Mono- and Dimeric Phosphine Complexes of Cyclopentadienylvanadium(II) Halides

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Preparation of CH₂COC₅(CO)₂NCCH₅. Bulk Electrolysis. CH₂COC₅(CO)₂ (0.10 g, 0.35 mmol) was electrolyzed in 30 cm³ of dry, degassed CH₂CN (0.1 mol dm⁻³ Bu₄NCIO₄) at -0.50 V until TLC and IR showed no increase in the amount of purple-gray dihalide complexes CpVX₂(PR₃)₁₆ from a concentrated CH₂CN solution were unsuccessful, and the solution and solid both slowly reverted to CH₂COC₅(CO)₂ at 0 °C (~50% over 12 h). This complex does not give rise to a molecular ion peak in its mass spectrum; the highest mass peak observed is at m/e 456 ([(CH₂COC₅(CO)₂)]ⁿ⁺). Anal. Calc'd for C₆₂H₄₀C₁₀O₂N₁₆P₂₀: C, 30.73; H, 1.29; N, 2.98. Found: C, 28.89; H, 2.15; N, 2.39. IR (CH₂CN): ν(CO) 2078 (w), 2030 (v), 2010 (s), 1990 (sh) cm⁻¹.

Thermal Reaction. CH₂COC₅(CO)₂ (0.14 g, 0.43 mmol) was refluxed in 25 cm³ of dry, degassed CH₃CN for 10 min. This reaction by TLC showed that the formation of the desired product was <30% and so this preparative route was not favored.

Reduction of CpVX₂(PR₃)₂ (X = Cl, R = Me, Et; X = Br, R = Et) with Al or Zn in THF gives dimeric vanadium(II) complexes [CpVX(PR₃)]₂. Methylcyclopentadienyl compounds are accessible by the same treatment. The dimers with an excess of PR₃ gives CpVX(PR₃)₃ and treating the dimers with bidentate phosphines, CpVCl(DMPE) and CpVCl(DPPE) are obtained. All compounds are paramagnetic with, in principle, three unpaired electrons on the metal atom. ¹H NMR spectra of the complexes show large downfield shifts of the cyclopentadienyl protons (range of 64-250 ppm). The phosphine ligands show smaller shifts, varying between ~4.0 ppm for the dimers [CpVX(PR₃)]₂ and between ~25.5 and ~17.0 ppm for CpVCl(DMPE). The complexes are very reactive and their reactions with a variety of substrates, e.g., dioxygen, cyclohexene oxide, alkynes, and carbon monoxide, proceed easily. With α-olefins no reaction (hydrogenation, isomerization, or oligomerization) was observed.

Introduction

In contrast to well-investigated low-valent titanium and chromium species, relatively little is known about vanadium(II) compounds. There are a few reports on the reduction of dinitrogen- and nitrogen-containing molecules by inorganic vanadium(II) complexes.¹ Vanadium(II) compounds also seem to be active in the reduction of epoxides and reductive coupling of allylic or benzylic halides.

Several metals can reduce vanadium(III). Thus VX₅-(THF) (X = Cl, Br) in THF reacts with various metals (e.g., Al, Zn, Fe, Mn) to form a dinuclear vanadium(II) cation, [VX₅(THF)]⁺.²⁻⁴

In this paper we report the preparation and reactivity of two series of well-defined vanadium(II) compounds containing one cyclopentadienyl and one halide ligand per vanadium atom using cyclopentadienyl vanadium(III) dihalide complexes CpVX(PR₃)₂ as starting compounds.⁵

Chromatography on silica gel plates eluted in hexane allowed recovery of CH₂COC₅(CO)₂NCCH₅ (0.06 g, 0.12 mmol, 40% yield). In an attempt to improve the yield the reaction was stirred at 60-75 °C for ~2 h but no significant difference in yield of the desired product was achieved.

BPK Reaction. BPK was added dropwise to an ~10⁻² mol dm⁻³ solution of CH₂COC₅(CO)₂ in CH₂CN. Monitoring of the reaction by TLC showed that the formation of the desired product was <30% and so this preparative route was not favored.

Registry No. CH₂COC₅(CO)₂, 10682-04-7; (CH₃)₂COC₅(CO)₂, 12584-37-3; (CH₂)₃COC₅(CO)₂, 12284-15-2; PhCOC₅(CO)₂, 15982-05-0; Ph₂COC₅(CO)₂, 11057-45-5; Ph₃COC₅(CO)₂, 14515-69-6; Ph₄COC₅(CO)₂NCCH₅, 8496-16-2; CH₂COC₅(CO)₂NCCH₅, 101011-53-4; PhCOC₅(CO)₂-dppm, 101141-55-3; [PhCOC₅(CO)₂]₃, 101141-59-7; PhCOC₅(CO)₂-dppe, 101101-54-5; [PhCOC₅(CO)₂]₃-dppm, 101011-55-6; PhCOC₅(CO)₂-dpme, 101011-56-7; PhCOC₅(CO)₂PPh₃, 13681-99-7; PhCOC₅(CO)₂(PPh₃)₂, 101011-57-8.

Mono- and Dimeric Phosphine Complexes of Cyclopentadienylvanadium(II) Halides

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Received August 28, 1985

Reduction of CpVX₂(PR₃)₂ (X = Cl, R = Me, Et; X = Br, R = Et) with Al or Zn in THF gives dimeric vanadium(II) complexes [CpVX(PR₃)]₂. Methylcyclopentadienyl compounds are accessible by the same procedure. The dimers with an excess of PR₃ gives CpVX(PR₃)₃, and treating the dimers with bidentate phosphines, CpVCl(DMPE) and CpVCl(DPPE) are obtained. All compounds are paramagnetic with, in principle, three unpaired electrons on the metal atom. ¹H NMR spectra of the complexes show large downfield shifts of the cyclopentadienyl protons (range of 64-250 ppm). The phosphine ligands show smaller shifts, varying between ~3.0 and ~4.60 ppm for the dimers [CpVX(PR₃)]₂ and between ~25.5 and ~17.0 ppm for CpVCl(DMPE). The complexes are very reactive and their reactions with a variety of substrates, e.g., dioxygen, cyclohexene oxide, alkynes, and carbon monoxide, proceed easily. With α-olefins no reaction (hydrogenation, isomerization, or oligomerization) was observed.

Experimental Section

General Remarks. All reactions were performed under purified nitrogen using Schlenk and glovebox techniques. Solvents were distilled under nitrogen from sodium (toluene) or sodium-potassium pellets (THF, ether, pentane) before use. CPVX₂(PR₃)₂ and CPVX₃(PR₃)₂ (CP = 5-C₅H₄-Me; CP = 5-C₅H₄-Me; X = Cl, Br; R = Me, Et), PMe₃ Ph₃P, and PMe₃ Ph₃P were prepared according to published procedures. Zinc powder (UCB), aluminium powder (Fluka), and DPPE (Strem) were used as purchased.

IR spectra (Nujol/KBr) were recorded on a JASCO-IRA-2 spectrophotometer. EPR spectra were recorded with a Varian E-4 EPR spectrometer. ¹H NMR spectra were recorded by Dr. R. J. Bouma in toluene-d₈ or benzene-δ with a Nicolet NT 200 EPR spectrometer. 'H NMR spectra were recorded by Dr. R. J. Bouma in toluene-d₈ or benzene-δ with a Nicolet Model 1180 data system. Chemical shifts are given relative to MelSi (internal standard, δ = 0, downfield shift) ppm. Molecular weights were determined by cryoscopy in benzene. Melting points were determined by DTA (heating rate 2 °C/min). Gas chromatography was performed...
Preparation of [CpVCl(PEt3)]2 (3). A solution of 30.0 g (67.0 mmol) of [CpVCl(PEt3)]2 was stirred with 20.0 g of aluminum in 100 mL of THF under reflux with 3.0 g of aluminium powder for 48 h. The purple-blue solution gradually changed to clear blue. On stripping the THF, a dark red solid remained, which was washed with 100 mL of pentane to remove the last traces of free phosgene. Extraction with 150 mL of ether resulted in a dark red solution which on concentrating to 40 mL and slow cooling to −80 °C yielded 0.40 g (0.88 mmol) of [CpVCl(PEt3)]2. Anal. Calc. for CpVCl(PEt3): C, 48.86; H, 7.58; Cl, 13.31; V, 8.78. Found: C, 48.5; H, 7.4; Cl, 13.26; V, 8.5.

Preparation of [CpVBr(PEt3)]2 (4). 4 was prepared analogous to 3: yield 47%; mp 121 °C. Anal. Calc. for CpVBr(PEt3): C, 50.51; H, 7.82; Cl, 17.98. Found: C, 50.50; H, 8.17; Cl, 17.74.

Preparation of [CpVBr(PEt3)]2 (5). 5 was prepared analogous to 3: yield 48%; mp 131 °C. Anal. Calc. for CpVBr(PEt3): C, 51.44; H, 6.42; Br, 25.44; V, 16.22. Found: C, 51.27; H, 6.47; Br, 25.50; V, 16.31.

Preparation of [CpVCl(PEt3)]2 (6). To a solution of 480 mg (0.88 mmol) of [CpVCl(PEt3)]2 in 20 mL of pentane was added 0.50 mL (7.3 mol-%) of PEt3 dropwise at room temperature. A clear blue solution was obtained. The compound was recrystallized from toluene to give analytically pure 6: yield 74%; mp 140 °C. Anal. Calc. for CpVCl(PEt3): C, 49.00; H, 7.48; Cl, 13.15; V, 18.82; mol wt, 560.

Preparation of [CpVCl(PEt3)]2 (7). Preparation of [CpVCl(PEt3)]2 (7). To a solution of 1.20 g (2.22 mmol) of [CpVCl(PEt3)]2 in 100 mL of toluene stirred at room temperature for 6 h, an excess of DMPE (1.5 mL, 8.9 mmol). On warming to 0 °C a black precipitate of polymeric residue. IR spectra show an increase of a new strong peak at 230 mol-' L cm-') and an increase of a new strong peak at 548 nm with e548 = 1.970 due to interaction of the electron with one vanadium (61V, I = 1/2, a = 68.7 G) and one phosphorus (32P, I = 1/2, a = 23.3 G) nucleus.

In a separate experiment a solution of 44.5 mg (0.083 mmol) of 3 in 3.05 g of benzene was reacted with 0.18 mmol of O2 at 6 °C. After reaction the freezing point of the solution was determined. No change in the freezing point of the solution after oxygen admission was observed.

Preparation of [CpVCl(PEt3)]2 (8) with Cyclohexene Oxide. To a solution of 415 mg (0.78 mmol) of 3, in 20 mL of ether at 0 °C, was added 72.1 mg (0.74 mmol) of cyclohexene oxide. After 10 min. The purple solution obtained was stirred for 1.5 h at 0 °C. The final solution was analyzed by GC. Quantitative conversion of cyclohexene oxycysteine to cyclohexene was found.

Preparation of [CpVCl(PEt3)]2 (6) with Alkynes. With Propyne. The reaction with propyne was performed under analogous conditions as described for ethyne. Only 5.9 mol of propyne/mol of dimer was consumed after 24 h. GC analysis of the solution showed 0.5 mol of PEt3/mol of dimer, in addition to the trimethylation products 1,5,5-trimethylbenzene (0.45 mol), 1,2,4-trimethylbenzene (1.68 mol), and 1,2,4,5-tetramethylbenzene (0.10 mol).

Results and Discussion

Monomeric vanadium(III) complexes [CpVCl(PR3)2], [CpVCl(PR3)2], [CpVBr(PEt3)]2, and [CpVCl(PEt3)]2 exhibit a dimeric structure, which was confirmed by variable-temperature 1H NMR spectroscopy. The complexes were found to be stable in solution and in the solid state. The electronic spectra of the complexes show a strong absorption band at 548 nm due to an intraligand charge-transfer transition. The EPR spectra of the complexes show a well-resolved 16-line signal at g = 2.0. These results were confirmed by X-ray crystallography, which showed a dimeric structure with a vanadium-vanadium bond length of 2.75 Å. The complexes were found to be air-stable and were not affected by exposure to air for extended periods of time.
compounds. The reduction takes place with metals like Na, Mg, Zn, and Al but is most convenient for Zn and Al since an excess of metal does not lead to further reduction. For strongly reducing metals (e.g., Na or Mg) further reduction beyond the vanadium(II) stage occurs readily. The products of these reductions were not identified. With stoichiometric amounts of Na/Hg, however, acceptable yields of 1–5 can be obtained. From the point of convenience the aluminum reduction method is to be preferred. The reduction of the triethylphosphate complexes with Zn or Al is complete within 24 h at room temperature, whereas the trimethylphosphine complexes react very slowly. In this case the reduction with Al or Zn has to be carried out in refluxing THF to obtain acceptable yields within 24 h. Reduction with 1 equiv of Na/Hg is more convenient here.

The stoichiometry of the reductions is represented in eq 1. The metal halide, MXₙ, has the role of forcing the nCPVX₂(PR₃)₂ + M → MXₙ + 1/2n[CPVX(PR₃)]₂ + 1/2nPR₃ (1) reaction to the dimeric vanadium(II) complexes through complexion of the liberated phosphines (formation of ZnX₈(PR₃)₂ and AlX₃(PR₃) was established). For M = Zn the stoichiometry is such that all of the phosphine liberated during the reduction can be complexed by the zinc halide. For M = Al considerable amounts of free phosphine remain in solution, thus complicating the synthesis of the dimeric complexes by participating in an equilibrium (eq 2). For R = Et, the equilibrium is at the left-hand side [CPVX(PR₃)]₂ + 2PR₃ ⇔ 2CPVX(PR₃)₂ (2) as can be concluded from the purple-red color of the solutions. For R = Me the equilibrium is at the right and the clear blue color of the reaction mixture is in accordance with this. The dimeric species 1–5 can be obtained from solutions containing an excess of phosphine by slow evaporation under vacuum.

Monomeric complexes CPVCl(PMe₃)₂ (6), CPVCl(DMPE) (7), and CPVCl(DPPE) (8) are made by treating 3 with excess of PMe₃ or the appropriate diphenphosphine. Formation of a monomeric complex CPVCl(PPh₃) from 3 in solution can be concluded from the characteristic blue color following addition of extra PPh₃. Attempts to isolate the compound failed due to the preferred crystallization of 3. Addition of PMe₃ to 3 in toluene also produces a deep blue color due to the formation of 6. Evaporation of the toluene resulted in the removal of the very volatile PMe₃ leading to the isolation of 3. Addition of a large excess of PMe₃ to a pentane solution of 3 gave precipitation of analytically pure 6. The solubility of 6 in pentane and benzene is quite low. It dissolves in THF, but all attempts to crystallize 6 from this solvent failed, and only the dimer 1 could be isolated.

Bidentate phosphines (DMPE and DPPE) react readily with 3 to give 7 and 8. These complexes are thermally stable and can be recrystallized from toluene. Their solubility in common organic solvents is quite low, and molecular weight determinations by cryoscopy in benzene failed. The monomeric character is indicated by the mass spectrum and magnetic properties of 7. The highest m/e value is 300, corresponding with the molecular ion minus H₂(M – H)⁺. Magnetic susceptibility measurements (Table 1) at various temperatures (10–300 K) show that 7 is a magnetically dilute compound following the Curie–Weiss law (10–300 K, θ = +7.7 K) with μeff = 3.80 μB (calculated spin only for d³ = 3.87 μB).

Table 1. Magnetic Susceptibilities* of CPVCl(DMPE) (7) at Various Temperatures

<table>
<thead>
<tr>
<th>T, K</th>
<th>10^5χ_mol cgsu</th>
<th>T, K</th>
<th>10^5χ_mol cgsu</th>
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<tr>
<td>9.5</td>
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<td>16.5</td>
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<td>6.79</td>
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<tr>
<td>65.9</td>
<td>24.0</td>
<td>295.6</td>
<td>5.99</td>
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</table>

*Corrected for diamagnetism (χ_dia = 0.20 × 10^−6 cgsu).

The dimeric nature of compounds 1–5 follows from molecular weight determinations for 2 and 3. The effective magnetic moments at room temperature are much lower (ca. 3.0 μB for 1) than expected for d³ systems, and on cooling they show antiferromagnetic behavior. A detailed study of the molecular structure and the magnetic properties of the dimers is in progress. Preliminary results of an X-ray diffraction study on 3 show bridging halide ligands and a cisoid (Z) arrangement of Cp and phosphine ligands. The V₂Cl₂ ring is puckered (Figure 1).

The dimers 1–5 are thermally very stable. The melting points of the triethylphosphine complexes are substantially higher than those of the monomeric vanadium(III) parent compounds CPVX₂(PMe₃). Differential thermal analysis showed no decomposition effects up to 250 °C.

The IR spectra of the complexes are all quite similar and show the expected Cp (Cp') and phosphine absorptions. For diagnostic purposes two characteristic features are mentioned here. The first is the very strong out of plane vibration, δ_m(dia)(CH), of the Cp ligand between 770 and 785 cm⁻¹, in the range expected for 15e vanadium cyclopentadienyl compounds. The second is the intense CH₃ rocking mode of the phosphate ligands, which is found at about 950 cm⁻¹ for PMe₃ and around 1040 cm⁻¹ for PPh₃ complexes.

(10) For a 16-electron V(III) compound, the strong band of the C–H oop deformation of an n⁵-C₅H₅ group is normally found in the range 790–810 cm⁻¹ (cf. 805 cm⁻¹ in CPVX₆(PMe₃)₂). For a 17-electron V(IV) compound this band is above 820 cm⁻¹ (cf. 824 cm⁻¹ in CPVC₅ and 822 cm⁻¹ in CPVCl₃).

Figure 1. Molecular structure of [CPVCl(PEt₃)]₂ (3).

Figure 2. ¹H NMR spectrum of CPVCl(DMPE) in toluene-d₈ at 20 °C. Solvent peaks are omitted.
**Table II.** 'H NMR Spectral Data* (δ) of [CpVCl(PEt3)]2 (3), [CpVCl(PEt3)]4 (4), and CpVCl(DMPE) (7)

<table>
<thead>
<tr>
<th>compd</th>
<th>isomer</th>
<th>Cp</th>
<th>Cp'</th>
<th>MeCp'</th>
<th>α-H(PEt3)</th>
<th>β-H(PEt3)</th>
<th>Me(DMPE)</th>
<th>CH3(DMPE)</th>
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<tr>
<td>3</td>
<td>Z</td>
<td>64</td>
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<tr>
<td>4</td>
<td>Z</td>
<td>75</td>
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<tr>
<td>7</td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
<td>-25.5</td>
<td>17.0</td>
</tr>
</tbody>
</table>

*At 20 °C in benzene-d₆ (7 in toluene-d₄); isotropic shifts relative to Me₄Si (δ 0, downfield shifts positive).

**Figure 3.** Proposed structure of CpVCl(DMPE) (7).

1H NMR spectra of the dimeric, formally 30-electron (i.e., 15e/vanadium) species 3 and 4 and of the monomeric, 15e compound 7 were recorded, and the data are given in Table II. The isotropic shift of the Cp protons of 7 (δ 250) seems normal for a divalent cyclopentadienyl vanadium(II) complex (cf. Cp₂V, δ 315). The DMPE resonances are shifted less dramatically. Both methyl and methylene resonances are split into two signals with a 1:1 ratio. The methyl groups are at +2.5 and −25.5 ppm and the methylene protons at +17.0 and +17.9 ppm (Figure 2). This magnetic inequivalence is consistent with a DMPE ligand in a more or less fixed position (Figure 3), such that the protons are divided in two groups: half the protons are on the Cp side and the other half on the Cl side of the molecule, like has been found in the related compound CpVMe(DMPE).12 Twisting of the DMPE vanadium ring is possible without changing Cp and Cl side positions of the protons. If the ring were completely rigid, four resonances for the methyl and also for the methylene protons would be expected. The fact that only two resonances are seen does not permit conclusions with respect to fluxionality of the DMPE–vanadium ring system. It is possible that the chemical shifts of the various protons are so little different that overlap of the rather broad signals (width at half-height is ca. 300 Hz) in effect results in one peak. A higher temperatures (105 °C) the signals show the expected Curie shifts toward diamagnetic positions but the two separate methyl (e.g., methylene) resonances still remain. It is clear that there is no low-energy process leading to equivalent methyl (and methylene) groups of the DMPE ligand, e.g., dissociation of one of the phosphine groups and rotation.

The isotropic shifts of the cyclopentadienyl protons in the dimeric complexes 3 and 4 (δ 140–64) are considerably smaller than for the monomeric cyclopentadienyl vanadium(II) compounds (Figure 4). This smaller shift is a consequence of antiferromagnetic exchange interactions between spins of two vanadium atoms in the dimeric complexes. The spectra of 3 and 4 indicate at room temperature the presence of two paramagnetic species in about 1:2 ratio. At higher temperatures (ca. 70 °C) the corresponding resonances coalesce. Due to the complicated dependence of the isotropic shifts and line widths on temperature a quantitative analysis was not attempted. A plausible explanation of the observed phenomena is the presence of isomers rather than a monomer–dimer equilibrium. Against the latter is the fact that molecular weight determinations in benzene are too close to the value expected for exclusively dimeric species in solution. Moreover, both species show an increase in absolute isotropic shift when the temperature is raised. This is exactly what is expected for antiferromagnetically coupled species, thus supporting the idea that both species are dimers. The most likely explanation is the presence of Z and E isomers (Scheme I). Since the crystal structure of [CpVCl(PEt3)]2 (3) show that the Z isomer is present in the solid state, we assume it also to be the most abundant in solution. Another argument in favor of this assignment is that antiferromagnetic coupling is expected to be larger on geometrical grounds for the Z isomer with its puckered V₂Cl₂ ring than for the E isomer where a centrosymmetric geometry (i.e., planar) of the V₂Cl₂ ring is likely. This difference in antiferromagnetic coupling will lead to a larger paramagnetism for the E isomer and consequently to larger isotropic shifts, and this is what is observed for the less abundant species. The merging of the various resonances at high temperature indicates that the interconversion of the Z and E isomers is rather slow on the NMR time scale. A more quantitative study of the kinetics and mechanism of this equilibrium is in progress.

**Chemical Properties.** As indicated in eq 2 dimeric complexes [CpVX(PR₃)₂] (1–5) react with phosphines to give monomeric complexes CpVX(PR₃)₂. Attempts to isolate these failed due to preferential crystallization of the dimers. Bidentate phosphines (e.g., DMPE, DPPE) give easy and complete displacement of the original PR₃. These results show that the phosphine ligands are quite labile and that the halogen bridges are easily opened.

All complexes are extremely air sensitive. Attempts have been made to study this by controlled oxidation and identification of the products. A solution of 3 in benzene at room temperature immediately turns intensely purple on slow admission of dioxygen. A very rapid further reaction was observed, if slightly more than 1 mol of O₂/mol of dimer was added. Within seconds the intensely purple solution turned dark green. A dark green product is also formed on slow decomposition of the purple complex at room temperature. Cryoscopy in benzene shows that the purple O₂ complex is still dimeric. Its IR spectrum shows

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Mono- and Dimeric Phosphine Complexes of CpVX₂

Scheme II

\[
\begin{align*}
\text{CpVCl(PEt₃)} & \quad \text{M} \quad \text{[CpVCl(PEt₃)]₂} \\
\text{CpV(PEt₃)} & \quad \text{CpVCO₄} \\
\text{CpVCl(PEt₃)} & \quad \text{CpVCO₄(PEt₃)}
\end{align*}
\]

no \( \nu(V=O) \) bands. The strong \( \delta_{\text{op}}(\text{CH}) \) band of the Cp group is shifted to 806 cm\(^{-1}\), indicating formation of a V(III) compound.\(^{10}\) These observations suggest that a peroxo-bridged compound is formed. The presence of a \( \nu(O=O) \) band in the range of 790–890 cm\(^{-1}\)\(^{13}\) could not be established unequivocally due to the presence of several bands in this range.

The green decomposition product shows a very strong \( \nu(V=O) \) band at 950 cm\(^{-1}\). On the basis of the stoichiometry of the reaction and the IR and EPR spectra (vide supra) we formulate this product as an oxo vanadium compound, CpV(OCl)₂PEt₃.

No IR evidence was found for the formation of phosphorus-oxygen bonds, i.e., formation of free Et₃P=O or Et₃P─O─O complexes.\(^{14}\) Also in NMR spectra no Et₃P─O was observed. NMR spectra and GC show that no PEt₃ is liberated, and we conclude that the phosphine remains coordinated.

The strong oxygen affinity of vanadium is also demonstrated by the absence of oxygen transfer to organic substrates like olefins or to metals like zinc. These results indicate that the dimers might be active in the reverse reaction, i.e., deoxygenation of oxygen-containing organic substrates. Indeed, 3 reacts with cyclohexene oxide under deoxygenation and formation of cyclohexene. The reaction is quite fast (half-time ca. 10 min) and stoichiometric, one mole of cyclohexene oxide reacts per mole of 3. This suggests the formation of a \( \mu\)-oxo-bridged vanadium complex as also has been observed for V(acac)₃ reactions,\(^{15}\) but we could not identify the oxidation product(s). Complexes 1–5 show little reactivity toward olefins. As an example, no isomerization or oligomerization was observed when 3 was refluxed in 1-hexene. Under hydrogen, neither isomerization nor hydrogenation was observed and 3 was recovered unchanged.

Functionalized olefins like 2-vinylpyridine or fumric acid did not react.

\[\text{[CpVCl(PEt₃)]₂}\] (3) does react with small alkynes under formation of trimerization product and polymers. In reaction with ethyne (1 bar) in toluene at 0 °C black polyacetylene (34 mol of ethylene/dimer) precipitated in 24 h. Benzene (4.5 mol of ethylene/dimer) was also formed, but no cyclooctatetraene was detected.

The reaction with propyne is slower. After 1 day only 5.9 mol of propyne/dimer were converted into oligomers; 2.23 mol was found as the trimerization products 1,3,5-trimethylbenzene (0.45 mol), 1,2,4-trimethylbenzene (1.68 mol), and 1,2,3-trimethylbenzene (0.10 mol). In both reactions a substantial amount of PEt₃ is liberated. This suggests that the elimination of a phosphine ligand is a key step in these reactions.

The small amount of 1,2,3-trimethylbenzene shows that the trimerization reaction should be considered neither as a process in which three alkynes combine in one move\(^{16}\) nor as an insertion of alkyne into a vanadacyclopentadienyl ring.\(^{17}\) Since these two reaction types can only account for 1,2,4- and 1,3,5-trisubstituted benzenes. A possible formation of the 1,2,3-trisubstituted benzenes from monosubstituted ethynes was suggested by Maitlis\(^{18}\) in alkyn oligomerization by palladium complexes.

\[\text{[CpVCl(PEt₃)]₂}\] (3) gives a fast reaction with carbon monoxide at room temperature in toluene solution. At 22 °C the half-time of the reaction was about 15 min and a total uptake of up to 3 mol of CO/dimer was measured.\(^{19}\) NMR spectra of the resulting reaction mixtures in benzene-\(d₆\) show the presence of diamagnetic CpV(CO)₃(PEt₃) but also of a paramagnetic product. During chromatography on Florisil the paramagnetic product decomposed. Two bands were collected after elution, and the compounds were identified by NMR as CpV(CO)₃ and CpV(CO)₃(PEt₃). These two compounds account for the total CO consumption, indicating that the paramagnetic product does not contain CO.

The formation of V(III) complexes in the reaction of 3 with CO is probably accompanied by the formation of a V(III) species. This can explain why in the zinc or aluminum reduction of CpVCl₂(PMe₃)₂ under CO, CpV(CO)₃(PMe₃) is formed in excellent yield.\(^{19}\) NMR experiments in THF-\(d₈\) indicate the formation of up to 95% of CpV(CO)₃(PMe₃) in the zinc reduction reaction and 90% in the aluminum reaction, within 1 day at ambient conditions. No formation of CpV(CO)₂ was observed.

Normally, zinc or aluminum reduction of V(III) only leads to V(II) species. CpVCl₂(PMe₃)₂ itself does not react with CO under the moderate conditions applied. Probably step 1 of the reaction is formation of \[\text{[CpVCl(PEt₃)]₂}\], subsequent reaction (2) with CO gives CpV(CO)₃(PMe₃) and a V(III) species, which is reduced, (3), to \[\text{[CpVCl(PEt₃)]₂}\] and again reacts with CO etc. as shown in Scheme II. The formation of CpV(CO)₄, (4), is only a minor side reaction.

The results show that CpVCl₂(PMe₃)₂ or \[\text{[CpVCl(PEt₃)]₂}\] are excellent starting materials for the preparation of CpV(CO)₃(PMe₃) in high yield at ambient conditions.

The study of the vanadium complexes \[\text{[CpVCl(PEt₃)]₂}\], CpVCl₂(PR₃)₂, and CpVCl(dme) is continued at the moment with attempts to substitute the chlorine ligand by an alkyl, allyl, or allyl group. So far, reactions of CpVCl(dme) (7) have led to CpV(dme) (8) and CpVCl(dme) (9).

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