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Phosph(on/in)ate-Bridged Vanadium(IV) Dimers: Synthesis and Characterization

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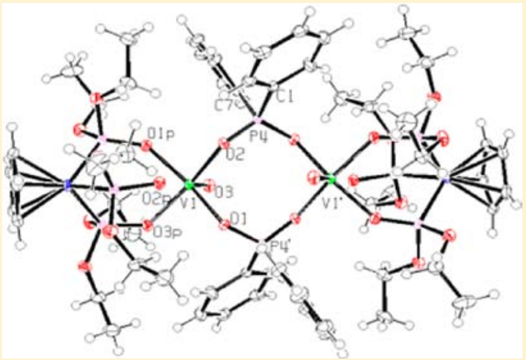
S Supporting Information

ABSTRACT: A series of dinuclear organophosphorus-bridged complexes of the general formula $\{(LVO(\mu\text{-}O_2PRR'))\}_2$ [L = η^5-cyclopentadienyltris(diethylphosphito-κ^1P) cobaltate(III)] has been synthesized as a structural model for the industrially used vanadium phosphate oxidation catalysts. These dimeric species contain two vanadium centers in a VO_6 environment bridged by O−P−O units. These complexes have been characterized via spectral and magnetic analyses. Structural parameters have been analyzed through X-ray diffraction. The dimers generally exist in either a *cis/cis*-anti or retracted chair conformation in the solid state. The syntheses, structural, spectral, and magnetic data are presented and discussed here.



■ INTRODUCTION

Understanding structures on an extended scale and the related structure/function relationships is an important goal to chemists and materials scientists as they attempt to create superior materials. One set of extended solids that are of great interest are oxidation catalysts. The industrially used oxidation catalysts often have poorly understood, extended structures and poorly defined compositions, thus making it very difficult to study the actual catalytic process,[1,2] although the engineering necessary to produce these catalysts is well understood.[3−6] Such catalysts are used extensively in industry to produce billions of tons of products each year, and catalytic materials with superior properties are continuously being sought. Currently, vanadium-containing catalysts are widely employed in academic and industrial settings as oxidation catalysts. For example, V_2O_5 is used in the production of sulfuric acid,[7] V compounds are useful for epoxidations of olefins and aromatic hydrocarbons,[8,9] V(IV) and V(V) complexes oxidize catechols to quinones,[10,11] and a vanadyl phosphate catalyst, nominally "$VOPO_4$", catalyzes the oxidation of C_4H_{10} to maleic anhydride.[3,5]

Investigation into the solid-state structure of $VOPO_4$ reveals an infinite lattice of vanadia octahedrally coordinated to oxygen atoms and phosphate tetrahedra.[12] The metal centers are in a mixture of V^{4+}/V^{5+} oxidations states.[13] Although the structure of the species has been characterized and understood for some time, mechanistically, the processes through which catalysis and oxidations occur remain convoluted. To study a representative motif of an extended solid on a structurally simpler level, we have adopted the method of "dimensional reduction," first described by Long et al.,[14−16] but employed earlier by solid-state chemists.[17−19] Using this method we represent the truncated structure and oxidative activity of layered vanadium phosphate catalysts with a series of dinuclear organophosphorus-bridged model molecules. These model complexes employ the use of the facially coordinating, O,O,O-binding monoanionic ligand, η^5-cyclopentadienyltris(diethylphosphito-κ^1P) cobaltate(III), $[CpP^{OEt}Co]^-$, first reported by Klaui and co-workers.[20,21] Use of this ligand gives the complexes structural and electronic similarities to industrially used catalysts;[13] the molecules contain octahedrally coordinated vanadium centers and tetrahedral phosph(on/in)ate moieties in addition to metal centers in the desired (+4) oxidation state. A related complex synthesized by Carrano and co-workers made use of the N,N,N-binding ligand hydrotris(pyrazolyl)borate ligand, Tp^-,[22] and that group has reported a series of such dimers with phosphates and phosphonates.[22−27] During our efforts to model this widely used catalyst, several novel octahedral vanadium(III/IV) complexes were synthesized and structurally characterized. The synthesis, characterization, and reactivity of the octahedrally coordinated vanadium(III) complex $[CpP^{OEt}Co]VCl_2(DMF)$ (DMF = *N,N*-dimethylformamide) (**1**) were recently communicated by us.[28] We have since made a number of dimers with a series of organophosphinates, organophosphonates, and organophosphates bridging the vanadium metal centers (Scheme 1), which we report here. These dinuclear molecules were synthesized with the intention of modeling the structure and oxidative catalytic activity of the catalyst $VOPO_4$. Here we report the spectroscopic, electronic, and structural results of the investigations of a series of vanadium(IV) organophosph(on/in)ate dimers.

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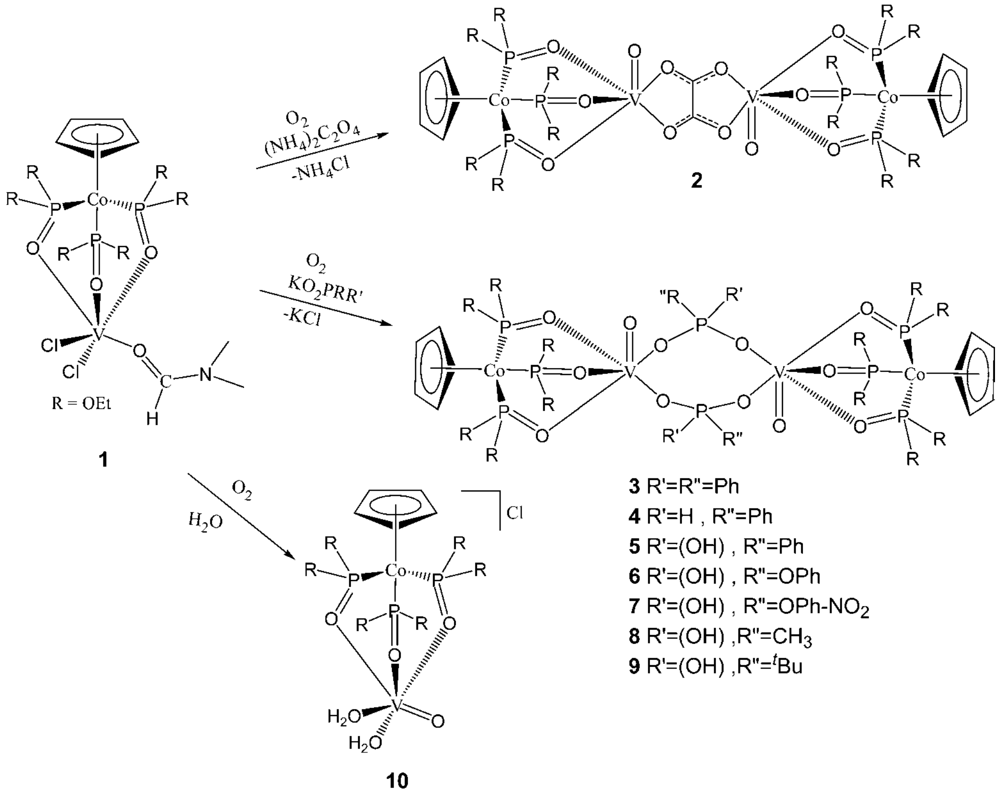
Scheme 1. Synthetic Strategy to Afford the Dimeric Species 2−9, and Decomposition Product 10



EXPERIMENTAL SECTION

General Considerations. Where indicated, air-free manipulations were carried out in an inert atmosphere glovebox, or using standard Schlenk techniques under a nitrogen atmosphere.[29] Dichloromethane and *N,N*-dimethylformamide were of BakerDRY quality and were deoxygenated before use. Reagent grade methanol was deoxygenated before use. Tetrahydrofuran (THF) was distilled over Na^0/benzophenone and deoxygenated before use. Deionized water was freeze-pumped-thawed before use. Reagent grade chloroform (Fisher, 99.9%), diethyl ether (Fisher, 99.9%), and acetonitrile (Fisher, 99.9%) were used as received. Vanadium(III) chloride (Acros, 99%), sodium hexafluorophosphate (Aldrich, 98%), potassium bicarbonate (Fisher, 99%), potassium carbonate (Fisher, 99%), vanadyl sulfate hydrate (Strem, 99%), barium chloride dihydrate (Baker 99%), diphenylphosphinic acid (Acros, 99%), biscyclohexylammonium 4-nitrophenyl phosphate monohydrate (Acros, 99%+), phenylphosphonic acid (Acros, 98%), phenylphosphinic acid (Acros, 99%), sodium phenyl phosphate sesquihydrate (Acros, 93%), and ammonium oxalate (Fisher, 99%) were used as received. The sodium salt of η^5-cyclopentadienyltris(diethylphosphito-κ^1P) cobaltate(III), NaCp-P^{OEt}Co was prepared according to literature procedures.[20,21] Potassium salts of *tert*-butyl phosphonate, phenyl phosphonate, methyl phosphonate, aminomethyl phosphonate, and aminoethyl phosphonate were obtained by aqueous neutralization of corresponding acids with $KHCO_3$. $(CpP^{OEt}Co)VCl_2(DMF)$, **1**, was prepared according to the literature procedure.[28] A slight modification to the literature procedure[30] was used to obtain $[(CpP^{OEt}Co)VO]_2(\mu\text{-ox})$, **2**.

NMR spectra (^1H, ^{13}C, ^{31}P, ^{51}V) were collected on a 400 MHz Bruker spectrometer and were referenced to residual solvent,[31] external phosphoric acid (^{31}P) or external $VOCl_3$ (^{51}V). EPR spectra were recorded with a Bruker EMX-080 spectrometer in solution at room temperature. Melting points were recorded using a MEL-TEMP apparatus. Infrared spectra (IR) were collected using a Perkin-Elmer FTIR spectrophotometer as KBr pellets. Magnetic susceptibility measurements were carried out using a Johnson Matthey magnetic susceptibility balance or analysis of solvent shift using a 400 MHz Bruker spectrometer.[32] Microanalyses were conducted by the Microanalytical Laboratory, School of Chemical Sciences, University of Illinois, Urbana−Champaign and Midwest Microlab. Electronic absorption spectra (UV−vis) were collected on an Agilent 8453 diode array spectrophotometer. Cyclic voltammograms were collected on a BAS CV-50W using a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode at scan rates of 25−100 mV s^{-1}. The electrolyte used was a 0.1 M solution of $(Bu_4N)(PF_6)$ in acetonitrile. The voltammograms were externally referenced to the ferrocene/ferrocenium couple.

$[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2PPh_2)]_2$, 3. An amount of 1.3783 g of **1**, $(CpP^{OEt}Co)VCl_2(DMF)$,[28] (1.887 mmol) was dissolved in 20 mL of H_2O. An amount of 0.4240 g of diphenylphosphinic acid (1.943 mmol) was mixed with 10 mL of H_2O. An amount of 0.2968 g of potassium carbonate was added to the diphenylphosphinic acid solution. The solution of diphenylphosphinic acid was transferred to the $(CpP^{OEt}Co)VCl_2(DMF)$ solution. A green solid immediately precipitated. The solution was allowed to dry by evaporation. The resulting solid was extracted into dichloromethane (∼ 10 mL) and gravity filtered. The dichloromethane solution was allowed to dry by evaporation. An amount of 0.9800 g (0.598 mmol, 61.6%) of light green solid, **3**, was isolated. Mp dec 178 °C. Anal. Calcd for $C_{58}H_{90}O_{24}Co_2P_8V_2$: C, 42.51; H, 5.54. Found: C, 42.20; H, 5.46. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}) 235 (60000), 333 (7000), 443 (37), 659 (33). ^1H NMR δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.2 (br), 1.7 (s), 3.7 (s), 4.5 (br), 4.7 (br), 5.2 (s). IR (cm^{-1}): 3490, 3056, 2978, 2363, 1498, 1387, 1037, 971, 935, 833, 726, 589. Mag. Suscept. μ_{eff} (μ_B): 0.969; $\chi_m = 3.97 \times 10^{-4}$ erg·G^{-2} mol^{-1} ($\chi_m T = 0.117$). Single crystals of this compound were additionally analyzed by X-ray diffraction.

$[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2PPhH)]_2$, 4. An amount of 0.202 g of phenylphosphinic acid (1.42 mmol) was mixed with 25 mL of H_2O. An amount of 0.243 g of potassium carbonate (1.76 mmol) was added to the phenylphosphinic acid mixture. The resulting solution was allowed to stir until no solid remained. An amount of 1.059 g (1.450 mmol) of **1**, $(CpP^{OEt}Co)VCl_2(DMF)$,[28] was added to the phenylphosphinic acid/potassium carbonate solution. A green solid

Table 1. Crystallographic Parameters for Complexes 3−5, 7, 9, 10

	3·2H_2O	4·2H_2O	5	7	9	10
empirical formula	$C_{58}H_{94}Co_2O_{26}P_8V_2$	$C_{46}H_{86}Co_2O_{26}P_8V_2$	$C_{92}H_{159}Co_4O_{52}P_{16}V_4$	$C_{46}H_{80}Co_2N_2O_{32}P_8V_2$	$C_{42}H_{90}Co_2O_{26}P_8V_2$	$C_{34}H_{84}Cl_2Co_2O_{27}P_6V_2$
moiety formula	$C_{58}H_{90}Co_2O_{24}P_8V_2$, 2($H_2O$)	$C_{46}H_{82}Co_2O_{24}P_8V_2$, 2($H_2O$)	2 ($C_{46}H_{82}Co_2O_{26}P_8V_2$)	$C_{46}H_{80}Co_2N_2O_{32}P_8V_2$	$C_{42}H_{90}Co_2O_{26}P_8V_2$	2($C_{17}H_{39}CoO_{12}P_3V$), 3(H_2O), 2(Cl)
formula weight	1674.83	1522.65	1518.11	1640.62	1478.64	1401.47
temperature, K	173(2)	100(2)	173(2)	93(2)	173(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$Pbca$	$P2_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	11.7238(7)	13.1414(6)	12.2986(12)	13.904(2)	11.9251(8)	11.8684(17)
b (Å)	11.8877(7)	15.3604(7)	25.4641(24)	16.653(3)	15.7419(10)	16.456(2)
c (Å)	15.2380(13)	32.0801(14)	20.5721(20)	15.653(3)	18.0135(12)	17.146(3)
α (deg)	96.2240(10)	90	90	90	90	116.304(3)
β (deg)	103.7480(10)	90	95.6840(15)	111.036(2)	109.224(1)	98.167(4)
γ (deg)	113.8880(10)	90	90	90	90	90.754(4)
V (Å^3)	1835.4(2)	6475.6(5)	6411(1)	3382.7(10)	3193.0(4)	2960.6(7)
Z	1	4	2	2	2	2
D_{calcd} (Mg m^{-3})	1.515	1.562	1.573	1.611	1.538	1.572
μ (mm^{-1})	0.941	1.058	1.068	1.026	1.066	1.186
F(000)	870	3160	3142	1692	1540	1456
final R indices [$I > 2\sigma(I)$]						
R_1[a]	0.0313	0.0644	0.0582	0.0410	0.0616	0.0349
wR_2[b]	0.0796	0.1817	0.1371	0.1025	0.1291	0.0916

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3$; X, Y = 0.0443, 1.6566 (**3**), 0.1299, 43.7854 (**4**), 0.0599, 14.0785 (**5**), 0.0556, 4.9967 (**7**), 0.0000, 17.8532 (**9**), 0.0570, 0.0000 (**10**).

immediately evolved. The solution was allowed to dry by evaporation. The resulting solid was extracted into about 10 mL acetone and gravity filtered. The acetone solution was allowed to dry by evaporation. An amount of 0.487 g (0.330 mmol, 46%) of dark green solid of **4** was isolated. MP, dec 140−150 °C. Anal. Calcd for $C_{46}H_{88}Co_2O_{24}P_8V_2$: C, 37.01; H, 5.94. Found: C, 36.23; H, 5.31. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}): 217 (42000), 242 (53000), 333 (6200), 448 (40), 672 (26), 798 (24). NMR δ_H(400 MHz; $CDCl_3$; Me_4Si): 0.8 (br) 1.2 (br), 1.8 (br), 4.5 (br), 4.7 (br), 7.3 (br). IR (cm^{-1}): 2980, 2930, 2905, 1637, 1478, 1438, 1388, 1202, 1131, 1061, 1037, 986, 962, 938, 834, 774, 762, 699, 603, 499, 461, 416 Mag. Suscept. μ_{eff} (μ_B): 2.63; χ_m = 2.89 × 10^{-3} erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.862). Single crystals of this compound were additionally analyzed by X-ray diffraction.

[(CpP^{OEt}Co)V(O)(μ-O_2P(OH)Ph)]$_2$, 5. An amount of 0.115 g of phenylphosphonic acid (0.727 mmol) was mixed with 10 mL of H_2O. An amount of 0.1378 g (0.9843 mmol) of potassium carbonate was added to the phenylphosphonic acid mixture. The resulting solution was allowed to stir until no solid remained. An amount of 0.513 g of **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] (0.703 mmol) was dissolved in 10 mL of H_2O. The resulting green clear solution was added to the phenylphosphonic acid/potassium carbonate solution. A tan solid immediately evolved. The solid was collected by suction filtration and washed with H_2O (3 × 5 mL). An amount of 0.4466 g (0.2941 mmol, 84%) was isolated. MP, dec 130 °C. Anal. Calcd for $C_{46}H_{82}Co_2O_{26}P_8V_2$: C, 36.38; H, 5.44. Found: C, 35.09; H, 5.84. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}): 333 (7500), 656 (30), 794 (23). NMR δ_H (400 MHz; $CDCl_3$; Me_4Si): 1.2 (br), 2.0 (br), 4.5 (br), 4.9 (br). IR (cm^{-1}): 3449, 2979, 2932, 2896, 1478, 1452, 1441, 1385, 1361, 1131, 1098, 1074, 1034, 1014, 974, 963, 938, 921, 830, 751, 721, 697. Mag. Suscept. μ_{eff} (μ_B): 1.23; χ_m = 0.00064 erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.19). Single crystals of this compound were additionally analyzed by X-ray diffraction.

{(CpP^{OEt}Co)V(O)[μ-O_2P(OH)(OPh)]}$_2$, 6. An amount of 0.303 g of **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] (0.415 mmol) was dissolved in 15 mL of H_2O. An amount of 0.1039 g (0.424 mmol) of of sodium phenylphosphate sesquihydrate was dissolved in 15 mL of H_2O. The phosphate solution was added to the (CpP^{OEt}Co)VCl_2(DMF) solution. A brown solid evolved after several seconds. The solution was allowed to stir for several minutes. The residue was collected by suction filtration and washed with H_2O (3 × 5 mL). The solid was dissolved in about 15 mL of acetone, gravity filtered, and allowed to dry. An amount of 0.1792 g (0.116 mmol, 56%) of **6** was isolated as a dark brown solid. MP, 109−111 °C. Anal. Calcd for $C_{46}H_{80}Co_2O_{28}P_8V_2$: C, 35.63; H, 5.33. Found: C, 35.49; H, 5.53. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}): 241 (56000), 334 (8800), 354 (45), 555 (27), 663 (22), 848 (18), 859 (17), 1033 (4). NMR δ_H (400 MHz; $CDCl_3$; Me_4Si): 0.5 (br), 1.2 (s), 4.4 (s, br), 4.55 (s, br), 4.8 (s), 6.7 (br), 7.0 (br). IR (cm-1): 3425, 3120, 2980, 2929, 2896, 1497, 1398, 1387, 1384, 1289, 1247, 1194, 1160, 1104, 1074, 1034, 975, 934, 830, 769, 732, 690, 609, 534. Mag. Suscept. μ_{eff} (μ_B): 2.62; χ_m = 0.0029 erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.86).

{(CpP^{OEt}Co)V(O)[μ-O_2P(OH)(OPh-4-NO_2)]}$_2$, 7. An amount of 0.501 g of **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] (0.686 mmol) was dissolved in 10 mL of H_2O. An amount of 0.3039 g of biscyclohexylammonium 4-nitrophenylphosphate (0.698 mmol) was mixed with 10 mL of H_2O. The (CpP^{OEt}Co)VCl_2(DMF) solution was added to the phosphate solution. The reaction was allowed to stir for several minutes, and the resulting brown solid was collected by suction filtration. An amount of 0.1096 g (0.0710 mmol, 21%) was isolated. MP, dec 100 °C. Anal. Calcd for $C_{46}H_{80}Co_2$ $N_2O_{32}P_8V_2$: C, 33.67; H, 4.91; N, 1.71. Found: C, 33.01; H, 4.99; N, 1.40. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}): 310 (9300), 457 (37), 664 (25), 857 (19), 1042 (7). NMR δ_H (400 MHz; $CDCl_3$; Me_4Si): 1.3 (s), 1.8 (br), 4.6 (br), 4.7 (br), 4.8 (br), 4.9 (sh), 8.0 (br). IR (cm^{-1}): 3449, 2981, 2346, 1342, 1265, 1110, 976, 940, 836, 756, 610. Mag. Suscept. μ_{eff} (μ_B): 2.503; χ_m = 0.002665 erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.784). Single crystals of this compound were additionally analyzed by X-ray diffraction.

{(CpP^{OEt}Co)V(O)[μ-O_2P(OH)CH_3]}$_2$, 8. An amount of 0.498 g of **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] (0.682 mmol) was dissolved in 15 mL of H_2O. An amount of 0.111 g (0.834 mmol) of potassium methylhydrogenphosphate salt was dissolved in 15 mL of H_2O. The (CpP^{OEt}Co)VCl_2(DMF) solution was added to the phosphate solution. The solution was allowed to stir for 24 h. The resulting solid was collected by suction filtration and washed with H_2O (3 × 5 mL). An amount of 0.1018 g (0.0731 mmol, 21%) was isolated. MP, dec 128 °C. Anal. Calcd for $C_{36}H_{78}Co_2O_{26}P_8V_2$: C, 31.01; H, 5.64. Found: C, 30.73; H, 5.45. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}): 333 (8000), 362 (47), 487 (36), 656 (28), 800 (21). NMR δ_H

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3−5, 7, 9

	3	4	5[a]	7	9
V═O	1.6005(14)	1.589(3)	1.582(4)	1.591(2)	1.585(3)
V---V	4.667	4.894	5.3455(13)	5.4481(11)	5.331
			5.2916(12)		
V−O_{trans}	2.2214(14)	2.209(3)	2.355(4)	2.295(2)	2.303(3)
V−$O_{P\mu}$	1.9982(13)	2.006(3)	1.988(4)	2.0163(19)	1.997(3)
	2.0122(13)	2.008(3)[b]	2.009(4)	2.036(2)	1.997(3)
V-OP_{Co}	2.0279(13)	2.024(3)	2.022(4)	2.0206(19)	2.303(3)
	2.0334(13)	2.019(2)	2.028(4)	2.0180(19)	2.038(3)
P---P	4.403	4.288	3.8906(19)	3.6711(14)	3.709
			3.8502(18)		
$V(OPO)_2V$ conformation	retracted chair	retracted chair	planar *cis*/*cis*-anti	planar *cis*/*cis*-anti	planar *cis*/*cis*-anti
space group	$P\bar{1}$	*Pbca*	$P2_1$	$P2_1/n$	$P2_1/c$

[a] Average values of 4 crystallographically unique sites. See Supporting Information, Table S2. [b] Main residue of a disordered structure.

(400 MHz; $CDCl_3$; Me_4Si): 1.2 (br), 5.0 (br). IR (cm^{-1}): 2980, 2346, 1106, 1075, 973, 939, 835, 771, 608. Mag. Suscept. μ_{eff} (μ_B): 1.67; χ_m = 0.0012 erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.35).

{(CpP^{OEt}Co)V(O)[μ-O_2P(OH)C(CH_3)]}$_2$, 9. An amount of 0.5059 g of **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] (0.6928 mmol) was dissolved in 10 mL of DMF. An amount of 0.152 g of potassium *tert*-butylphosphate (0.710 mmol) was dissolved in 10 mL of DMF. The solution of (CpP^{OEt}Co)VCl_2(DMF) was transferred to the butylphosphate solution. The resulting green solution turned brown after 20 min of stirring in air. The solution was allowed to stir for 24 h yielding a green solution with a green precipitate. The mixture was gravity filtered and reduced to dryness in vacuo. The resulting green solid was collected. An amount of 0.1895 g (0.128 mmol, 37%) of olive-green solid, **9**, was isolated. MP, dec 114 °C. Anal. Calcd for $C_{42}H_{90}Co_2O_{26}P_8V_2$: C, 34.11; H, 6.13. Found: C, 33.58; H, 6.11. UV−vis λ_{max} (CH_3CN)/nm (ε = M^{-1} cm^{-1}) 242 (53000), 333 (7200), 362 (43), 487 (33), 656 (26). NMR δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.5 (br), 1.9 (s), 2.4 (s), 2.5 (s), 4.9 (br), 8.0 (s). IR (cm^{-1}): 1654, 1113, 1039, 976, 940, 836, 774, 600. Mag. Suscept. μ_{eff} (μ_B): 1.30; χ_m = 7.16 × 10^{-4} erg·G^{-2} mol^{-1} ($\chi_m T$ = 0.212). Single crystals of this compound were additionally analyzed by X-ray diffraction.

X-ray Crystallography. Single crystals of **2** (ether), **3** (CH_2Cl_2/hexane), **4** (acetone), **5** (acetone/ether), **7** (hexane/toluene), and **9** (DMF) were grown by slow evaporation of a supersaturated solution in air. Crystallization attempts of **6** and **8** have, thus far, only afforded decomposition products with properties quite different than the bulk isolated material- most obviously the color and infrared spectra (see Supporting Information for further details). Single crystals of the oxidation product of (CpP^{OEt}Co)VCl_2(DMF), that is, [(CpP^{OEt}Co)(H_2O)$_2$OV]Cl·H_2O, **10**, were grown from slow evaporation of a moist acetone solution of **1** in air. Intensity data were collected at −173 °C on a Bruker SMART Apex diffractometer equipped with a CCD area detector using graphite monochromated Mo Kα radiation. Data were reduced and corrected for absorption using the SAINT+ Software Suite.[33] Structure solutions were obtained by direct methods and were refined on F^2 with the use of full-matrix least-squares techniques.[34] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined with a riding model. Selected crystallographic details for complexes **3**−**5**, **7**, and **9**−**10** are shown in Table 1. More extensive crystallographic details for complexes **2**−**5**, **7**, and **9**−**10** are included in the Supporting Information.

RESULTS AND DISCUSSION

Syntheses. These dimeric cluster syntheses were based on previously reported vanadium phosph(on)ate dimers and involve self-assembly reactions between compound **1**, (CpP^{OEt}Co)VCl_2(DMF),[28] and the appropriate phosph(on/in)ate salt in solution in air at ambient atmospheric conditions.[24] This synthesis was based on methods employed in our laboratory and others' involving related work with hydrotris(pyrazolyl)borate complexes.[35−38] Several serendipitously oxidized species were isolated during the course of our work with V(III) species[28] so we began to investigate the oxidized species more deliberately. Conception of this series began with the isolation of [(CpP^{OEt}Co)VCl]$_2$(μ-ox), **2a**,[30] where ox = oxalato, which was originally obtained by accidental air oxidation of a V(III) complex **2** analogue, namely, [(CpP^{OEt}Co)VCl]$_2$(μ-ox).[28] During synthesis of this analogue complex, crystals suitable for X-ray diffraction appeared serendipitously from rotary evaporation of wash ether portions yielding complex **2a**. Isolation of this species sparked an interest in the behavior of the V(IV) dimeric molecules. This dinuclear series was assumed to have more activity as an oxidation catalyst, owing to its similarity in oxidation state with the modeled solid state catalyst.

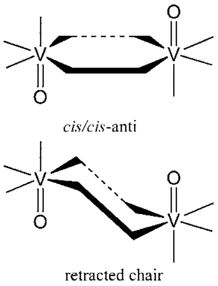
The synthesis of the series of complexes **3**−**9** was straightforward and involved the combination of a 1:1 molar mixture of **1**, (CpP^{OEt}Co)VCl_2(DMF), with the appropriate bridging ligand (as a salt) in DMF in aerobic conditions. The synthetic strategy is summarized in Scheme 1. The synthesis was presumed to involve a slow conversion of an initial V(III) species to the desired V(IV) molecule via air oxidation. Efforts to isolate the target molecules through use of a V(IV) starting material, namely, a nominal $VOCl_2$,[39] through an ion metathesis in aqueous media seem to be successful but tend to afford mixtures of products. Water was the solvent chosen for the syntheses of complexes **3**−**9** with the presumption that the products would be insoluble in water and would precipitate out of solution as formation occurred. The anticipated byproduct, chloride salts, are water-soluble and were easily removed via filtration.

As obvious from the synthetic procedures, the complexes all undergo oxidation in air to afford the V(IV) species from the starting compound **1**, a V(III) species. We have attempted to isolate the intermediate oxidized species without success, instead isolating complex **10** in the process. Presumably the bound water ligands and the waters of hydration were present in the acetone. The expected oxidation product of **1** was (CpP^{OEt}Co)VOCl(DMF); however, because of the known oxophilicity of vanadium,[40] the water present in the solvent preferentially bound to the vanadium and forced the chloride to exist as an unbound anion.

X-ray Crystallography. X-ray diffraction quality crystals of each complex were obtained by slow evaporation from saturated solution or vapor diffusion methods as described. Structural details for complex **2** are described in the Supporting

Information. For complexes **3**−**9**, the basic structures of the series of dimers are described below. Relevant crystallographic information is included in Table 1 and in the Supporting Information. Pertinent bond distances and angles are contained in Table 2. Each consists of a dimeric $V_2O_4P_2$ core. The bridging nature of the phosph(in/on)ate moieties allows for systematic classification of the $V(OPO)_2V$ core as first investigated and implemented by Carrano and co-workers.[23] While originally devised as a means to predict structural interactions with DNA binding, this classification system is ideal for our purposes of identifying structural frameworks and electronics. Although Carrano and co-workers have discussed a variety of theoretical and experimentally observed core shapes,[23] all of the dinuclear complexes under investigation here exhibit only one of two of the possible cyclic conformations. These conformations, known as the retracted chair and planar *cis/cis*-anti conformations are shown in Scheme 2.[23] One can imagine two isomers of some of the complexes but the only isolated structures examined by X-ray crystallography contain a quasi-inversion center, not the isomer containing an idealized mirror plane, although some disorder is noted in **4**. Some species have been resistant to crystallization efforts and one might imagine this is a result of the easily imagined mixture of isomer products. Yellow/orange crystals of a decomposition product, namely, $(CpP^{OEt}Co)_2Co$, could occasionally be isolated from the crystallization efforts as well.[41] Specific details on each structure are included below.

Scheme 2. Naming Scheme for Bridging Dimer Species



Structure of $(CpP^{OEt}Co)_2[\mu\text{-}O_2PPh_2]_2V_2O_2$, 3. Green plate-shaped single crystals suitable for X-ray diffraction were grown from a slow evaporation of a saturated acetone solution of **3**. Complex **3** crystallized in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit. As expected, the molecule exhibits a shortened bond between the metal center and the terminal oxo ligand and the bond oriented *trans* to the terminal oxo ligand is lengthened relative to the other vanadium−oxygen bonds. The molecule crystallized in a manner in which the cyclic core has adopted the retracted chair conformation.[23] The bridging phosphorus and oxygen atoms lie within a plane with the two vanadium atoms oriented above and below the plane. A displacement ellipsoid plot of complex **3** is shown in Figure 1. Selected bond distances and angles are shown in Table 2.

Structure of $(CpP^{OEt}Co)_2[\mu\text{-}O_2PPhH]_2V_2O_2$, 4. X-ray quality crystals were grown from a slow evaporation of a saturated acetone solution of **4**. Complex **4** crystallized in an orthorhombic cell in the space group *Pbca* with four molecules per asymmetric unit. All non-hydrogen atoms were refined anisotropically. A phosphorus atom as well as an oxygen atom within the bridging phosphinate moiety are disordered over two positions each with occupancies of 81.8% and 18.2% . The cyclic core of the molecule can be categorized as the retracted chair conformation.[23] A displacement ellipsoid plot of complex **4** is shown in Figure 2. Selected bond distances and angles are shown in Table 2.

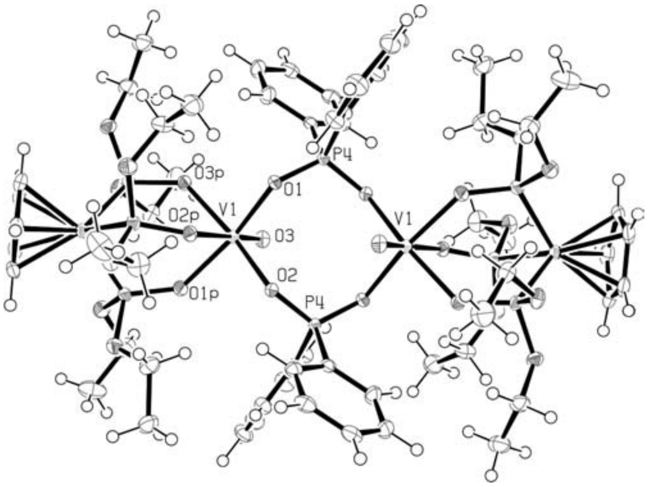


Figure 1. Displacement ellipsoid plot of $[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2PPh_2)]_2$, **3**. For this and all subsequent figures, displacement ellipsoids are shown at 50% and hydrogen atoms are shown as spheres of arbitrary size. ^{i}Symmetry code: −*x*, −*y*, −*z*.

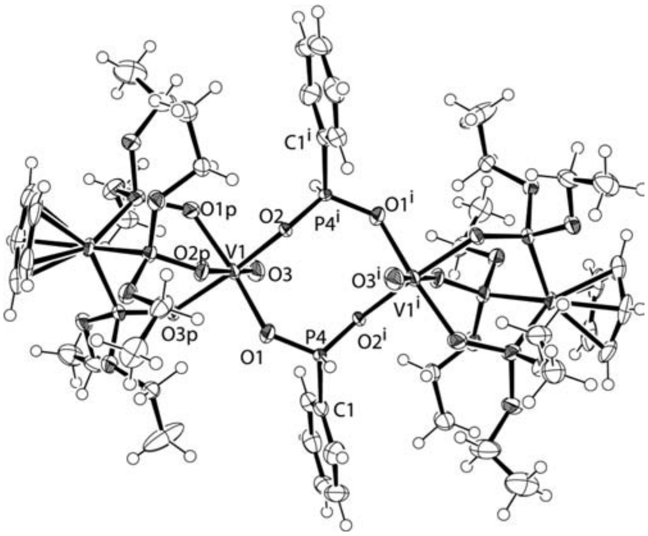


Figure 2. Displacement ellipsoid plot of $[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2PPhH)]_2$, **4**. ^{i}Symmetry code: −*x*, 1 − *y*, −*z*.

Structure of $(CpP^{OEt}Co)_2[\mu\text{-}O_2(OH)PPh]_2V_2O_2$, 5. Single X-ray quality crystals of complex **5** were grown from slow evaporation of a saturated ether/acetone solution of **5**. Despite the fact that complex **5** could ideally contain an inversion center, complex **5** crystallized in the space group $P2_1$ with two molecules in the asymmetric unit. This phenomenon is brought about by the asymmetry induced by the phenyl rings. In one molecule in the asymmetric unit, the rings lie in the same plane. In the other molecule, the rings lie at a canted angle, oriented approximately 90° out of plane. Solving the molecule centrosymmetrically gives an R_{int} of 28%. Both molecules, regardless of phenyl ring orientation exhibit the planar *cis/cis*-anti conformations among their cyclic cores. A displacement

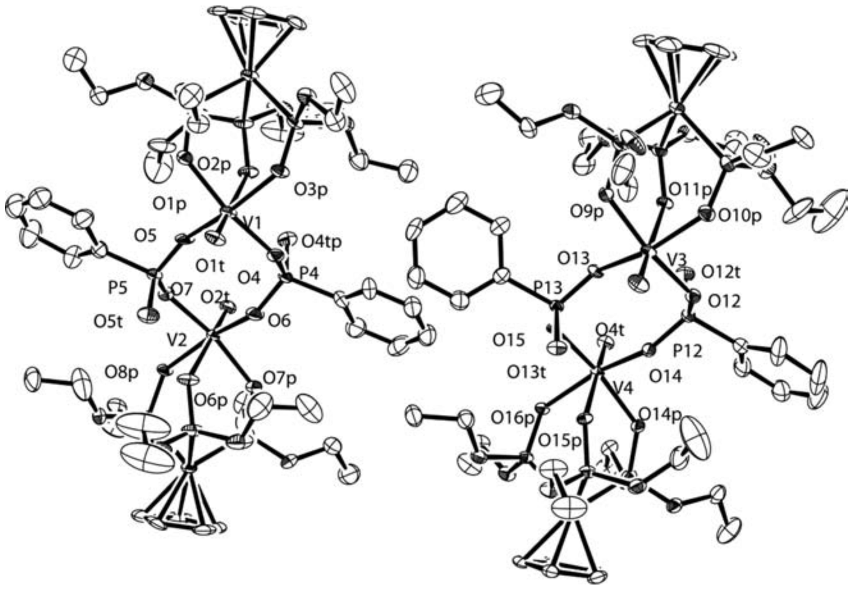


Figure 3. Displacement ellipsoid plot of $[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2P(OH)Ph)]_2$, 5. All H atoms have been removed for clarity.

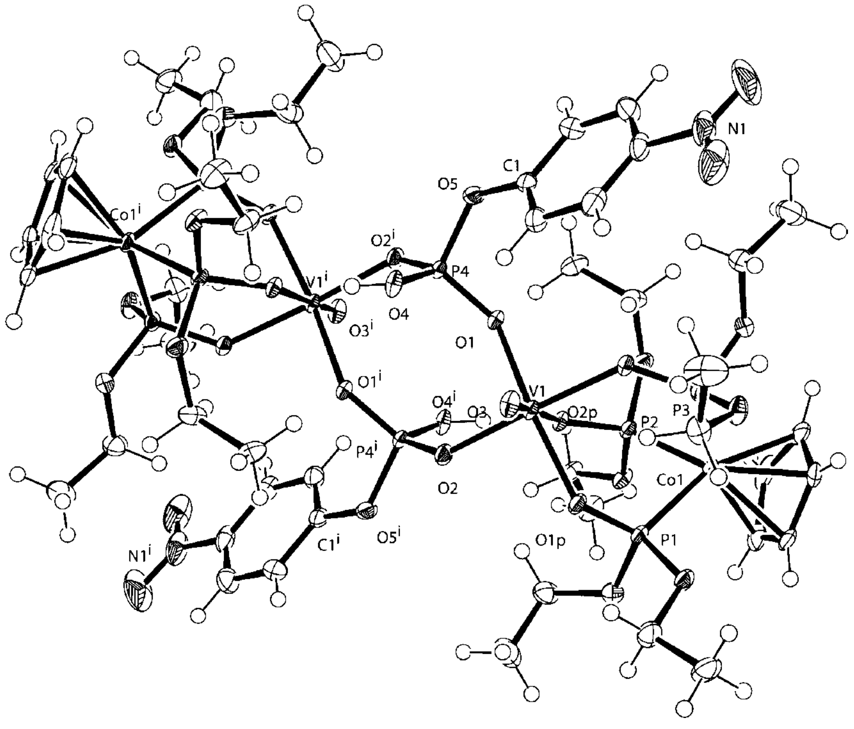


Figure 4. Displacement ellipsoid plot of $\{(CpP^{OEt}Co)V(O)[\mu\text{-}O_2P(OH)(OPh\text{-}4\text{-}NO_2)]\}_2$, 7. ^{i}Symmetry code: $-x$, $2 - y$, $-z$.

ellipsoid plot of 5 is shown in Figure 3. Selected bond distances and angles for 5 are shown in Table 2.

Structure of $(CpP^{OEt}Co)_2[\mu\text{-}O_2P(OH)(4\text{-}NO_2PhO)]_2V_2O_2$, 7. A single X-ray quality crystal was isolated from a slow evaporation of a saturated pentane/toluene solution of 7. Complex 7 crystallized in the monoclinic space group $P2_1/n$ with one molecule per asymmetric unit. The cyclic core of this molecule adopts the planar *cis*/*cis*-anti conformation. A displacement ellipsoid plot of 7 is shown in Figure 4. Selected bond distances and angles for 7 are shown in Table 2.

Crystallization Efforts of Structure of $(CpP^{OEt}Co)_2[\mu\text{-}O_2P(OH)CH_3]_2V_2O_2$, 8. Attempts to crystallize complex 8 yielded two types of crystals, but neither with properties matching the bulk material. Details on the isolated cluster species are reported in Supporting Information.

Structure of $(CpP^{OEt}Co)_2$ $[\mu\text{-}O_2P(OH)C(CH_3)_3]_2V_2O_2$, 9. Single crystals of 9 were isolated from a slow evaporation of a saturated acetone solution of 9. The molecule crystallized in the monoclinic space group $P2_1/c$ with two molecules per asymmetric unit. The central ring portion has adopted the planar *cis*/*cis*-anti conformation described by Carrano and co-workers.[23] This conformation has both metal centers and bridging oxygens oriented within the same plane. The phosphorus atoms lie above and below the plane created by the vanadium and oxygen atoms. A displacement ellipsoid plot

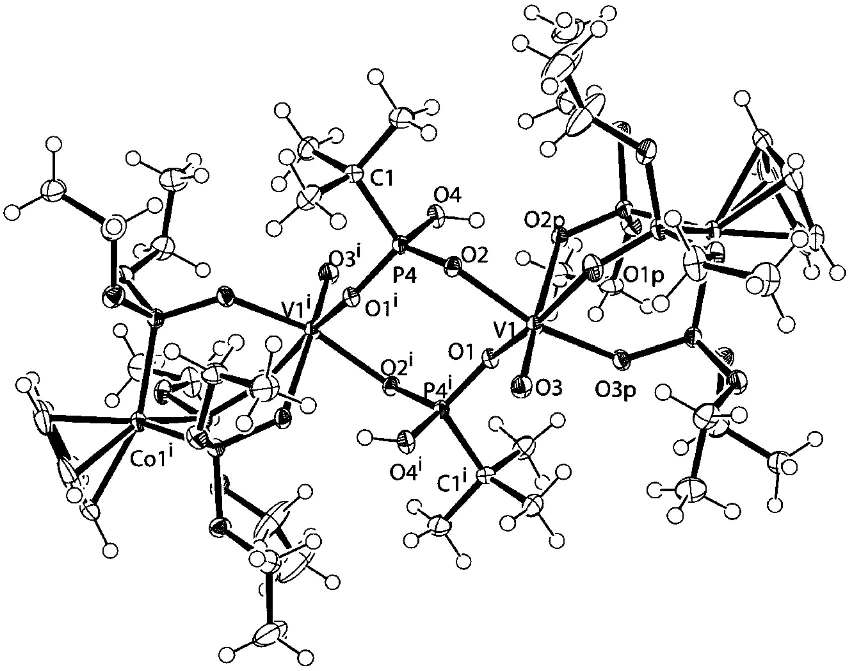


Figure 5. Displacement ellipsoid plot of $\{(\mathrm{CpP^{OEt}Co})\mathrm{V(O)}[\mu\text{-}\mathrm{O_2P(OH)}{}^t\mathrm{Bu}]\}_2$, **9**. ^{i}Symmetry code: $-x$, $2 - y$, $-z$.

of complex **9** is shown in Figure 5. Selected bond distances and angles are shown in Table 2.

Structure of $[(\mathrm{CpP^{OEt}Co})(\mathrm{H_2O})_2\mathrm{OV}]\mathrm{Cl}\cdot\mathrm{H_2O}$, 10. X-ray quality crystals of **10** were grown from acetone evaporation and were found to be non-merohedrally twinned. Complete details are found in the Supporting Information. A displacement ellipsoid plot of half of the asymmetric unit of **10** is shown in Figure 6 and Supporting Information, Figure S3.

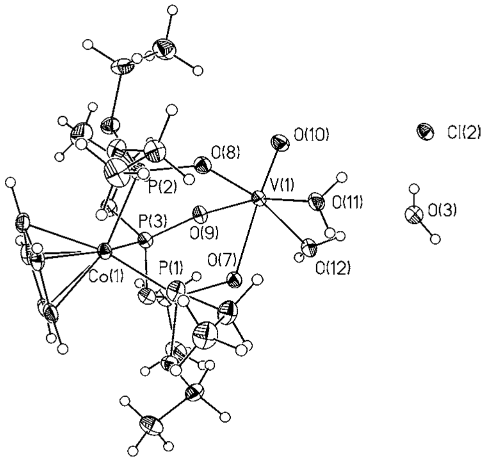


Figure 6. Displacement ellipsoid plot of $[(\mathrm{CpP^{OEt}Co})(\mathrm{H_2O})_2\mathrm{OV}]\text{-}\mathrm{Cl}\cdot\mathrm{H_2O}$, **10**.

Characterization. In addition to structural determination by X-ray crystallography, species were characterized using spectral methods, including UV−vis spectroscopy, infrared spectroscopy, magnetic resonance, as well as physical measurements including C, H, N analyses, magnetic measurements, melting point determination, and cyclic voltammetry. Ring conformation, magnetic susceptibility, infrared vanadyl vibrational stretches, and electronic absorbances are summarized in Table 3.

Infrared Spectroscopy (IR). IR spectra of the dimeric complexes display the expected peaks indicative of the V═O stretch[42] at approximately 975 cm^{-1} as a sharp shoulder peak to ligand absorbances at approximately 935 cm^{-1}.[11,21,43]

Electronic Absorption Spectroscopy (UV−vis). UV−vis spectra among the series indicate absorbances at approximately 333 nm with molar absorptivity values of approximately 8000 M^{-1} cm^{-1}. This is similar to the trend exhibited by an analogous tetrameric series that absorb at the same wavelength with twice the absorptivity.[44] Also, complex **7** experiences a hypsochromic shift to a λ_{max} of 310 nm, presumably from the electron withdrawing nature of the *p*-nitrophenyl substituent on the bridging phosphorus atoms. As would be expected for V(IV)-oxo species,[45] there also exist several much weaker absorbances ($\varepsilon < 40$ M^{-1} cm^{-1}) in the region from 400 to 1000 nm.

Elemental Analyses. Elemental analyses (C/H/N) were conducted on bulk samples via combustion analysis. The results are largely satisfactory for H and N, but shown the reduced carbon percentage commonly seen in combusting vanadium-containing species owing to the facile formation of vanadium carbide upon combustion.[46] Examination of the V/P contents via EDAX-equipped SEM supports the proposed compositions.

Nuclear Magnetic Resonance Spectroscopy (NMR). ^{1}H NMR spectra display a mixture of broadened and sharp peaks. The broadening can be attributed to the paramagnetic nature of the vanadium metal centers (vide infra).[47] Although peak broadening renders the spectra of no practical value for structural diagnostics, similarities in spectra among the series suggest the formation of the target molecules as all molecules in the series share a structural framework. All spectra exhibit broad peak sets between 0.5 and 2.0 ppm and between 4.0 and 5.0 ppm. These shifts likely arise from methyl and methylene portions of the phosphite functionalities on the ligand. Molecules with phosphate bridges that contain aromatic moieties exhibit broadened peaks within the expected region of 6.5 to 7.5 ppm.

Table 3. Summary of Pertinent Characterization Data for Complexes **3**−**9**

	3	**4**	**5**	**6**	**7**	**8**	**9**
$V(OPO)_2V$ conformation	retracted chair	retracted chair	planar *cis*/*cis*-anti	[a]	planar *cis*/*cis*-anti	[a]	planar *cis*/*cis*-anti
magnetic moment (μ_B)	0.969	2.62	1.23	2.62	2.50	1.67	1.30
V═O stretch (cm^{-1})	971	986	974	975	976	973	976
UV−vis λ_{max}	235, 333, 443, 659	242, 333, 448, 672, 798	333, 656, 794	334, 354, 555, 663, 848, 859, 1033	310, 457, 664, 857, 1042	333, 362 487, 656, 800	242, 333, 362, 487, 656
1st $E_{1/2}$[b]	660	800	520	1090[c]	1130[c]	650	690
2nd $E_{1/2}$[b]	990	1140	940	1470[c]	1550[c]	1010	1120

[a] Not collected. [b] vs Ag/AgCl. Potentials are quasi-reversible, see text and Supporting Information, Table S10. [c] Irreversible, E_{pa}.

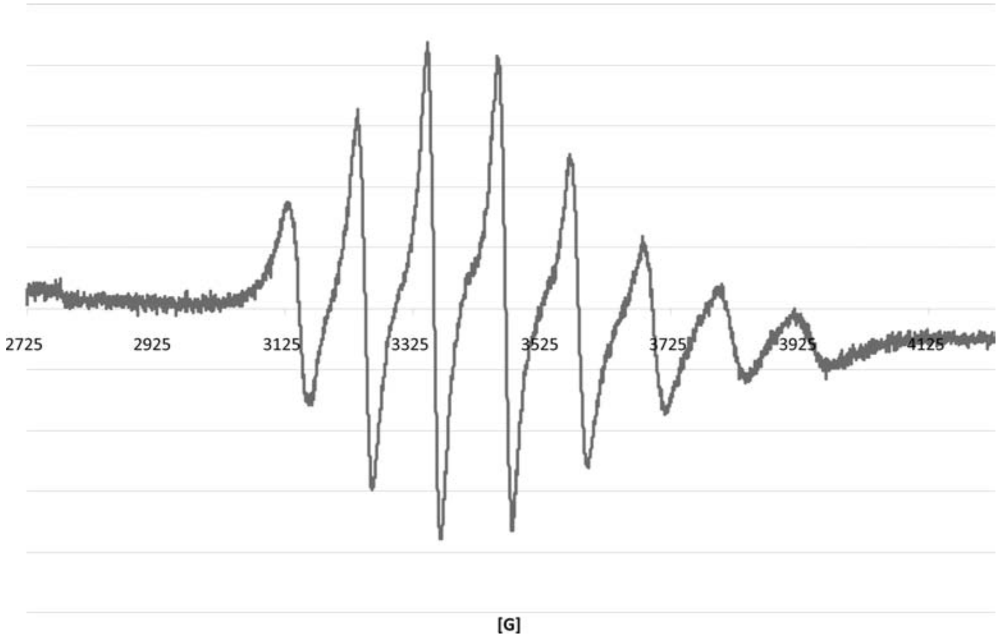


Figure 7. EPR spectrum of $[(CpP^{OEt}Co)V(O)(\mu\text{-}O_2PPh_2)]_2$, **3**, collected at 298 K in CH_2Cl_2. This spectrum is typical for **3**, **5**−**9**.

Electron Paramagnetic Resonance Spectroscopy (EPR). Whereas the unpaired electron found on the metal centers of these molecules complicates nuclear magnetic resonance, the unpaired electron can be analyzed using EPR techniques. EPR measurements were performed on all dimeric cluster molecules at ambient temperatures in dichloromethane. EPR spectra for complexes **3** and **5**−**9** showed eight line spectra consistent with the coupling of the single unpaired electron of V(IV) with the 7/2 spin value of the ^{51}V nucleus. All complexes demonstrated a broadening of signal at higher field ends of spectra, which can be explained by the quadrupolar nature of the vanadium nucleus. The appearance of the expected eight line signal suggests independent unpaired electrons in similar chemical environments. Strong antiferromagnetic coupling would yield a ground state of zero spin, causing EPR measurements to be silent. Conversely, strong ferromagnetic coupling would yield a ground state of $S = 1$, also causing EPR measurements to be silent.[48] If the dimers contained a mixture of oxidation states, that is, a V(IV)/V(V) species, we would expect to see a 15 line spectrum.[48] The obtained spectra suggest systems with little to no exchange through the organophosphorus bridges at ambient temperatures. The EPR spectrum for complex **3** is typical for the series and is shown in Figure 7.

Magnetic Measurements. Magnetic susceptibility measurements among the series produced mixed results at room temperature, with magnetic moments ranging between 0.969 and 2.62 μ_B (Table 3). Not all values were clearly indicative of independent, uncoupled vanadium(IV) centers in the dimers[49] but all measurements further suggest the isolation of paramagnetic species. Trends in deviation from predicted spin-only values do not correlate with the V···V distances in isolated X-ray structures. A diamagnetic impurity, namely, a V(V) species, cannot be completely ruled out, but there is strong evidence against either a V(IV)/V(V) mixed species and a V(V)/V(V) species. Cyclic voltammetry studies do not seem to indicate the presence of other redox-active species, a V(V) species is not observed in any of the ^{51}V NMR spectra, which are all silent, and the EPR spectra do not display the 15 line spectrum we would expect for a mixed valence species. The interesting magnetic properties and electrochemical properties of these dimers have led us to initiate investigations utilizing solid-state NMR and variable-temperature SQUID techniques. On the basis of preliminary SQUID results, we have concluded that these systems are much more complex than a simple antiferromagnetically coupled system. These studies are currently underway with collaborators and will be reported elsewhere.[50]

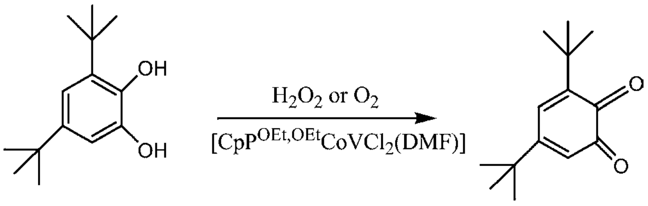
Electrochemical Properties. The electrochemical behavior of complexes **3**−**9** was investigated using cyclic voltammetry and differential pulse voltammetry. Results are summarized in

Table 3 and Supporting Information, Table S10 and shown in Supporting Information, Figure S6. Electrochemical studies show two unique, quasi-reversible oxidation events for most of the dimers. For example, complex **3** shows two quasi-reversible oxidations with $E_{1/2}$ values of 0.67 and 0.99 V vs Ag/Ag^{+}. The two vanadium centers are believed to be in identical environments (vide supra) so it is believed that the two peaks most likely correspond to the one electron oxidation of one metal center in the dinuclear species (namely V(IV)/V(IV) to V(IV)/V(V)) followed by the subsequent oxidation of the second vanadium center (i.e., V(IV)/V(V) to V(V)/V(V)). A similar outcome has been reported for a hydrotrispyrazolylborate (Tp^{-}) analogue to **4**.[51] Attempts to correlate the trends across several stereoelectronic parameters (Hammett/Taft σ, Kabachnik's σ, Tolman's χ, QALE)[52−54] show no obvious correlation with the observed electrochemistry oxidations. Nor do the values correlate with the V···V or P···P distances in the isolated solid-state structures. Such an observation is also noted in a similar dimer series with $[CpP^{OMe}Co]^{-}$ as the ligand, but the two series *do* correlate in their effect.[55] The lack of a bridging ligand effect would lead one to believe that the electrochemical behavior is dominated by the $[(CpP^{OEt}Co)VO]$ portion of these species.

Bond Valence Sum Analysis. The oxidation state assignments in complexes **2**−**5**, **7**, and **10** were confirmed through bond valence sum (BVS) analysis. The values used for these calculations were obtained from the bond distance tables reported here as well as published R_o values.[56−59] The results of these calculations are shown in Supporting Information, Tables S3−S9. All the BVS data support the assignment of the suspected oxidation states, namely, V(4+) for the metal centers and a nominal P(+5). We also used BVS to infer the presence of a proton on the bridging phosph(on)ates in complexes **4**, **5**, **7**, and **9** (vide supra).[60]

Catechol Catalysis. $(CpP^{OEt}Co)VCl_2(DMF)$ and several vanadium(IV) $CpP^{OEt}Co$ complexes have previously been shown to be effective catalysts in the oxidation of 3,5-di-*tert*-butylcatechol to the corresponding quinone (Scheme 3).[11,28,61]

Scheme 3. Oxidation of 3,5-Di-*tert*-butylcatechol



To examine the catalytic activity of our complexes, the formation of quinone was monitored through the use of UV−vis spectroscopy and gas chromatography. A gas chromatograph with an FID was used to quantitate the formation of quinone; pentadecane was used as the internal standard. The catalytic reactions consisted of 1 equiv of catechol, 2 equiv of hydrogen peroxide, and 1.5% catalyst in 20 mL of THF. Preliminary catalytic results show only weakly positive results for dimer in our hands for the oxidation of catechol. Likely the steric bulk of the dimer does not allow an open coordination site needed for catalysis. A space-filling diagram from the X-ray structure of complex **7** is shown in the Supporting Information, Figure S5. In contrast, our monomer complex, **1**, is known to be mildly effective as a precatalyst under the same conditions.[28] Catalytic efforts with less bulky substituents are underway.

■ CONCLUSION

A series of $CpP^{OEt}CoV{=}O$ dimers described above has been structurally and spectroscopically characterized. As model complexes for the oxidation catalyst $VOPO_4$, the series of $CpP^{OEt}Co$ dimers serve as effective structural models owing to the VO_6 octahedron rather than the VO_3N_3 octahedron in the Tp analogue. Much remains to be done in generating a functional model. Structural and spectroscopic investigations of the dimer series may elucidate electronic behavior and the effects of structure differences on coupling patterns.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Electrochemistry details, BVS data, and X-ray crystallographic data for **2**, **3**, **4**, **5**, **7**, **9**, **10** (CIF) and details on the treatment of the twinning of **10**. Structural details for $K_4\{[(CpP^{OEt}Co)VO]_2[\mu\text{-}O_2P(O)CH_3]\}_2(VO)_4[\mu_3\text{-}O_2P(O)CH_3]_4(\mu\text{-}OH)_4$, **8a**, and $K_6\{[(CpP^{OEt}Co)VO]_3[\mu_3\text{-}O_3PCH_3](\mu_3\text{-}O_3PCH_3)_3\}_2[(VO)_6(\mu\text{-}OH)_6)](\mu_3\text{-}O_3PCH_3)\cdot 6H_2O$, **8b**, are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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