulation and phase-sensitive detection. Temperatures below room temperature were achieved with an Oxford Instruments CF 935 cryostat and an ITC 502 temperature controller. (cf. supra for an analysis of the EPR measurements.)

(5) Comparative Reactions of 9-Fuorenone with Lithium Vanadium(I) Dihydride (13) Prepared from VCl_4 or from VCl_3: To order to compare the reactivities of $LiVH_2$ (**13**), prepared either from VCl_4 or from VCl_3, toward a typical carbonyl substrate, a standard solution of 9-fluorenone (**20**, 650 mg, 3.6 mol) in 10 mL of anhydrous THF under argon was treated with 3.6 mmol of $LiVH_2$ in 40 mL of THF at room temp. and stirred for 12 h. In run a the $LiVH_2$ was prepared from VCl_4, in run b the $LiVH_2$ originated from VCl_3. Typical hydrolytic workup of each run and addition of diethyl ether allowed the separation of the organic layer, which after drying with anhydrous Na_2SO_4 and removal of volatiles by rotary evaporation left a residue that was analyzed by ^{1}H and ^{13}C NMR spectroscopy.

Results from Run a: Weight of residue: 430 mg, consisting of 37% of 9-fluorenol, 38% of fluorene, 12% of 9*H*, 9′*H*-9,9′-bifluorenyl, 9% of 9,9′-bifluorenylidene and 4% of 9,9′-bifluorenyl-9,9′-diol.

Results from Run b: Weight of residue: 440 mg, consisting of 57% of 9-fluorenol, 13% of fluorene, 12% of 9*H*, 9′*H*-9,9′-bifluorenyl, 1% of 9,9′-bifluorenylidene and 6% of 9,9′-bifluorenyl-9,9′-diol. In addition, 11% of 9-fluorenone was recovered unchanged.

From the recovery of 9-fluorenone and the amount of 9-fluorenol (57% vs. 37%), it is clear that the $LiVH_2$ prepared from VCl_3 (run b) exhibited a weaker overall reducing action than the $LiVH_2$ prepared from VCl_4. This is consistent with other infrared spectroscopic and acetolytic gasometric analyses indicating that the $LiVH_2$ derived from VCl_3 is thermally unstable even in solution at room temp.

By contrast, reaction of 9-fluorenone with $LiVH_2$ in a 1:2 molar ratio in THF at room temp. very similar results regardless of

whether $LiVH_2$ from VCl_4 or VCl_3 is employed. Dimeric reduction products were not observed and 83–86% of 9-fluorenol and 12–15% of fluorene were formed with 1–2% of 9-fluorenone remaining.

Chemical Trapping and Characterizing Reactions of Vanadium(I) Chloride (12)

(1) Isomerization of *cis*-Stilbene: A solution of VCl (**12**, 4.2 mmol) in 30 mL of THF was treated with *cis*-stilbene (2.52 mg, 1.4 mmol) at room temp. for 24 h. Hydrolytic workup gave an organic residue of 90% of *trans*-stilbene, 4% of *cis* stilbene and 6% of bibenzyl, cf. Equation (16).

(2) Polymerization of Styrene: A solution of VCl (**12**, 2.8 mmol) in 10 mL of THF was treated with styrene (146 mg, 1.4 mmol) at room temp. for 12 h. Hydrolytic workup gave only atactic polystyrene as a light brown solid, as determined by IR and NMR spectroscopy, cf. Equation (17). ^1H NMR ($CDCl_3$): δ = 7.30–7.07 (br. m), 6.8–6.3 (br. m), 2.3–1.7 (m, CH), 1.6–1.1 (m, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 146.0–145.1 (br), 127.9–127.1 (br), 125.8–125.5 (br.), 40.3–40.1 (br.) ppm.

(3) Reduction of 9-Fluorenone (18): A solution of VCl (**12**, 3.4 mmol) in 40 mL of THF was treated with 9-fluorenone (300 mg, 1.7 mmol) at room temp. for 12 h. Hydrolytic workup of one-half of the reaction mixture gave 220 mg of a dark residue solid that by NMR spectroscopy consisted of 43% of 9,9′-bifluorenyl-9,9′-diol, 32% of 9,9′-bifluorenylidene, 16% of 9*H*,9′*H*-9,9′-bifluorenyl, 5% of 9-fluorenol and 4% of fluorene, cf. Equation (18).

Workup of the remaining half of the reaction mixture then showed that the 9-fluorenol was 95% deuteriated at C^9 and on O.

In a reaction run of 2.1 mmol of VCl and 1.7 mmol of 9-fluorenone in 40 mmol of THF conducted at reflux for 8 h led to 99% of 9,9′-bifluorenylidene, cf. Equation (19).

(4) Benzylic Chlorides: A solution of VCl (6.8 mmol) in 30 mL of THF was treated with benzyl chloride at room temp. for 12 h. Hydrolytic workup and ^1H and ^{13}C NMR spectroscopic analysis showed that 24% of toluene and 76% of bibenzyl had formed.

In a similar reaction between VCl and benzal chloride the reaction products were 77% of benzyl chloride and 23% of *meso*-1,2-dichloro-1,2-diphenylethane, cf. Equation (22). ^1H NMR ($CDCl_3$): δ = 7.38–7.24 (m, 10 H) 5.19–5.17 (d, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.3, 128.9, 128.4, 128.0, 65.6 ppm.

Chemical Trapping and Characterizing Reactions of Lithium Vanadium Dihydride (13)

(1) Isomerization of *cis*-Stilbene: A solution of $LiVH_2$ (3.2 mmol, from VCl_3) in 10 mL of THF was treated with *cis*-stilbene (576 mg, 3.2 mmol) at room temp. for 12 h. Hydrolytic workup yielded 510 mg of product that by ^1H NMR analysis consisted of 71% of *trans*-stilbene and 29% of bibenzyl.

When a solution of $LiVH_2$ (1.9 mmol) in 10 mL of THF was treated with an excess of *cis*-stilbene (3.42 g, 19.0 mmol) in a similar manner, 3.24 g of product were obtained, which consisted of 99% of *trans*-stilbene and 1% of bibenzyl.

(2) Polymerization of Styrene: A solution of $LiVH_2$ [4.1 mmol in 40 mL of THF converted styrene (210 mg, 2.0 mmol) into 100% of atactic polystyrene at 25 °C].

(3) Reactions of 9-Fluorenone with Lithium Vanadium(I) Hydride in a 1:2 Molar Ratio and Comparative Hydrolytic and Deuteriolytic Workup: A solution of 3.9 mmol of $LiVH_2$ in 40 mL of THF was treated with 9-fluorenone (**18**, 350 mg) at room temp. for 12 h. Hydrolytic workup gave 290 mg of a mixture of 84% of 9-fluorenol, (**19**), 12% of fluorene (**20**) and 4% of 9-fluorenone.

An identical reaction except that there was a workup with DCl in 97% D_2O gave 82% of 9-fluorenol, 14% of fluorene and 4% of 9-fluorenone. The 9-fluorenol was completely dideuteriated at C^9 and on O.

Acknowledgments

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with such protolyses that clearly have particulate metal (Ti, Zr, Hf, Cr and V), such metal remains unreacted after addition of HOAc.

[23] Although the by-product LiCl through its Cl^- and the solvent THF may well be coordinated with **12** and/or **13** in solution, the gasometric protolysis of solid samples of **12** or **13** demonstrates that such solvated THF can be removed in high vacuum. As to chemical complexation of LiCl with samples of **12** and **13** in the solid state, such stable complexes are unlikely. In previous work, samples of $TiCl_2$·2THF, $ZrCl_2$·2THF and$LiCrH_2$·2THF, free of LiCl, have been isolated from the solvent pair of THF and toluene, cf. ref.[8,13,19]

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