

Synthesis of [Bis(salicylaldehyde) ethylenediiminato]diphenylvanadium(IV)-Methanol, a Novel Organovanadium Compound

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Received December 5, 1985

The reaction of $VCl_2(\text{salen})$ ($H_2\text{salen}$ = the Schiff base of salicylaldehyde and ethylenediamine) and $PhLi$ results in the replacement of the chloro groups by phenyl groups. The product, purified in methanol, is $VPh_2(\text{salen})\cdot CH_3OH$. Side products resulting from the reaction of $PhLi$ and CH_2Cl_2 are Ph_2CH_2 and $LiCl$. The compound $VPh_2(\text{salen})\cdot CH_3OH$ is the first example of an organovanadium(IV) compound that is thermally stable at room temperature. Its IR and UV-visible spectra are reported as well as a preliminary survey of its electrochemistry.

Introduction

The focus of most reports on vanadium(IV) chemistry has long been ligand substitution reactions of the vanadyl ion, VO^{2+} . Recently, two types of reactions of the VO^{2+} cation itself have shown that this species is not as inert as is often assumed. Pasquali, Floriani, and co-workers^{1,2} were the first to report that the reaction of VO^{2+} with $SOCl_2$ produces VCl_2^{2+} . Jezierski and Raynor³ produced VBr_2^{2+} using $SOBr_2$ in a similar reaction. Callahan and Durand⁴ formed VBr_2^{2+} using $PPhBr_2$ as the brominating agent. Callahan, Durand, and Rieger^{4,5} also introduced the first thiovanadyl, VS^{2+} , complexes by treating vanadyl complexes with B_2S_3 . Recently, Money, Huffman, and Christou⁶ used hexamethyldisilthiane, $(Me_3Si)_2S$, to convert $[VO(\text{edt})_2]^{2+}$ to $[VS(\text{edt})_2]^{2+}$ (edt = ethane-1,2-dithiolate). Complexes of these three new cations, VCl_2^{2+} , VBr_2^{2+} , and VS^{2+} , are all moisture-sensitive, and most revert rapidly back to their oxo analogues.

Comparisons of the compounds of these cations to their oxo analogues have been reported in a few cases. The crystal structure of $VS(\text{acen})$ ($H_2\text{acen}$ = the Schiff base of acetylacetone and ethylenediamine) has been described,⁷ as has been its electrochemistry.⁸ In general, the compounds behave much like their oxo analogues but reflect weak V-S bonds.

Perhaps the greatest potential value of these new compounds is as intermediates leading to other types of vanadium compounds. Organovanadium compounds are an important example. Organovanadium compounds are found mostly in the low oxidation states of vanadium and are dominated by carbonyl and cyclopentadienyl derivatives.⁹ Most of the σ -bonded alkyl or aryl derivatives are unstable, and very little has been reported about them. For example, $V[\text{CH}(\text{Si}(\text{CH}_3)_3)_2]_3$ ^{9,10} and $[VPhCl_2\cdot ZnCl_2]^{19,11}$ have been prepared and are extremely air- and water-sensitive. Organovanadium(IV) compounds are quite rare.⁹ They have been found mostly in the form of VR_nCl_{4-n} (R = alkyl, aryl; n = 0-4,^{9,12-15} and only a few are found as VR_2Cp_2 ^{9,16,17} (Cp = cyclopentadienyl). σ -Alkyl and -aryl vanadium(IV) complexes are also quite unstable like those of the lower oxidation states. Vanadium-carbon bonds are cleaved, resulting in a coupling of the alkyl and aryl radicals.⁹

Metal-carbon σ -bonds have been shown to be stabilized by cyclopentadienyl ligands¹⁸ and also by the tetradentate Schiff base ligand $H_2\text{salen}$ (the Schiff base of salicylaldehyde and ethylenediamine) as in $Fe(\text{salen})R$ ¹⁹ (R = Ph, CH_2Ph), $R_2Sn(\text{salen})$ ²⁰ (R = Me, Ph), and $CH_3Co(\text{salen})\cdot L$ ²¹ (L = H_2O , py). Vanadium-carbon σ -bonds are also expected to be stabilized by the presence of the $H_2\text{salen}$ ligand. In fact, the first report of a V-C bond stabilized by a tetradentate Schiff base ligand in a vanadium(III) complex has just been reported. Gambarotta and co-workers²² reported the synthesis and crystal structure of the dimer $[V(\text{acen})CH_2Ph]_2$, in which one benzyl group is bound directly to each vanadium. We report here the synthesis of a mixed-ligand (σ -bonded phenyl and coordinating $H_2\text{salen}$ ligand) compound, $VPh_2(\text{salen})\cdot CH_3OH$, which is the first example of

an organovanadium(IV) compound that is thermally stable at room temperature. $[(CH_3)_2V(\text{acac})_2]$, acac = acetylacetonato anion, was reported to form and immediately decompose at 20 °C.²³ Infrared and UV-visible spectroscopy as well as the electrochemistry of $VPh_2(\text{salen})\cdot CH_3OH$ have been studied and compared to its oxo and dichloro analogues, $VO(\text{salen})$ and $VCl_2(\text{salen})$, respectively.

Experimental Section

The electrochemical instrumentation used has been described in detail previously.⁸ Infrared spectra were recorded with CsI windows and a Perkin-Elmer Model 683 IR spectrophotometer. Visible and UV spectra were recorded on a Hewlett-Packard Model 8450A spectrophotometer.

Reagents. Spectroanalytical grade methylene chloride (0.008% water), dimethyl sulfoxide (Me_2SO) (0.011% water), and dimethylformamide (DMF) (0.011% water) were obtained from Burdick and Jackson Laboratories. Spectral quality methanol (0.02% water) and benzene (0.05% water) were obtained from Fisher Scientific. All of the solvents were deoxygenated before use. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as previously described²⁴ and used as the supporting electrolyte in

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the electrochemical studies. SOCl_2 (reagent grade) was obtained from Fisher Scientific. Phenylmagnesium chloride (2.0 M THF) and phenyllithium (2.0 M cyclohexane/diethyl ether, 70/30) were obtained from Aldrich. Silica gel (230–400 mesh) was obtained from Sigma. Glassware was rinsed with methanol and dried at 110–120 °C before use.

All syntheses except those of H_2salen and $\text{VO}(\text{salen})$ were carried out in a dry/inert atmosphere of prepurified nitrogen. Manipulations under nitrogen atmosphere for the $\text{VCl}_2(\text{salen})$ synthesis were achieved by utilizing Schlenk glassware and a nitrogen stream. The synthesis of $\text{VPh}_2(\text{salen})\cdot\text{CH}_3\text{OH}$ was carried out in a glovebox.⁸ Samples for the spectroscopic study of air-sensitive compounds were prepared under nitrogen atmosphere in the glovebox.

Synthesis of Compounds. The H_2salen ligand and $\text{VO}(\text{salen})$ complex were prepared by the methods described by Selbin and co-workers.²⁵ $\text{VO}(\text{OAc})_2$ was used for the synthesis of $\text{VO}(\text{salen})$. This reagent was obtained by mixing 2.5 g (0.01 mol) of VOCl_2 and 1.64 g (0.02 mol) of NaOAc in methanol. After filtration of the NaCl precipitate, the $\text{VO}(\text{OAc})_2$ (in situ) was combined with the ligand in acetone. After the mixture was refluxed, $\text{VO}(\text{salen})$ was isolated.

The $\text{VCl}_2(\text{salen})$ complex was obtained from the reaction of $\text{VO}(\text{salen})$ and SOCl_2 as described in method A by Pasquali and co-workers.²

[Bis(salicylaldehyde) ethylenediiminato]diphenylvanadium(IV)-Methanol, $\text{VPh}_2(\text{salen})\cdot\text{CH}_3\text{OH}$. To solid $\text{VCl}_2(\text{salen})$ (1 g, 2.6×10^{-3} mol) was slowly added PhLi (5 mL, 2-fold excess). The blue $\text{VCl}_2(\text{salen})$ complex first turned green and then brown as time progressed. The reaction mixture was stirred at room temperature overnight. Methylene chloride was slowly added to the mixture to quench the unreacted PhLi . A gellike brown precipitate was filtered out, and the filtrate was evaporated to dryness under vacuum. Methylene chloride was added to redissolve the residue, and a pale yellow precipitate of LiCl was filtered out. The dark brown filtrate was loaded onto a silica gel column that was packed in methanol. The first few milliliters collected were discarded, and the subsequent eluent was evaporated to dryness to yield the final product. Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2\text{V}\cdot\text{CH}_3\text{OH}$: C, 69.18; H, 5.57. Found: C, 69.23; H, 5.56. The elemental analysis also showed no chlorine in the product.

Results and Discussion

Synthesis. It has been shown that chlorine ligands can be replaced by various nucleophiles.²⁶ For example, chlorine in Cp_2VCl_2 has been replaced by CN^- , N_3^- , NCO^- , SCN^- , and NCSe^- .²⁷ Chlorine can also be substituted by R groups (R = methyl, aryl) as in the conversion of Cp_2TiCl_2 to Cp_2TiR_2 .¹⁶ On the basis of these observations, the synthesis of $\text{VPh}_2(\text{salen})$ from $\text{VCl}_2(\text{salen})$ was attempted.

Although V–C σ -bonds are expected to be very labile, the presence of a tetradentate Schiff base salen ligand has been shown to stabilize transition-metal–carbon bonds.^{19–21} The salen ligand probably blocks the coordination sites that otherwise would be used in decomposition. Another factor that affects the stability of V–C bonds is the type of R groups. Aryl and bulky alkyl groups or those lacking β -hydrogen atoms usually form more stable metal–carbon bonds than do small alkyl groups.^{9,28} Two common decomposition pathways^{18,29} are (1) the homolytic fission of M–C bonds followed by the coupling of free organic radicals and (2) β -hydrogen transfer. Aryl and alkyl groups that have no β -hydrogen atoms cannot undergo the β -hydrogen-transfer reaction, thus stabilizing M–C bonds. Steric factors are also thought to be important for the existence of compounds like $\text{Co}(\text{1-nor})_4$ (1-nor = 1-norbornyl),²⁸ $\text{Cr}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_4$,²⁹ $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$,¹⁵ and $\text{V}(\text{CH}_2\text{C}_6\text{H}_5)_4$.¹⁵ Hence, the phenyl group was chosen as the R substituent in preparing $\text{VR}_2(\text{salen})$ from $\text{VCl}_2(\text{salen})$. It possesses both advantages, i.e. being inactive toward the β -hydrogen-transfer reaction and being bulky.

The reaction stoichiometry is

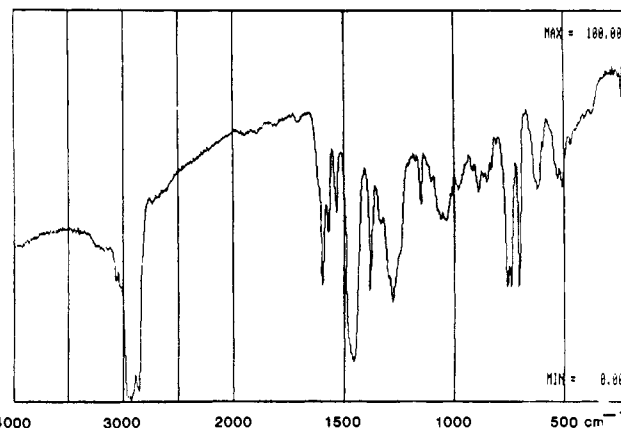
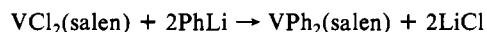


Figure 1. Infrared spectrum of $\text{VPh}_2(\text{salen})\cdot\text{CH}_3\text{OH}$ (4000–200 cm^{-1}) in Nujol.

The purification procedure led to isolation of the methanol adduct, $\text{VPh}_2(\text{salen})\cdot\text{CH}_3\text{OH}$.

Phenyllithium was found to be preferable to phenylmagnesium chloride as the phenylating agent.³⁰ PhLi was kept in two- to threefold excess to ensure complete substitution. (A 1:2 $\text{VCl}_2(\text{salen})\text{:PhLi}$ ratio was tried, but the final product contained some of the $\text{V}=\text{O}$ species.) The reaction of $\text{VCl}_2(\text{salen})$ and PhLi is quite exothermic. The $\text{VCl}_2(\text{salen})$ compound was reacted in its solid form because commonly used solvents, e.g. CH_2Cl_2 or THF, also react with PhLi . After the mixture was stirred overnight at room temperature, a jellylike precipitate was filtered with difficulty. The inorganic salt byproduct could be quantitatively separated from the desired product by first evaporating the filtrate to dryness under vacuum. Three to five mL of CH_2Cl_2 was then put into the flask that now contained mixed, brown and white, precipitates. The white precipitate, LiCl , was not soluble in CH_2Cl_2 and was filtered off. The brown filtrate was loaded onto a silica gel column in methanol, and the first few milliliters of the dark brown band was discarded³¹ as it was believed to contain an organic byproduct from the reaction of PhLi and CH_2Cl_2 (vide infra). The rest of the band was collected and yielded the final product upon solvent evaporation under vacuum.

On the basis of elemental analysis, the isolated product is believed to be a 1:1 methanol adduct, $\text{VPh}_2(\text{salen})\cdot\text{CH}_3\text{OH}$. The methanol molecule probably does not reside in the first coordination sphere since 7-coordinate vanadium(IV) complexes are not common. The methanol molecule was not removed from the structure upon drying in vacuo at room temperature or at 80 °C, as indicated by infrared spectroscopy. This suggests that the methanol is held quite tightly. The diphenyl derivative was soluble in CH_2Cl_2 , Me_2SO , DMF and methanol. It was relatively air-stable but over a period of days slowly reacted to give some $\text{VO}(\text{salen})$ as indicated by IR spectroscopy. In CH_2Cl_2 solution, there was no indication of decomposition, although in Me_2SO and DMF there was a color change to green indicative of $\text{VO}(\text{salen})$. Both the phenyl groups and the salen ligand probably contribute to the stability of the complex.

By loading of the brown filtrate onto a silica gel column packed with CH_2Cl_2 , the organic byproduct from quenching the PhLi was successfully separated as a yellow effluent. When PhLi was put directly into CH_2Cl_2 , a white precipitate (LiCl) was formed along with a yellow solution. A yellow solid was recovered from this solution. The yellow solid obtained from the yellow effluent showed an infrared spectrum similar to that of the yellow solid resulting from the direct reaction of PhLi and CH_2Cl_2 . The

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(30) Phenylmagnesium chloride was first used as the phenylating agent, but the product obtained always contained a considerable amount of chloride. The chloride-containing impurity was MgCl_2 , which could not be removed by washing with water because the vanadium product was moisture-sensitive. Other efforts to separate MgCl_2 from the desired product were unsuccessful.

(31) The column purification procedure led to low, variable yields, typically about 40%.

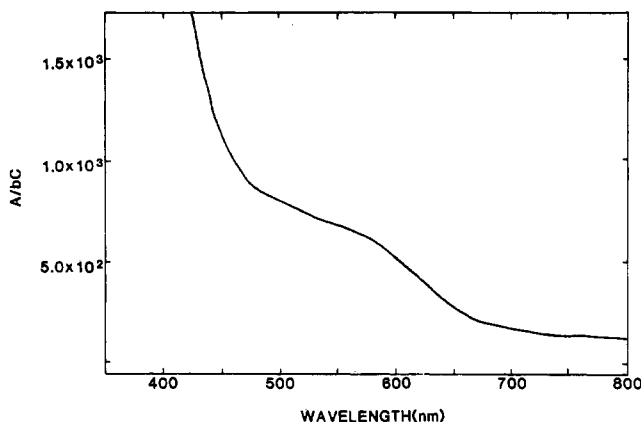
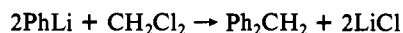


Figure 2. Visible spectrum of VPh₂(salen)·CH₃OH in CH₂Cl₂.

spectra in Nujol exhibited peaks expected for monosubstituted benzene, i.e. two peaks in the 600–900-cm⁻¹ region (705 and 743 cm⁻¹), which would account for ring C–H out-of-plane bends. An ¹H NMR spectrum in CDCl₃ exhibited peaks in the aromatic proton region (7–8 ppm) and peaks between 0.5 and 2.0 ppm. The integrated ratio of the former to the latter peaks was 5 to 1. The yellow byproduct is thus believed to be Ph₂CH₂ produced by the reaction



Spectroscopy. The infrared spectrum of VPh₂(salen)·CH₃OH was recorded and compared to those of VO(salen) and VCl₂(salen). The diphenyl derivative, VPh₂(salen)·CH₃OH, exhibits an infrared spectrum as shown in Figure 1. The main features of this spectrum are the bands between 675 and 900 cm⁻¹. A monosubstituted benzene ring is expected to exhibit two bands in this region while a disubstituted ring would exhibit only one band. These absorptions are ring C–H out-of-plane bends. Figure 1 shows bands at 707 and 744 cm⁻¹, which account for the presence of the phenyl substituent groups. These bands are comparable to those at 705 and 743 cm⁻¹ of the yellow organic byproduct, Ph₂CH₂. The band at 761 cm⁻¹ corresponds to the disubstituted benzene ring in the salen ligand, which was observed at 768 cm⁻¹ in the spectra of VO(salen)⁴ and VCl₂(salen).

Evidence that the salen ligand is intact and hence that the phenyl group must be bound to the vanadium atom comes from observation of the C=N stretching frequency of the ligand. Although C=N frequencies are higher in other compounds, it is well documented that this band appears between 1630 and 1600 cm⁻¹ for vanadyl Schiff base complexes.^{32–36} The observed frequencies for the species studied here are

species	$\nu_{\text{C=N}}$, cm ⁻¹	species	$\nu_{\text{C=N}}$, cm ⁻¹
H ₂ (salen)	1611	VCl ₂ (salen)	1603
VO(salen)	1614	VPh ₂ (salen)	1596

This suggests that in the latter two compounds strong V–N bonding weakens the C=N bond and shifts its frequency lower.

The O–H stretching frequency of the methanol adduct is observed at 3190 cm⁻¹, which is lower than the normal frequency range for methanol. This suggests an associated hydroxyl group that probably arises from intermolecular hydrogen bonding to another methanol molecule. A broad band at 1050 cm⁻¹ accounts for C–O stretching vibrations that cover up the ring C–H in-plane bends (1000–1200 cm⁻¹). The in-plane O–H bending appears as a broad band at about 1280 cm⁻¹ and is augmented by C–H in-plane bends.

The differences in the spectra of VPh₂(salen)·CH₃OH, VO(salen), and VCl₂(salen) are important. VO(salen)⁴ exhibits the characteristic V=O stretch at 986 cm⁻¹, which is absent from

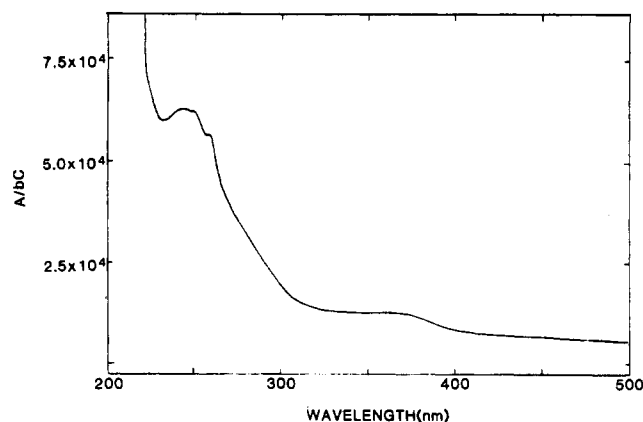


Figure 3. Ultraviolet spectrum of VPh₂(salen)·CH₃OH in CH₂Cl₂.

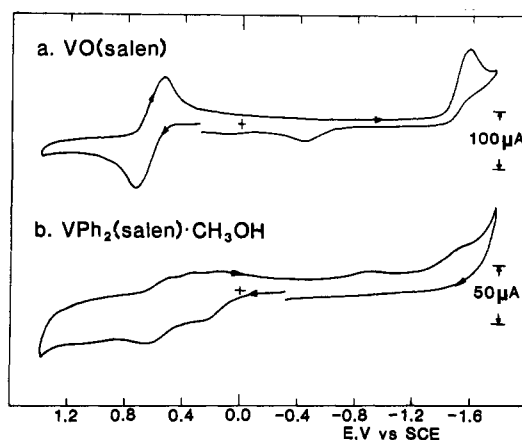


Figure 4. Cyclic voltammograms in 0.1 M TEAP/CH₂Cl₂ solutions of (a) 1.0 mM VO(salen) and (b) 1.3 mM VPh₂(salen)·CH₃OH (scan rate 200 mV/s).

each of the other two spectra. VCl₂(salen) exhibits a peak at 301 cm⁻¹, which is assigned to the V–Cl stretch. This peak is absent from the spectra of both the oxo and diphenyl compounds.

Pasquali and co-workers² determined the structure of VCl₂(sal-N-Bu)₂ to be a distorted octahedron with trans chloro groups. On the basis of the similarity of this compound to VCl₂(salen), the precursor of VPh₂(salen)·CH₃OH, we predict a similar structure for the diphenyl derivative. That is, the salen ligand probably is planar with phenyl ligands trans to each other above and below the plane. Gambarotta's work²² also supports this. Although his compounds were dimers, the structures included essentially planar Schiff base ligands and trans methyl, phenyl, or benzyl ligands.

The visible and ultraviolet spectra of VPh₂(salen)·CH₃OH in CH₂Cl₂ are shown in Figures 2 and 3, respectively, and are similar to those for VO(salen) and VCl₂(salen). The visible spectrum of VPh₂(salen)·CH₃OH shows only a broad shoulder that appears to be composed of two d–d transition bands at about 500 and 580 nm. These have relatively high molar absorptivities (about 800 and 650, respectively) since they are on the tail of an intense charge-transfer band. In the spectrum of VO(salen) the 580-nm peak is much more distinct, while for VCl₂(salen) (recorded in Me₂SO because of decomposition in CH₂Cl₂) only one broad band near 600 nm is observed.

In the UV region the phenyl groups of VPh₂(salen)·CH₃OH appear to increase the charge-transfer absorption intensities. For VPh₂(salen)·CH₃OH the absorbances are 375 nm ($\epsilon = 1.25 \times 10^4$) and 240 nm ($\epsilon = 6.0 \times 10^4$). For VO(salen) the values are 365 nm ($\epsilon = 8.0 \times 10^3$) and 285 nm ($\epsilon = 1.9 \times 10^4$).

Electrochemistry. The electrochemistry of VO(salen) and VCl₂(salen) in DMF have been reported by Kapturkiewicz.³⁷ We

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have reinvestigated these compounds in various solvents in order to compare to $VPh_2(\text{salen})\cdot\text{CH}_3\text{OH}$.

The electrochemistry of $VO(\text{salen})$ was carried out in Me_2SO and in CH_2Cl_2 . In Me_2SO there is a reversible oxidation (based on peak height ratio and peak potential separation) at +0.29 V vs. SCE and an irreversible reduction at -1.6 V. In CH_2Cl_2 these processes are observed at +0.64 and -1.6 V, respectively (Figure 4a). The results in Me_2SO are virtually identical with those reported by Kapturkiewicz²⁷ in DMF, while the oxidation couple is shifted positively about 0.3 V in CH_2Cl_2 .

Kapturkiewicz reported a reversible reduction of $VCl_2(\text{salen})$ at -0.450 V vs. SCE in DMF, although the compound was not stable in solution. We also found a transient couple at about -0.5 V in DMF, while in Me_2SO only the reduction peak was present. In both solvents, features corresponding to $VO(\text{salen})$ began to appear on the cyclic voltammograms within a few minutes.

The electrochemistry of $VPh_2(\text{salen})\cdot\text{CH}_3\text{OH}$ was studied in CH_2Cl_2 (Figure 4b) and was compared to that of $VO(\text{salen})$ in the same solvent (Figure 4a). The cyclic voltammogram of $VPh_2(\text{salen})\cdot\text{CH}_3\text{OH}$ shows several peaks, although none are distinct. This suggests some decomposition may have taken place, although the solution stayed red-brown for hours, unlike $VCl_2(\text{salen})$, which decomposed quickly. There are two oxidation waves on the initial positive scan, and the first one (0.2 V) could be due

to the diphenyl compound. The second oxidation peak (0.6 V) appears at almost the same potential as that for the $VO(\text{salen})$ couple, but its identity is unclear since electrolysis at 0.8 V did not produce the corresponding reduction peak expected for $VO(\text{salen})^+$. The reduction wave at -1.5 V also suggests that some decomposition to $VO(\text{salen})$ may have taken place. Since the absorption spectra indicate that the compound is stable in solution and since quantitative conversion to $VO(\text{salen})$ is not observed, the problem may be that efficient electron transfer between the electrode and the analyte does not occur in this system. To improve the quality of the electrochemical data for this system and others, we are pursuing the use of mediator titrants.

Conclusion

From the stable vanadyl ion, VO^{2+} , we have prepared VCl_2^{2+} by the method of Pasquali and co-workers.² This ion can then be used as a precursor for making the VPh_2^{2+} moiety. The compound $VPh_2(\text{salen})\cdot\text{CH}_3\text{OH}$ is the first organovanadium(IV) species that is stable at room temperature. This reaction pathway is straightforward and should be useful for making other organovanadium compounds such as $VR_2(\text{salen})$, where R = benzyl or *tert*-butyl.

Acknowledgment. Financial support for this work was provided by the Research Corp. and Miami University.

Contribution No. 3830 from the Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Organometallic Crown Ethers. 2. Syntheses of Phosphino Aza Crown Ether Ligands

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Received October 1, 1985

The syntheses of phosphino aza crown ethers $Ph_2P(CH_2)_m\overline{NCH_2(CH_2OCH_2)_nCH_2}$ ($n = 3, m = 0; n = 4, m = 0-3$) and $Ph_2PCH_2N(CH_2CH_2OCH_2CH_2O)_2(o-C_6H_4)$ using simple aza crown ethers $HNCH_2(CH_2OCH_2)_nCH_2$ ($n = 3, 4$) and $HN(CH_2CH_2OCH_2CH_2O)_2(o-C_6H_4)$ as starting materials are reported. These new ligands can bind to transition metals at phosphorus and alkali-metal ions at the aza crown ether.

Introduction

The migration of a metal alkyl ligand to a coordinated CO to generate a metal acyl is a fundamental reaction of organometallic chemistry¹ and a key step in metal-catalyzed carbonylation reactions.² This reaction is promoted by many types of Lewis acids including Li^+ ,³ AlX_3 ,⁴ BF_3 ,⁴ $CpFe(CO)_2^+$,⁵ $CpMo(CO)_3^+$,⁵ $CpW(CO)_3^+$,⁵ and amphoteric aluminophosphine ligands.⁶

We recently reported the synthesis of a phosphine-functionalized aza crown ether that is capable of holding Lewis acidic cations

close to transition metals.⁷ The first phosphine-functionalized crown ethers reported by Shaw and co-workers are rigid, and the positions of the binding sites are not optimum for interaction between a crown-ether-held cation and a phosphine-bound transition metal.⁸ Recently a number of more flexible phosphino crown ethers have been reported, particularly by Powell and co-workers.⁹ Examples include phosphino aza crown ethers,^{9a} chelating bis(phosphinites) with crown-ether-type properties,^{9b,c} and crown ethers with phosphorus(III) in the macrocycle ring.^{9d,10} As part of a program to study the effect of crown-ether-held cations on the rate of alkyl migration to CO, we have prepared a series of phosphine-functionalized aza crown ethers, $Ph_2P(CH_2)_n\overline{NCH_2(CH_2OCH_2)_4CH_2}$, in which the distance between

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