of the metal halides tried even at room temperature while $Hg(CF_3)_2$ usually requires elevated temperatures.

Bis(trifluorosilyl)mercury will undergo a ligand-exchange reaction at room temperature when reacted with group 4 and 5A metal halides such as germanium tetraiodide and arsenic triiodide.[18] The mercurial product is especially reactive toward low-valent, late-transition-metal complexes such as $PdBr_2(PMe_3)_2$ which will react rapidly at 0 °C to give $Pd(SiF_3)_2(PMe_3)_2$. This is especially exciting since the only other known route to a metal trifluorosilyl, besides the metal vapor technique, involves the reaction of SiF_3H or SiF_3I with a binuclear metal carbonyl. This reaction is extremely limited, requires high temperatures, and gives rise to a product containing only one trifluorosilyl group.[2,3]

Trifluorosilyl complexes prepared by using main-group metals were much less stable than their corresponding trifluoromethyl analogues. For example, $Te(CF_3)_2$ and $Bi(CF_3)_3$ are thermally quite stable at room temperature while $Te(SiF_3)_2$ and $Bi(SiF_3)_3$ decompose well below room temperature. In contrast, a very different trend may be observed for the transition metals since the silicon d orbitals can interact with filled metal d orbitals. For example, the trifluorosilyl nickel arene complex $(\eta^6\text{-toluene})Ni(SiF_3)_2$ is stable at room temperature while $(\eta^6\text{-toluene})Ni(CF_3)_2$ decomposes moderately fast at room temperature.[19] Unusually stable metal alkyls incorporating metals such as tungsten, tantalum, and uranium, just to mention a few, may result upon cocondensing these metals with trifluorosilyl radicals.

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Syntheses, Kinetics, and Mechanism of Ligand Substitution Reactions of 17-Electron Cyclopentadienyl and Pentadienyl Vanadium Carbonyl Complexes

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Abstract: Reported are the syntheses of bis(η^5-pentadienyl)vanadium carbonyls and corresponding triethylphosphine compounds. The CO substitution lability in the complexes $(\eta^5\text{-L})_2VCO$ (L = C_5H_5, C_5Me_5, C_5H_7, 2,4-C_7H_{11}) was investigated. The exchange reaction of $(\eta^5\text{-}C_5H_5)_2V^{13}CO$ or of $(\eta^5\text{-}C_5Me_5)_2V^{13}CO$ with CO is first-order in both CO and metal complex: for L = C_5Me_5, kinetic parameters in toluene are $\Delta H_2^\ddagger = 8.9 \pm 0.7$ kcal/mol, $\Delta S_2^\ddagger = -21 \pm 3$ cal/(mol K), and k_2 (0.0 °C) = 12.7 (±0.1) $M^{-1}\,s^{-1}$. The rate of CO addition to the 15-electron complex $Cp^*{}_2V$ is slower than the CO exchange rate for $Cp^*{}_2VCO$: $\Delta H^\ddagger = 6.3 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -37 \pm 4$ cal/(mol K), and k (0.0 °C, toluene) = 0.424 ± 0.005 $M^{-1}\,s^{-1}$. The vanadium carbonyl complexes containing one or two pentadienyl ligands react 10^3–10^4 times slower than the bis(cyclopentadienyl) complexes, and the CO exchange rates depend only slightly on CO concentration. The electronic and steric features in these complexes, which allow for associative reactions for $(\eta^5\text{-}C_5H_5)_2VCO$ and $(\eta^5\text{-}C_5Me_5)_2VCO$ but prohibit this pathway for the pentadienyl complexes, are discussed.

The reactivity of 17-electron organometallic complexes is of interest in view of the role of metal radicals as intermediates in catalytic, photochemical, and electrochemical reactions.[1-3] Kinetic studies have established associative mechanisms for ligand substitution in the 17-electron complexes $V(CO)_6$,[4] $Mn(CO)_5$,[5] $Mn(CO)_3(PR_3)_2$,[6] $Re(CO)_5$,[7] $[Cp'Mn(CO)_2L]^+$,[8] and $[Fe(CO)_3(PR_3)_2]^+$,[9] and associative mechanisms have also been implicated for $CpMo(CO)_3$,[10] $CpW(CO)_3$,[11] $[(py)W(CO)_5]^+$,[12] and $[(\eta^6\text{-}C_6Me_6)W(CO)_3]^+$.[13] The rapid rates of associative ligand substitution in these complexes compared to analogous 18-electron complexes have been attributed to the lower energy barrier for formation of a 19-electron transition state or intermediate from a 17-electron species, compared to the higher energy barrier for formation of a 20-electron species.

Dissociative mechanisms for CO substitution in 17-electron complexes are far less common. A dissociative mechanism was originally proposed to account for the reactivity of $Mn(CO)_5$ and, in analogy, other species such as $Co(CO)_4$ involved in radical chain processes.[14,15] Subsequent quantitative evidence for associative CO substitution in $Mn(CO)_5$ has led to speculation that CO

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dissociation from 17-electron species may not be as facile as was originally believed.[5,16]

In addition to $V(CO)_6$ and its derivatives, a number of stable 17-electron vanadium complexes may be formed by ligand addition to vanadocene and its ring-substituted derivatives. Of particular interest in this work are the 17-electron derivatives formed by addition of a π-acid ligand such as CO, acetylene, or olefin to Cp_2V.[17-24] Although Cp_2V binds π-acid ligands, it fails to react with more basic ligands such as phosphines and phosphites.

The chemistry of 17-electron pentadienyl analogues of these complexes has been largely unexplored. In addition to carbonyl derivatives, the phosphine and phosphite complexes $(pd)_2V(PR_3)$ and $Cp(pd)V(PR)_3$ (pd or pd′ = η^5-pentadienyl or η^5-2,4-dimethylpentadienyl) are known,[25,26] which suggests that the electronic effects of the pentadienyl ligand differ from cyclopentadienyl.

In previous communications, we noted that Cp_2*VCO undergoes rapid CO substitution with $MeO_2CC\equiv CCO_2Me$ and CO by an associative mechanism, whereas pd_2VCO undergoes CO exchange at slower rates that depend only slightly on CO concentration.[27,28] Recent theoretical and EPR studies,[29] and the kinetic studies reported in this work, have allowed us to characterize the different mechanisms of CO substitution for these and related 17-electron complexes.

Experimental Section

General Procedures. The vanadocene derivatives used in this work are air-sensitive and often pyrophoric. Solids were stored and manipulated in a Vacuum Atmospheres glovebox under N_2. Solutions were manipulated on a high vacuum line or on a Schlenk line under an atmosphere of N_2, Ar, or CO, which had been passed through an oxygen scavenger (Ridox or MnO/silica at 100 °C). Toluene, hexane, pentane, methylcyclohexane, ether, THF, and decalin were predried, saturated with N_2, and distilled from Na or Na/benzophenone before use. Solvents used for Cp_2V, Cp_2*V, and their derivatives were further degassed by three freeze–pump–thaw cycles and saturated with N_2. The ^{13}CO was obtained from Monsanto Research Corp. (Mound Facility) and contained <1% ^{12}CO and ~11% $^{12}C^{18}O$. Other compounds were purchased (from Strem or Aldrich) and dried or purified by conventional methods. Solution IR spectra were recorded in septum-sealed, N_2-purged CaF_2 or NaCl cells on a Nicolet FTIR or Perkin-Elmer 283 infrared spectrophotometer. Constant temperatures for kinetic studies were maintained with a Neslab RTE-8 refrigerated circulating bath or a Haake Model F circulator. Solutions for ligand substitution studies were kept in the dark.

Bis(η^5-cyclopentadienyl)vanadium(II). The synthesis described is derived from literature procedures.[30,31] A $VCl_3\cdot 3THF$ solvate, formed by refluxing VCl_3 (3.00 g, 19.1 mmol) in THF (40 mL) for 4 h, was reduced with Zn dust (2.9 g, 14.7 mmol) to form a green slurry containing $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$.[32] A slurry of NaC_5H_5 (3.38 g, 38.4 mmol) in THF (50 mL) was added dropwise; the reaction mixture was refluxed 4 h and stirred at 25 °C for 8 h. The volume was reduced to 50 mL, and the dark purple mixture was filtered through a THF-saturated column of Celite (3 in.) using 2 × 20 mL portions of THF. After removal of solvent from the filtrate, the dark purple solid was taken up in 3 × 20 mL hexane and filtered to remove insoluble impurities. Hexane was removed under vacuum, and the resulting solid Cp_2V was sublimed (80 °C, 0.01 mm) or recrystallized from cold (−20 °C) pentane, to yield dark violet crystals of Cp_2V. Yield: 50% after recrystallization. The melting point (167 °C),[31] mass spectrum (70 eV, parent ion at m/e 181)[33] and IR spectrum[34] (Nujol) agree with literature data. Visible spectral data (λ (ϵ_{max})): 408 (36.2), 494 (27.5), 577 nm (36.2 M^{-1} cm^{-1}).

Bis(η^5-pentamethylcyclopentadienyl)vanadium(II). The synthesis of Cp_2*V is described in the literature;[35,36] the modified procedure used to prepare Cp_2V (above) was adapted in this work, except LiC_5Me_5 was used instead of NaC_5H_5. The resulting red-violet Cp_2*V may be sublimed (110 °C, 0.01 mm) or recrystallized from cold (−78 °C) pentane. Yield: 65%. The melting point (300 °C), mass spectrum, (70 eV, parent ion at m/e 321), infrared spectrum (Nujol), and UV–vis spectrum agree with literature results.[36]

Carbonylbis(η^5-cyclopentadienyl)vanadium(II) and Carbonylbis(η^5-pentamethylcyclopentadienyl)vanadium(II). The complexes Cp_2VCO and Cp_2*VCO have been described in the literature[17,35] and form readily on passing a stream of CO over a stirred hexane solution of Cp_2V or Cp_2*V. The color changes to deep green within 3 min for Cp_2V + CO and within 20 min for Cp_2*V + CO. The complexes were crystallized by slowly cooling (to −20 °C) a saturated hexane solution under a CO atmosphere and were isolated by filtration. The carbonyl complexes are soluble in hexane, and additional crystals may be obtained after concentrating the filtrate, saturating with CO, and cooling. Sublimation results in partial CO loss to give mixtures of the vanadocene precursor and the carbonyl complex. Yields after recrystallization: 79% for Cp_2VCO and 90% for Cp_2*VCO. IR of Cp_2VCO (cm^{-1}): ν_{CO} at 1890 (Nujol), 1882 (toluene); other bands (Nujol) 1105 (w); 1009 (m), 788 (s). IR of Cp_2*VCO (cm^{-1}); ν_{CO} at 1852 (Nujol), 1842 (toluene); other bands (Nujol 1060–1100 (mult w), 1020 (m), 800 (s). Visible spectral data (λ (ϵ_{max})) for Cp_2VCO: 550 (50.8), 720 nm (19.1 M^{-1} cm^{-1}). For Cp_2*VCO: 530 nm (41.4 M^{-1} cm^{-1}). EPR data (toluene, 24 °C): for Cp_2VCO, $g = 2.005 \pm 0.002$, $a_V = 2.87 \pm 0.02$ mT, a_C (^{13}CO-labeled complex) $= 1.00 \pm 0.02$ mT; for $Cp*_2VCO$, $g = 2.004 \pm 0.002$, $a_V = 1.86 \pm 0.02$ mT, $a_C = 1.14 \pm 0.02$ mT.

(Triethylphosphine)(cyclopentadienyl)pentadienylvanadium(II), $(C_5H_5)(C_5H_7)V(PEt_3)$. This compound was synthesized by dissolving $(C_5H_5)VCl_2(PEt_3)_2$[37] (0.50 g, 1.2 mmol) in 40 mL of THF under nitrogen. The addition of 0.0386 g of Zn dust (0.590 mmol) this blue solution, along with 2 h of refluxing, produced a purple solution of $[(C_5H_5)VCl(PEt_3)]_2$. After this solution was cooled to −78 °C, 0.15 g (1.4 mmol) of $K(C_5H_7)$ dissolved in 40 mL of THF was added dropwise with stirring. The mixture was slowly warmed to room temperature and stirred overnight to give a golden brown solution. After the solvent was removed in vacuo, the product was extracted with five 20-mL portions of hexane. The combined golden extracts were filtered under nitrogen and the solution volume reduced in vacuo to approximately 40 mL. Very air-sensitive golden green crystals were isolated by cooling to −90 °C, yield 0.34 g (ca. 96%). Purification of the product (mp/129–131 °C) was achieved by either sublimation in vacuo (ca. 50 °C) or recrystallization from hexane at −90 °C. This compound was also synthesized in an alternative fashion by dissolving 0.50 g (1.2 mmol) of $(C_5H_5)VCl_2(PEt_3)_2$ in 40 mL of THF and cooling to −78 °C. A solution of 0.28 g (2.6 mmol) of

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$K(C_5H_7)$[38] dissolved in 40 mL of THF was added dropwise to this solution. After the addition was complete, the mixture was slowly warmed to room temperature and stirred overnight. Workup was carried out as before, yielding 0.25 g of product (ca. 70%). Complete infrared data (Nujol mull): 3109 (mw), 3094 (w), 3039 (ms), 3004 (sh), 1425 (ms), 1376 (sh), 1255 (m), 1212 (m), 1114 (m), 1092 (m), 1033 (s), 1024 (ms), 1013 (ms), 999 (m), 983 (ms), 954 (m), 916 (m), 898 (mw), 863 (w), 842 (s), 834 (s), 798 (vs), 776 (mw), 752 (s), 723 (w), 698 (s), 634 (m), 614 (ms) cm^{-1}. Mass spectrum: *m/e* (relative intensity): 39 (37), 40 (13), 41 (40), 43 (13), 45 (13), 47 (11), 49 (59), 51 (19), 53 (14), 55 (19), 57 (24), 59 (28), 61 (60), 62 (100), 65 (12), 66 (23), 67 (31), 68 (13), 75 (14), 84 (35), 86 (24), 90 (70), 103 (18), 116 (10), 118 (33), 181 (11). Magnetic susceptibility (Evans method, THF): 1.7 μ_B. EPR data (toluene, 23 °C): $>$ = 1.981 ± 0.001, a_V = 6.87 ± 0.03 mT, a_p = 2.65 ± 0.03 mT. Anal. Calcd for $C_{16}H_{27}PV$: C, 63.78; H, 9.03. Found: C, 63.81; H, 9.19.

(Triethylphosphine)(cyclopentadienyl)(2,4-dimethylpentadienyl)vanadium(II), $(C_5H_5)(2,4\text{-}C_7H_{11})V(PEt_3)$. This compound was synthesized in manners analogous to those used for the $(C_5H_5)(C_5H_7)V(PEt_3)$ complex. In one route 1.00 g (2.36 mmol) of $(C_5H_5)VCl_2(PEt_3)_2$[37] dissolved in 50 mL of THF was refluxed for 2 h with 0.0787 g (1.20 mmol) of Zn dust. The purple solution was cooled to −78 °C, and 3.38 g (2.8 mmol) of $K(2,4\text{-}C_7H_{11})$[38] in 40 mL of THF was added dropwise with stirring. After the addition was complete, the mixture was slowly warmed to room temperature and was then stirred overnight to give a golden brown solution. Workup followed in an entirely analogous fashion as before, yielding 0.72 g (ca. 92%). Alternatively, 0.50 g (1.2 mmol) of $(C_5H_5)VCl_2(PEt_3)_2$ was dissolved in 40 mL of THF and cooled to −78 °C. To this solution was added dropwise 0.35 g (2.6 mmol) of $K(2,4\text{-}C_7H_{11})$ in 40 mL of THF. Workup was carried out as before, yielding 0.37 g of product (ca. 95%). The very air-sensitive golden crystals (mp 151–154 °C) were purified by either sublimation in vacuo (ca. 70 °C) or recrystallization from hexane at −90 °C. Complete infrared data (Nujol mull): 3050 (sh), 3040 (w), 1430 (ms), 1253 (m), 1117 (m), 1025 (s), 1007 (ms), 998 (ms), 905 (ms), 865 (ms), 853 (s), 837 (ms), 794 (vs), 748 (vs), 713 (w), 691 (s), 638 (m), 614 (s) cm^{-1}. Mass spectrum: *m/e* (relative intensity) 39 (13), 41 (21), 51 (20), 55 (16), 57 (19), 59 (24), 61 (55), 62 (100), 75 (13), 79 (12), 81 (13), 90 (71), 103 (16), 116 (88), 118 (37), 181 (16), 207 (26), 209 (58), 211 (21). Magnetic susceptibility (Evans method, THF): 1.6 μ_B. EPR data (toluene, 23 °C): g = 1.981 ± 0.001, a_V = 6.72 ± 0.03 mT, a_p = 2.66 ± 0.03 mT. Anal. Calcd for $C_{18}H_{31}PV$: C, 65.64; H, 9.49. Found: C, 65.70; H, 9.58.

Carbonyl(cyclopentadienyl)(pentadienyl)vanadium(II), $(C_5H_5)(C_5H_7)VCO$. A variable quantity of $(C_5H_5)(C_5H_7)V(PEt_3)$ dissolved in hexane was exposed to an excess of gaseous CO. A rapid change in color from golden to green occurred, indicating the formation of the product. The very air-sensitive solution was filtered under nitrogen and the volume reduced in vacuo. The product (mp 161–165 °C) was purified by either sublimation in vacuo (ca. 30 °C) or recrystallization from hexane at −90 °C, yielding dark green crystals. Complete infrared data (Nujol mull): 3049 (sh), 1937 (vs), 1894 (vw), 1259 (mw), 1217 (m), 1113 (vw), 1092 (ms), 1059 (w), 1013 (s), 1004 (s), 978 (m), 956 (mw), 925 (ms), 910 (w), 894 (w), 863 (s), 850 (s), 796 (vs), 758 (m) cm^{-1}. Mass spectrum: *m/e* (relative intensity) 39 (30), 40 (11), 41 (25), 49 (42), 51 (23), 53 (10), 65 (13), 66 (18), 67 (21), 68 (11), 84 (26), 86 (15), 90 (19), 105 (14), 116 (66), 181 (100), 182 (12), 183 (19), 211 (6). Magnetic susceptibility (Evans method, THF): 1.7 μ_B. EPR data (toluene, 23 °C): g = 1.991 ± 0.001, a_V = 6.28 ± 0.03 mT. Anal. Calcd for $C_{11}H_{12}OV$: C, 62.57; H, 5.73. Found: C, 62.76; H, 5.34.

Carbonyl(cyclopentadienyl)(2,4-dimethylpentadienyl)vanadium(II), $(C_5H_5)(2,4(C_7H_{11})VCO$. This compound was synthesizd in a manner analogous to that used for the $V(C_5H_5)(C_5H_7)CO$ complex. The product (mp 64–66 °C) was purified by either sublimation in vacuo (ca. 30 °C) or recrystallization from hexane at −90 °C to yield dark green crystals. Complete infrared data (Nujol mull): 3054 (sh), 1991 (vw), 1934 (vs), 1894 (w), 1261 (w), 1154 (w), 1115 (w), 1125 (s), 1114 (s), 1002 (s), 891 (m), 866 (m), 798 (vs) cm^{-1}. Mass spectrum: *m/e* (relative intensity) 39 (12), 41 (14), 51 (23), 55 (12), 67 (15), 69 (10), 79 (11), 81 (10), 90 (21), 95 (33), 96 (10), 116 (90), 129 (10), 207 (41), 208 (11), 209 (100), 210 (14), 211 (48), 239 (12). Magnetic susceptibility (Evans method, THF): 1.7 μ_B. EPR data (toluene, 23 °C): g = 1.992 ± 0.001, a_V = 6.15 ± 0.03 mT. Visible spectral data (λ (ϵ_{max})): 430 (207), 770 nm (30 M^{-1} cm^{-1}). Anal. Calcd for $C_{13}H_{16}OV$: C, 65.27; H, 6.74. Found: C, 65.04; H, 6.67.

(Triethylphosphine)bis(pentadienyl)vanadium(II), $(C_5H_7)_2V(PEt_3)$. A mixture of 3.50 g (9.37 mmol) of $VCl_3(THF)_3$ and 0.37 g (5.7 mmol) of zinc powder in 30 mL of THF was refluxed for 3 h. The solution was then cooled to −78 °C, and 2.5 mL (16.8 mmol) of triethylphosphine was added via syringe. Stirring was continued for 30 min, at which time 2.00 g (18.8 mmol) of potassium pentadienide in 60 mL of THF was added over a period of 30 min. The reaction mixture was then allowed to warm slowly to room temperature with stirring over 5 h. After the solution was stirred for an additional 2 h, the solvent was removed in vacuo and the remaining residue extracted with four 20-mL portions of hexanes and filtered thru Celite. Cooling the hexane solution of −90 °C overnight led to the crystallization of the green compound (mp 113.5–114.5 °C). The product was recrystallized a second time from hexanes before being used in subsequent reactions. A yield of 1.80 g (64%) was obtained. Infrared data (Nujol mull): 3075 (w), 3050 (w), 1502 (m), 1267 (w), 1253 (w), 1222 (m), 1104 (m), 1032 (ms), 1024 (sh), 1000 (vw), 988 (vw), 952 (w), 921 (m), 864 (w), 843 (s), 800 (m), 754 (s), 702 (sh), 694 (ms) cm^{-1}. Mass spectrum (EI, 17 eV): *m/e* (relative intensity) 40 (15), 41 (16), 61 (29), 62 (94), 66 (10), 67 (76), 68 (15), 79 (10), 90 (100), 91 (17), 92 (20), 93 (13), 103 (21), 118 (69), 119 (15), 134 (10), 181 (14), 185 (13). EPR (toluene, 23 °C): g = 1.980 ± 0.001, a_V = 7.83 ± 0.03 mT, a_P = 2.14 ± 0.03 mT. Magnetic susceptibility (Evans method, THF): 1.7 μ_B. Anal. Calcd for $C_{16}H_{29}PV$: C, 63.36; H, 9.64. Found: C, 63.28; H, 9.79.

Carbonylbis(pentadienyl)vanadium(II), $(C_5H_7)_2VCO$. A solution of 1.0 g (3.2 mmol) of $(C_5H_7)_2VP(C_2H_5)_3$ in 30 mL of hexane was exposed to 1 atm of CO for ca. 2 min, during which time the color changed from yellow-green to green-blue. The solution was pumped to dryness to remove $P(C_2H_5)_3$ and the residue dissolved in 30 mL of hexane, which then was exposed to 1 atm of CO for another 2 min. The solution was then filtered thru Celite and stored at −90 °C overnight to afford 0.51 g (75%) violet crystals. The product readily sublimes at ca. 40 °C and may be further purified in this manner if desired. The crystalline carbonyl product, as well as solutions of this compound, were observed to be thermochromic. UV–vis data (λ (ϵ_{max}): 295 K, 568 (185), 388 nm (2990 M^{-1} cm^{-1}); 80 K, 555 (280), 388 nm (3650 M^{-1} cm^{-1}). Infrared data (Nujol mull): 3080 (w), 1958 (vs), 1502 (m), 1263 (mw), 1224 (m), 1100 (w), 923 (mw), 822 (w), 861 (w), 841 (w) cm^{-1}. Mass spectrum (17 eV): *m/e* (relative intensity): 39 (16), 40 (16), 41 (21), 51 (30), 67 (50), 90 (24), 116 (76), 115 (25), 181 (100), 182 (10), 185 (39), 213 (16). EPR (toluene, 23 °C): g = 1.987 ± 0.001, a_V = 7.91 ± 0.03 mT. Magnetic susceptibility (Evans method, THF): 1.7 μ_B. Anal. Calcd for $C_{10}H_{14}VO$: C, 61.98; H, 6.62. Found: C, 61.66; H, 7.05.

CO Exchange Experiments. The compounds $(pd)_2V^{13}CO$, $Cp(pd)V^{13}CO$, and $Cp(pd')V^{13}CO$ were prepared from the $(\eta^5\text{-}L)_2V(PEt_3)$ precursor under an atmosphere of ^{13}CO, and $Cp_2V^{13}CO$ and $Cp_2{}^*V^{13}CO$ were prepared from the metallocene as described in the previous sections. IR ($\nu_{^{13}CO}$ (cm^{-1})) for $(pd)_2V^{13}CO$ at 1914; $Cp(pd)V^{13}CO$, 1895; $Cp(pd')V^{13}CO$, 1892 in decalin. $Cp_2V^{13}CO$, 1839; $Cp_2{}^*V^{13}CO$, 1799 in toluene.

The apparatus used for the CO exchange reaction is similar to that described by Berry and Brown.[39] The CO or CO/N_2 gas mixture was bubbled through the solution by using a coarse-fritted tube, and the CO atmosphere in the closed system was continuously recirculated by using a Masterflex tubing pump. The reaction vessel was equipped with connections for CO addition, a manometer for initial filling of the vessel, and a septum-sealed stopcock for withdrawing aliquots for IR analysis.

For the low-temperature experiments the toluene solvent (~10 mL) was degassed in the reaction vessel, thawed to the desired reaction temperature, and saturated with the CO/N_2 mixture. Three standardized tanks of CO were obtained from Matheson consisting of 99.99% CO, 9.992% CO in N_2, and 1.002% CO in N_2. Other mixtures were obtained by mixing the calibrated standard with N_2 using a Matheson gas mixer and rotameter, and the gas was passed through an oxygen scavenger (MnO on silica) before entering the reaction vessel. Following saturation of the solvent ($P_{tot.}$ = 1.0 atm), the reaction vessel was closed off to the gas addition line, manometer, and exit bubbler. With the circulating pump on, a small aliquot of a stock solution of the ^{13}CO-labeled complex (0.5 mL of a 0.10 M solution prepared under N_2) was added to the vessel by syringe. Small aliquots for IR analysis were withdrawn by syringe, and reaction progress was monitored by the increase in the IR carbonyl absorbance of the $(\eta^5\text{-}L)_2VCO$ complex and the decrease in absorbance of $(\eta^5\text{-}L)_2V^{13}CO$ as the mixture approached equilibrium.

The procedure for the higher temperature reactions of pentadienyl complexes is similar, except the solvent (decalin) was presaturated with the desired CO mixture and added to the reaction vessel containing 1.0 atm of the same CO mixture at the reaction temperature.

Data were analyzed by using a version of the McKay equation for isotope exchange reactions (eq. 1) which takes into account the $CO_{soln} \rightleftharpoons CO_{vapor}$ exchange.[40,41]

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$$\ln\left[\frac{A - A_\infty}{A_0 - A_\infty}\right] = -(k_1 + k_2[\mathrm{CO}]_{\mathrm{sol}})\left[\frac{[\mathrm{MCO}]}{C} + 1\right]t \qquad (1)$$

In this equation, A is the $(\eta^5\text{-L})_2\mathrm{V}^{13}\mathrm{CO}$ absorbance (similar expressions may be written for the increase in absorbance of the unlabeled complex or for the fraction of exchange which has occurred) and k_1 and k_2 are the ligand- (CO-) independent and ligand-dependent rate constants, respectively. The total vanadium carbonyl concentration is given by $[\mathrm{MCO}] = [(\eta^5\text{-L})_2\mathrm{VCO}] + [(\eta^5\text{-L})_2\mathrm{V}^{13}\mathrm{CO}]$, $[\mathrm{CO}]_{\mathrm{sol}}$ is the CO solubility, and C is the total moles of CO + ^{13}CO in the reaction vessel (solution + vapor) divided by the solution volume. Solubility data for CO in toluene,[42] decalin,[43] ether,[44] THF,[45] hexane,[46] and methylcyclohexane[42] were taken from the literature and corrected for the temperature and P_{CO} used in the experiments.[42] The constant C may be estimated from the volume of the vessel and solution, temperature, and P_{CO}. For reactions with low CO concentrations, the reaction to displace ^{13}CO is not driven completely to the right and C may be determined from the equilibrium concentrations of the metal carbonyl complexes; in this case the ratio $[\mathrm{MCO}]/C$ is given by $(A_{\mathrm{M^{13}CO}}/A_{\mathrm{MCO}})_\infty$. For the higher CO concentrations used in reactions of the pentadienyl complexes, $[\mathrm{MCO}]/C$ is small compared to 1 and the previous estimate holds.

A plot of the quantity on the left-hand side of eq 1 vs. time gives a straight line (correction coefficient ≥ 0.995) with slope equal to k_{obsd} (eq 2).

$$k_{\mathrm{obsd}}\left[\frac{[\mathrm{MCO}]}{C} + 1\right]^{-1} = k_1 + k_2[\mathrm{CO}]_{\mathrm{soln}} \qquad (2)$$

Kinetics of Reaction between $\mathrm{Cp_2^*V}$ and CO. Solutions of $\mathrm{Cp_2^*VCO}$ (4×10^{-3} to 1.5×10^{-2} M) under CO pressures of 0.50–1.50 atm were prepared in a 50-mL flask attached to a 1-cm Pyrex cell. The reaction temperature was maintained with a jacketed, flow-through cell holder. The solution in the cell was photolyzed for ~4 min by using a Hanovia high-pressure mercury arc lamp and then transferred immediately to a Perkin-Elmer 320 UV–vis spectrophotometer. The absorbance increase at 440 nm corresponding to the re-formation of $\mathrm{Cp_2^*VCO}$ was monitored with time. Similar measurements at other wavelengths and photolysis times ranging between 1 and 20 min gave reproducible pseudo-first-order rate constants from plots of $\ln(A_\infty - A_t)$ vs. time.

$\mathrm{Cp^*VCO/Cp^*_2V}$ Equilibrium. No detectable dissociation of $\mathrm{Cp^*_2VCO}$ to $\mathrm{Cp^*_2V}$ and CO is observed from −10 to 30 °C in toluene solutions of $\mathrm{Cp^*_2VCO}$ saturated with greater than 0.5 atm of CO. At lower P_{CO}, the equilibrium constant for dissociation (eq 4) was estimated from the IR (ν_{CO}) and UV–vis spectra of a 1.74×10^{-2} M solution of $\mathrm{Cp^*_2V}$ saturated with 9.99% and 1.002% CO in $\mathrm{N_2}$ and equilibrated for several hours at 25 °C. For $P_{\mathrm{CO}} = 0.11$ atm ($[\mathrm{CO}]_{\mathrm{sol}} = 8.7 \times 10^{-4}$ M) $\mathrm{Cp^*_2V/Cp^*_2VCO} = 0.024$, and for $P_{\mathrm{CO}} = 0.011$ atm ($[\mathrm{CO}]_{\mathrm{sol}} = 8.7 \times 10^{-5}$ M) $\mathrm{Cp^*_2V/Cp^*_2VCO} = 0.037$; $K_{\mathrm{eq}}(\mathrm{av}) = 3 \times 10^{-5}$ M at 25 °C. Similar measurements starting with 5.0×10^{-3} M $\mathrm{Cp^*_2V}$ gave $K_{\mathrm{eq}} = (4 \pm 2) \times 10^{-5}$ M at 25 °C, and $K_{\mathrm{eq}} = (5 \pm 1) \times 10^{-6}$ at 0.0 °C.

Rates of CO Addition to $\mathrm{Cp_2V}$, $\mathrm{(pd)_2V}$, and $\mathrm{Cp(pd')V}$. Toluene solutions of $(\eta^5\text{-L})_2\mathrm{VCO}$ (5.0×10^{-3} M) were prepared under 1 atm of CO. Recombination of CO and the metallocene after photolysis was too rapid to measure by the technique used for $\mathrm{Cp_2^*V}$. Rate estimates were obtained from flash photolysis experiments using a computer-interfaced apparatus.[47] The increase in absorbance at the following wavelengths was measured: $\mathrm{Cp_2V}$, 450 nm; $\mathrm{(pd)_2V}$, 440 nm; $\mathrm{Cp(pd')V}$, 600 nm.

Results

The reaction of $\mathrm{CpVCl_2(PEt_3)_2}$ or $[\mathrm{CpVCl(PEt_3)_2}]_2$ with 2 equiv of the pentadienyl or 2,4-dimethylpentadienyl anion in the presence of excess triethylphosphine leads directly to the formation of the respective complexes $\mathrm{Cp(pd)V(PEt_3)}$ or $\mathrm{Cp(pd')V(PEt_3)}$ in good yields. These compounds exist as monomeric 17-electron complexes having one unpaired electron, as judged from magnetic susceptibility and EPR data (see Experimental Section), as well as an X-ray diffraction study of $\mathrm{Cp(pd)V(PEt_3)}$.[26a] Both compounds react immediately with CO, leading to 17-electron monocarbonyl complexes, which have been similarly characterized. The C–O stretching modes appear at 1937 cm^{-1} for Cp(pd)V(CO) and at 1934 cm^{-1} for Cp(pd′)V(CO) (cf. 1881 cm^{-1} for $\mathrm{Cp_2V(CO)}$).

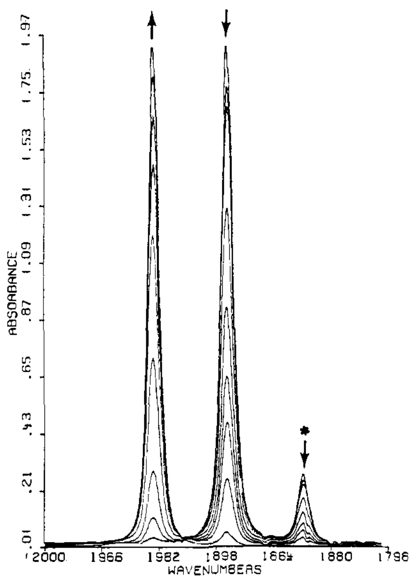

Figure 1. Infrared spectral changes for the reaction $\mathrm{Cp(pd')V^{13}CO + CO \rightarrow Cp(pd')VCO + {}^{13}CO}$ in decalin at 50.0 °C ($p_{\mathrm{CO}} = 1.0$ atm). The peak marked with an asterisk results from $\mathrm{Cp(pd')VC^{18}O}$.

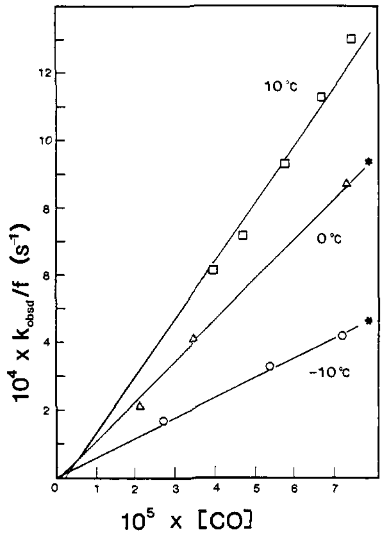

Figure 2. Plot of k_{obsd}/f vs. CO concentration for the reaction $\mathrm{Cp^*_2V^{13}CO + CO \rightarrow Cp^*_2VCO + {}^{13}CO}$ in toluene. The asterisk denotes data at higher CO concentrations (not shown) were also obtained.

Although bis(pentadienyl)vanadium compounds such as $\mathrm{(pd)_2V}$ have not been isolated, access to ligand adducts may be attained through $\mathrm{(pd)_2V(PEt_3)}$, which may be prepared from the reaction of a divalent vanadium complex with 2 equiv of the pentadienyl anion in the presence of excess phosphine. Again, spectroscopic data indicate the presence of a monomeric, 17-electron species. In the EPR spectrum, one observes coupling due to both the vanadium (7.83 mT) and the phosphorus (2.14 mT) centers, whose magnitudes are respectively larger and smaller for those found in $\mathrm{Cp(pd)V(PEt_3)}$ (6.87, 2.65 mT). Exposure of $\mathrm{(pd)_2V(PEt_3)}$ to CO leads instantly to the formation of the 17-electron monocarbonyl complex, whose C–O stretching mode appeared at 1958 cm^{-1} in the infrared spectrum. As successive replacement of cyclopentadienyl ligands by pentadienyl ligands in the series $\mathrm{Cp_2VCO}$, Cp(pd)VCO, and $\mathrm{(pd)_2VCO}$ leads to increasingly higher C–O stretching frequencies, it would appear that the pentadienyl

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Table I. Rates of CO Exchange for $Cp_2^*\ V^{1o}CO$ and $Cp_2V^{13}CO$

T, °C	10^5[CO]	$10^4k_{obsd}/f$,[a] s^{-1}	k_2, $M^{-1}\ s^{-1}$
	$Cp^*_2V^{13}CO$		
toluene[b]			
−10.0	2.62	1.70	
	5.24	3.34	6.06 (± 0.02)
	7.11	4.21	
	71.1	43.2	
0.0	2.12	2.060	
	3.33	4.146	
	7.23	8.700	12.7 (± 0.1)
	72.3	91.8	
10.0	3.99	6.09	
	4.70	7.13	
	5.67	9.24	
	6.52	11.34	21.5 (± 0.9)
	7.31	13.07	
diethyl ether			
0.0	16.9	7.55	4.5 (± 0.6)
10.0	16.5	8.54	5.2 (± 0.5)
methylcyclohexane			
0.0	10.0	7.58	7.6 (± 0.2)
10.0	9.88	11.5	11.7 (±0.5)
	Cp_2VCO		
toluene			
−15.0	3.42	7.91	
	7.04	10.2	15.6 (± 0.5)
	70.2	110.5	
−10.0	3.99	10.9	
	7.11	17.1	16.9 (± 0.1)
	70.9	133	
0.0	1.40	14.0	
	5.88	25.0	27 (± 3)
	7.23	30.6	

[a] f = [MCO]/C + 1; [MCO] ≅ 5 × 10^{-3} M. [b] Activation parameters in toluene: $\Delta H^\ddagger$ = 8.9 (±0.7) kcal/mol; $\Delta S^\ddagger$ = −21 (±3) cal/(mol K).

groups seem to withdraw more electron density than does the cyclopentadienyl ligand.

The CO exchange reaction (eq 3) may be monitored by following changes in the IR carbonyl absorbances of the CO- and ^{13}CO-labeled species (Figure 1). Rate constants for exchange reactions of Cp_2^*VCO and Cp_2VCO appear in Table I, and data for $(pd)_2VCO$, $Cp(pd)VCO$, and $Cp(pd')VCO$ are given in Table II.

$$(\eta^5\text{-L})_2V^{13}CO + CO \rightleftharpoons (\eta^5\text{-L})_2VCO + {}^{13}CO \qquad (3)$$

Results for CO exchange in Cp^*_2VCO support an associative mechanism, with activation parameters $\Delta H^\ddagger$ = 8.9 (± 0.7) kcal/mol and $\Delta S^\ddagger$ = −21 (± 3) cal/(mol K).[28a] No evidence for a dissociative (CO-independent) pathway was obtained (Figure 2) despite experience with this complex which indicated that solutions of Cp^*_2VCO in the absence of added CO may exist in equilibrium with small quantities of Cp^*_2V (eq 4). Investigation

$$Cp^*_2VCO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Cp^*_2V + CO \qquad (4)$$

of the recombination between Cp^*_2V and CO following photolysis of toluene solutions of Cp^*_2VCO showed that the rate of CO addition to Cp^*_2V occurs *slower* than the rate of associative CO exchange: at 25 °C in toluene, k_2 = 1.42 $M^{-1}\ s^{-1}$ for CO addition to Cp^*_2V (Table III), k_2 = 48 $M^{-1}\ s^{-1}$ for CO exchange (extrapolated). The activation parameters for CO addition to Cp^*_2V are $\Delta H^\ddagger$ = 6.3 (± 0.1) kcal/mol and $\Delta S^\ddagger$ = −37 (± 4) cal/(mol K). The slower rate for this reaction compared to CO exchange is reflected in the larger (negative) entropy of activation.

The equilibrium constant for eq 4 is about 10^{-5} M at 25 °C and 10^{-6} M at 0 °C, which may be equated with the kinetic constant, k_f/k_r. Using k_r = 1.42 $M^{-1}\ s^{-1}$ at 25 °C, the rate constant for CO dissociation (k_f) is calculated to be 1.4 × $10^{-5}\ s^{-1}$. The slow CO dissociation from Cp^*_2VCO together with slow CO addition to Cp^*_2V indicates that the dissociative process does not compete with the more facile associative pathway for CO exchange.

The solvent dependences for the reactions of eq 3 and the reverse of eq 4 were also examined. The rate of CO addition to Cp^*_2V at 25 °C is slower in THF than in toluene or hexane (Table III), which suggests that the coordinating ability of THF may stabilize the Cp^*_2V formed upon photolysis of Cp^*_2VCO. A similar trend is observed for CO exchange, where the rate decreases in the order toluene > methylcyclohexane > diethyl ether (Table I). Small rate variations for this process are not unusual for associative ligand substitution reactions and may only reflect the accuracy with which the CO solubilities are known.

Table II. Rates of CO Exchange for $pd_2V^{13}CO$, $Cp(pd')V^{13}CO$, and $Cp(pd)V^{13}CO$ in Decalin

complex	T, °C	10^4[CO]	$10^4k_{obsd}/f$,[a] s^{-1}	k_1,[b] s^{-1}	k_2,[c] $M^{-1}\ s^{-1}$
$(pd)_2V^{13}CO$[b]	60.0	56.1	0.294	0.81 × 10^{-5}	3.8 × 10^{-3}
		5.61	0.102		
$(pd)_2V^{13}CO$[b]	70.0	55.2	0.869		
		5.52	0.384	2.82 × 10^{-5}	10.7 × 10^{-3}
		0.552	0.250		
$(pd)_2V^{13}Co$[b]	81.0	54.1	0.70		
		5.41	1.25	10.6 × 10^{-5}	30.4 × 10^{-3}
		0.541	1.05		
$Cp(pd')V^{13}CO$[c]	50.0	56.9	0.956		
		28.5	0.904	8.41 × 10^{-5}	2.2 × 10^{-3}
$Cp(pd')V^{13}CO_c$	60.0	56.1	3.87		
		28.1	3.44	31.0 × 10^{-5}	13 × 10^{-3}
		5.61	3.20		
$Cp(pd')V^{13}CO$[c]	70.0	55.2	12.5		
		27.6	11.9	113 × 10^{-5}	22 × 10^{-3}
		5.52	11.4		
$Cp(pd)V^{13}CO$[d]	50.0	56.9	0.697		6.97 × 10^{-5}
		28.5	0.696		
$Cp(pd)V^{13}CO$[d]	60.0	56.1	2.73		
		28.1	2.73		27.3 × 10^{-5}
		5.61	2.42[e]		
$Cp(pd)V^{13}CO$[d]	70.0	55.2	10.1		101 × 10^{-5}
		27.6	10.1		

[a] f = [MCO]/C + 1; [MCO] ≅ 5 × 10^{-3} M. [b] Activation parameters from ligand-independent rates: $\Delta H_1^\ddagger$ = 28.1 (± 0.4) kcal/mol; $\Delta S_1^\ddagger$ = 2 (± 1) cal/mol K) Activation parameters from ligand-dependent rates: $\Delta H_2^\ddagger$ = 22.7 (± 0.5) kcal/mol; $\Delta S_2^\ddagger$ = −2 (± 1) cal/mol K). [c] Activation parameters from ligand-independent rates: $\Delta H_1^\ddagger$ = 27.9 (± 0.8) kcal/mol; $\Delta S_1^\ddagger$ = 9 (± 2) cal/(mol K). Activation parameters calculated from ligand-dependent rates have large uncertainties: $\Delta H_2^\ddagger$ ≅ 25 (± 8) kcal/mol; $\Delta S_2^\ddagger$ = 7 (± 20) cal/(mol K). [d] Activation parameters from ligand-independent rates: $\Delta H_1^\ddagger$ = 28.8 (± 0.3) kcal/mol; $\Delta S_1^\ddagger$ = 11.2 (± 0.8) cal/(mol K). The CO concentration dependence for this reaction is small and was not investigated in detail. k_2 estimated from data at 60.0 °C is 6 (± +) × 10^{-3} $M^{-1}\ s^{-1}$. [e] Omitted in calculation of k_1.

Table III. Rates of CO Addition to $Cp^*{}_2V$[a]

T, °C	$10^3[CO]$	$10^3 k_{obsd}$, s^{-1}	k_2, M^{-1} s^{-1}
toluene[b]			
15.0	7.48	7.07	0.945
25.0	3.95	7.01	
	7.60	12.13	1.42
	11.4	17.61	
30.0	7.65	14.35	1.88
40.0	7.75	20.32	2.62
hexane[c]			
15.0	15	7.04	0.47
25.0	13	10.4	0.72
35.0	11	14.2	1.3
45.0	9	19.8	2.2
tetrahydrofuran			
19.0	26	7.05	0.27
25.0	38	10.5	0.28

[a] $[Cp^*{}_2V] \cong 5 \times 10^{-3}$ M. [b] Activation parameters in toluene: $\Delta H^{\ddagger} = 6.3\ (\pm\ 0.1)$ kcal/mol; $\Delta S^{\ddagger} = -37\ (\pm\ 4)$ cal/(mol K). [c] Activation parameters in hexane: $\Delta H^{\ddagger} = 9\ (\pm\ 1)$ kcal/mol; $\Delta S^{\ddagger} = -30\ (\pm\ 4)$ cal/(mol K).

Table IV. Rates of CO Addition to $(\eta^5\text{-}L)_2V$ in Toluene at 25 °C

complex	k_2,[a] M^{-1} s^{-1}	rel rate
$Cp_2{}^*V$	1.42 (± 0.01)	1
Cp(pd′)V	34 (± 5)	24
$(pd)_2V$	42 (± 5)	30
Cp_2V	91 (± 5)	64

[a] $[(\eta^5\text{-}L)_2V] = 5 \times 10^{-3}$ M; $[CO] = 7.60 \times 10^{-3}$ M (1 atm).

Rates for CO exchange in Cp_2VCO are about 3 times faster than for $Cp^*{}_2VCO$ (Table I). Rates measured at higher temperatures were not reproducible because of the rapid rate of this reaction.

Rates of CO addition to Cp_2V, $(pd)_2V$, and Cp(pd′)V in toluene were determined by flash photolysis of the carbonyl complexes (Table IV). Recombination of CO with these 15-electron complexes is faster than for the analogous reaction with $Cp^*{}_2V$. The complexes $(pd)_2V$, Cp(pd)V, and Cp(pd′)V are difficult to purify, and precise characterization (by UV-vis spectroscopy) of the processes occurring on photolysis was not possible.

Carbon monoxide exchange in the pentadienyl complexes $(pd)_2VCO$, $(pd')_2VCO$, Cp(pd)VCO, and Cp(pd′)VCO is remarkably slower than in Cp_2VCO or $Cp^*{}_2VCO$. At 25 °C, complete equilibration of the pentadienyl vanadium carbonyls with 1 atm of ^{13}CO requires days ($k_{obsd} = 10^{-5}\text{–}10^{-6}$ s^{-1}). Kinetic data for the exchange of CO with the ^{13}CO-labeled complexes was obtained in decalin at 50–80 °C. Observed rate constants (Table II) were obtained as described for CO exchange in $Cp^*{}_2VCO$. The nonzero slopes (k_2) and intercepts (k_1) obtained from plots of the left-hand side of eq 2 vs. $[CO]_{sol}$ suggest both CO-independent and CO-dependent processes contribute to the rate. The enthalpies of activation for the CO-independent process are similar for $(pd)_2V(CO)$, Cp(pd)VCO, and Cp(pd′)VCO ($\Delta H_1{}^{\ddagger} = 28.1 \pm 0.4$, 27.9 ± 0.8, and 28.8 ± 0.3 kcal/mol, respectively) and are typical for a CO-dissociative process; entropies of activation are small and positive. The large enthalpies of activation for the CO-dependent pathway ($\Delta H_2{}^{\ddagger}$) and the similarities in $\Delta S_1{}^{\ddagger}$ and $\Delta S_2{}^{\ddagger}$ suggest that CO exchange occurs by a dissociative interchange (I_d) mechanism, in which vanadium–carbonyl bond breaking is advanced in the transition state.[48-50]

The kinetics of CO substitution in Cp(pd′)VCO by $P(OMe)_3$ were also examined. Even with a 500-fold excess of $P(OMe)_3$, the reaction (eq 5) is not driven to completion unless the CO

$$Cp(pd')VCO + P(OMe)_3 \rightleftharpoons Cp(pd')V[P(OMe)_3] + CO \quad (5)$$

liberated is purged from the reaction vessel. The reverse reaction is rapid, and Cp(pd′)VCO is almost completely regenerated on passing a CO atmosphere over solutions that contains up to 0.8 M $P(OMe)_3$. The low CO concentrations (the CO solubility under these conditions is $\sim 8 \times 10^{-3}$ M) needed to drive the reaction to the left illustrates a strong preference for CO coordination in this complex. The forward reaction shows only a slight dependence on phosphite concentration, and the activation parameters estimated from initial rate data are $\Delta H^{\ddagger} = 2m\ (\pm\ 1)$ kcal/mol and $\Delta S^{\ddagger} = 5\ (\pm\ 3)$ cal/mol K. These values are the same as those obtained for the ligand-independent pathway for CO exchange ($\Delta H^{\ddagger} = 27.9\ (\pm\ 0.8)$ kcal/mol, $\Delta S^{\ddagger} = 9\ (\pm\ 2)$ cal/(mol K)) in Cp(pd′)VCO and provide additional support for a CO-dissociative mechanism.

By analogy with $Cp^*{}_2VCO$, rates of the reaction between $(pd')_2VCO$ and $MeO_2CC{\equiv}CCO_2Me$ were measured. Reaction rates are independent of acetylene concentration and similar to rates of CO exchange for the other pentadienyl complexes. Unfortunately, the product of this reaction does not appear to be a simple π-olefin complex and could not be isolated in pure form. However, the absence of a ligand-dependent term and the activation parameters for this process ($\Delta H_1{}^{\ddagger} = 27.2\ (\pm\ 0.4)$ kcal/mol, $\Delta S_1{}^{\ddagger} = 11\ (\pm\ 1)$ cal/(mol K)) suggest that the rate-determining step in this reaction involves CO dissociation.

Discussion

The 17-electron complexes Cp_2VCO, $Cp^*{}_2VCO$, Cp(pd)VCO, Cp(pd′)VCO, $(pd)_2VCO$, and $(pd')_2VCO$ undergo CO substitution reactions at rates that span over 4 orders of magnitude (Table V). The vanadocene and decamethylvanadocene carbonyls are labile, and substitution proceeds by an associative mechanism. The pentadienyl complexes $(pd)_2VCO$ and $(pd')_2VCO$ are more inert and react at elevated temperatures by a CO-dissociative pathway. The mixed η^5-ligand complexes Cp(pd)VCO and Cp(pd′)VCO behave like $(pd)_2VCO$. Thus, replacement of one cyclopentadienyl ligand in Cp_2VCO with a pentadienyl ligand is sufficient to shut off associative reactions at the metal.

Because mechanistic studies of other 17-electron metal carbonyl complexes have shown that CO substitution occurs by a facile associative process, it is of interest to consider the structural and electronic features which prohibit this reaction pathway for the pentadienyl complexes but allow it for Cp_2VCO and $Cp^*{}_2VCO$. Structural results for two pentadienylvanadium complexes indicate vanadium–(η^5-ligand) bonding is strong. The vanadium–carbon distance of the η^5-ligand in $(pd')_2V$ is shorter than in Cp_2V ($V\text{–}C(C_7H_{11}) = 2.21$ Å, $V\text{–}C(D_5H_5) = 2.28$ Å),[51] and in Cp(pd)V(PEt$_3$) these distances are 2.21 Å for the pentadienyl ligand and 2.30 Å for the cyclopentadienyl ligand.[26] In addition to the shorter vanadium–pentadienyl bond distances, the greater girth of the pentadienyl ligand compared to cyclopentadienyl may impose steric constraints on the reactivity of these complexes. One indication of this effect is the stability of the 16-electron complex $(pd)_2TiCO$; a dicarbonyl species analogous to $Cp_2Ti(CO)_2$ is not known.[52] The U conformation for pentadienyl ligands bound to transition metals appears typical,[25,26] although complexes containing η^5-bound S-shaped ligands[53] and η^3-coordinated pentadienyls are also known.[54-57] Although the mode of coordination for the pentadienyl ligands in $(pd')_2VCO$, $(pd)_2VCO$, Cp(pd)VCO, and Cp(pd′)VCO has not been confirmed by structural studies, the

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Table V. Summary of Results for CO Exchange Reactions of $(\eta^5\text{-L})_2VCO$ Complexes[a]

complex	k_1, s^{-1}	$\Delta H_1^‡$	$\Delta S_1^‡$	k_2, M^{-1} s^{-1}	$\Delta H_2^‡$	$\Delta S_2^‡$	rel rate[b]	ν_{CO}, cm^{-1}	P[c]
$(pd)_2VCO$	8.1×10^{-6}	28.1	2	0.0038	22.7	−2	1	1959	91.3
$(pd')_2VCO$[e]	2.1×10^{-3}	27	11				70	1944	94.1
Cp(pd)VCO[d]	2.7×10^{-4}	28.8	11	0.006			9	1938	90.2
Cp(pd')VCO[d]	3.1×10^{-4}	27.9	9	0.013	ca. 25		13	1935	87.3
Cp_2VCO[f]	ca. 10^{-4}			ca. 800	ca. 6	ca. −30	5×10^4	1881	82.9
$Cp_2{}^*VCO$[f]	ca. 10^{-4}			ca. 260	8.9	−21	2×10^4	1842	80.0

[a] Rate constants are for reactions at 60.0 °C. Activation enthalpies in kcal/mol; entropies in cal/(mol K). [b] Relative rate for reactions under 1 atm of CO = $k_1 + k_2/[CO]$ relative to pd_2VCO. [c] P (in units of 10^{-4} cm^{-1}) reflects the localization of the unpaired spin on the metal. Lower values of P indicate greater delocalization.[29] [d] Kinetic parameters and ν_{CO} measured in decalin. [e] Kinetic parameters estimated from data for CO substitution by $MeO_2CC{\equiv}CCO_2Me$ in toluene.[28a] [f] Kinetic parameters extrapolated from data in toluene.

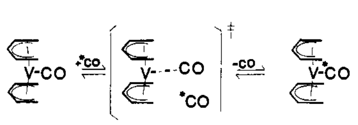

Figure 3. Dissociative interchange mechanism for CO exchange reactions of $(pd)_2VCO$, Cp(pd)VCO, and Cp(pd')VCO.

analogous complexes $(pd')_2V(PF_3)$, $(pd')_2Zr(PEt_3)$, $(pd')_2Nb(PEt_3)$, $(pd')_2Ti(PMe_3)$, and $Cp(pd)V(PEt_3)$ contain η^5-coordinated U-shaped ligands in which the open side of the pentadienyl ligand faces the metal–phosphorus bond. The dihedral angle formed by the planes of the pd' ligands and metal atom in the $(pd)_2ML$ complexes is large (~180°), which may result from repulsions between the syn-eclipsed atoms on the 2,4-dimethylpentadienyl ligands.[26,53]

A larger number of Cp_2VL_n (n = 1 or 2) have been characterized. Typical vanadium–Cp distances in Cp_2VL complexes (L = Cl[58] or the side-bound ligands $RC{\equiv}CR$,[21,22] $RCH{=}CHR$,[21] $H_2C{=}O$,[23] $RN{=}C{=}NR$[59]) are 1.95–1.96 Å; in $Cp^*{}_2VCO$ this distance is 1.93 Å.[37] The Cp–M–Cp angle depends on the size of the ligand; for Cp_2VL complexes it is usually 135–140° and in $Cp^*{}_2VCO$ it is 153°. The flexible CpVCp moiety can accommodate two additional ligands, and in addition to the 17-electron Cp_2VX_2 complexes (X = halide, pseudohalide, alkyl[60–66]), many 18-electron complexes containing bulkier ligands are known, such as $Cp^*{}_2V(t\text{-}BuNC)(CN)$, $[Cp^*{}_2V(t\text{-}BuNC)_2]^+$, $[Cp^*{}_2V(CO)_2]^+$, $[Cp_2V(CO)_2]^+$, and $[Cp_2V(CO)(P\text{-}n\text{-}Bu_3)]^+$.[18,37] In contrast, except for $(pd)_2Zr(CO)_2$,[67] no bis(η^5-pentadienyl) complexes of the titanium, vanadium, or chromium triads, which contain more than one additional ligand, are known.

Mechanism of CO Exchange in the Pentadienyl Complexes. Kinetic parameters for CO exchange in $(pd)_2VCO$, Cp(pd)VCO, and Cp(pd')VCO are summarized in Table V. Under our experimental conditions, the CO exchange reaction shows a small CO concentration dependence (eq 2). Activation parameters for the dissociative process ($\Delta H_1^‡$, $\Delta S_1^‡$) and the CO-dependent process ($\Delta H_2^‡$, $\Delta S_2^‡$) are similar and suggestive of a dissociative interchange (I_d) pathway in which vanadium–carbonyl bond breaking is well-advanced in the transition state (Figure 3). A distinct associative (A or S_N2) process occurring in addition to a CO-dissociative (D or S_N1) pathway should be reflected in a more negative value for $\Delta S_2^‡$. The large enthalpies of activation ($\Delta H_1^‡$ and $\Delta H_2^‡$ = 23–30 kcal/mol) are typical for dissociative reactions of other metal carbonyl complexes.[48–50,68]

In addition to the structural constraints, which could prohibit associative reactions for the pentadienyl complexes, the results of EPR studies and SCF-Xα-DV calculations[29] suggest that electronic factors contribute as well. The greater electron-withdrawing ability of the pentadienyl ligand compared to cyclopentadienyl yields a more positively charged vanadium atom, which leads to decreased vanadium–carbonyl π-bonding and reduced delocalization of the unpaired spin from the metal center in $(pd)_2VCO$. These trends are reflected in higher IR carbonyl stretching frequencies and the absence of detectable ^{13}C hyperfine interaction in the EPR spectra of the ^{13}CO-substituted pentadienyl vanadium carbonyl complexes. If the associative substitution reactions observed for $Cp^*{}_2VCO$ and Cp_2VCO occur via CO attack on the largely metal-based singly occupied orbital, delocalization of the unpaired electron from the vanadium atom should facilitate associative reactions for Cp_2VCO over $(pd)_2VCO$. The generally enhanced associative substitution lability of 17-electron metal carbonyl complexes, compared to their 18-electron analogues, is attributed to a more facile nucleophilic attack on the partially occupied metal orbital in the 17-electron complexes compared to the filled orbital in 18-electron complexes.[4,5,9,69,83] Since the higher energy LUMO in these complexes is oriented toward the ligands and has little metal character, it seems unlikely that associative attack on $Cp^*{}_2VCO$ or Cp_2VCO involves this orbital directly. A detailed description of the bonding and the results of EPR studies on these complexes will be presented in a future publication.[29] The electronic and steric factors that prohibit associative reactions for the pentadienyl complexes are also reflected in the failure of these complexes to abstract halide atoms from PCl_3 or CCl_4, which occurs rapidly for the bis(cyclopentadienyl) complexes.[70]

In contrast, other pentadienyl transition-metal complexes show enhanced reactivity compared to their cyclopentadienyl analogs. For example, η^5–η^3 conversion of the pentadienyl ligands has been observed in reactions of $(pd)Mn(CO)_3$[56b] or $(pd')Co(PR_3)_2$[57d] with nucleophiles. Coupling reactions of pentadienyl ligands[71] in other complexes may occur via η^4-diene–radical intermediates. Because associative reactions are slow for pentadienyl vanadium carbonyl complexes, despite evidence that pentadienyl ligands should be more likely to undero η^5–η^3 transformations or accept an electron from the metal, this suggests their inertness results from steric and electronic constraints that prohibit nucleophilic attack at the vanadium. Our experience[72] with both inert and labile cyclo-

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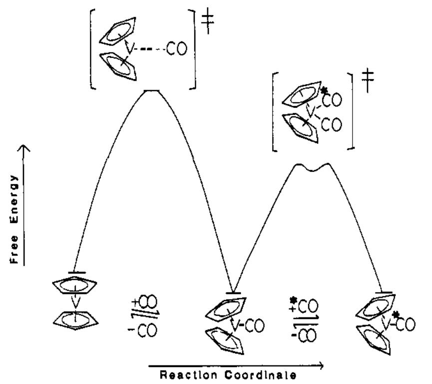

Figure 4. Proposed reaction profile for Cp^*_2VCO. (Methyl groups on Cp* ligands omitted for clarity.)

pentadienyl and indenyl metal carbonyl complexes has led us to believe that the ability of a nucleophile to closely approach the metal center is important in promoting associative ligand substitution reactions presumed to involve η^5–η^3 ring slippage.

Addition of CO to 15-Electron Metallocenes. The energy barrier for CO addition to 15-electron Cp^*_2V complex is surprisingly larger than the energy required to add a second CO to Cp^*_2VCO in the associative CO exchange reaction. This barrier is reflected in the unfavorable entropy of activation for this process: $\Delta S^\ddagger = -37 \pm 4$ cal/(mol K), $\Delta H^\ddagger = 6.3 \pm 0.1$ kcal/mol, and $\Delta G^\ddagger = 17.2 \pm 0.6$ kcal/mol at 25 °C. (For CO exchange, $\Delta S^\ddagger = -21 \pm 3$ cal/(mol K), $\Delta H^\ddagger = 8.9 \pm 0.7$ kcal/mol, and $\Delta G^\ddagger$ (25 °C) = 15 ± 1 kcal/mol.) Addition of CO to Cp^*_2V requires significant structural and electronic reorganization compared to the CO exchange reaction, since the rings must bend back to a greater extent to accommodate the CO ligand, and spin pairing is required to form Cp^*_2VCO (one unpaired electron) from Cp^*_2V (three unpaired electrons). Similar explanations have been used to account for the tendency of photogenerated Cp_2Mo, Cp_2W, and Cp_2V to resist recombination with CO in low-temperature CO matrices[73] and the tendency for Cp_2CrCO to dissociate to Cp_2Cr and CO in solution.[74] The similarity in the rates for CO addition to Cp_2V, pd_2V, and Cp(pd)V (Table IV) suggest that structural deformations may be more important than the spin-pairing energy in accounting for the rates of CO addition to the 15-electron complexes. This hypothesis is consistent with the observation that the "half-open metallocenes" generally seem to exhibit a much greater tendency toward coordination than do either metallocenes or "open metallocenes".[75]

A proposed reaction profile for Cp^*_2VCO is shown in Figure 4. The activation parameters determined for CO addition to Cp^*_2V and for CO exchange in Cp^*_2VCO allow a quantitative sketch of the reaction coordinate. Although the energy barrier for addition of CO to Cp^*_2V is large, the resultant Cp^*_2VCO complex is at least several kilocalories more stable than Cp^*_2V. This is reflected in the small equilibrium constant for eq 4, which is approximately 10^{-5} M at 25 °C. If Cp^*_2VCO is more than 2 kcal/mol lower in energy than Cp^*_2V, the associative CO exchange will be favored over a dissociative mechanism, and this has been confirmed experimentally. For reactions between Cp^*_2VCO and ligands other than CO (such as more crowded or poorer π-acid ligands) a CO dissociative mechanism may be preferred.

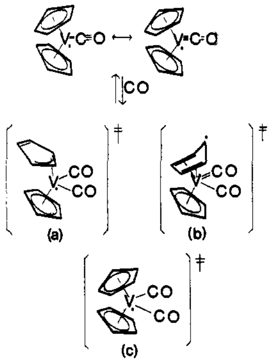

Figure 5. Possible transition states for associative CO exchange reactions of Cp^*_2VCO and Cp_2VCO.

Three alternative descriptions of the transition state or intermediate in the associative CO exchange reaction are illustrated in Figure 5. Possibility *A* is a 17-electron complex resulting from η^5–η^3 Cp ring slippage, *B* is an 18-electron complex resulting from localization of one electron on the Cp ring, and *C* is a formally 19-electron complex. Associative ligand substitution reactions of several other cyclopentadienyl transition-metal complexes are proposed to involve η^5–η^3 ring slippage,[72,76] and CO addition to bis(η^5-indenyl)vanadium gives the slipped indenyl complex (η^3-indenyl)(η^5-indenyl)$V(CO)_2$ as a stable crystalline solid.[77] However, the presence of this pathway for indenyl ligands does not imply that this is a low-energy pathway for complexes containing Cp (or Cp*) ligands, since associative reactions of indenyl metal carbonyls are several magnitudes times faster than associative reactions of cyclopentadienyl metal carbonyls.[72,78] Furthermore, the slipped cyclopentadienyl complex (η^3-Cp)(η^5-Cp)$W(CO)_2$ is *not* formed by CO addition to Cp_2WCO, except in very small quantities under extreme conditions.[79] The relatively high-energy barriers for associative reactions of other cyclopentadienyl metal carbonyls, which have been attributed to ring slippage, as compared to the facile associative reactions of Cp_2VCO, and especially Cp^*_2VCO suggest that other, lower energy, possibilities besides η^5–η^3 ring slippage may explain the enhanced reactivity of these radicals.

An alternative method of avoiding an unfavorably high electron count on vanadium localizes the odd electron on a Cp-ring carbon to give the diene radical shown in *B* (Figure 5). A similar intermediate has been proposed to account for the reactivity of the photogenerated $CpFe(CO)_2$ radical with donor ligands.[80] The reaction between $Cp_2V(Ph)$ and CO results in phenyl migration to the cyclopentadienyl ligand to give (η^5-Cp)(η^4-C_5H_5Ph)V-$(CO)_2$.[81] The mechanism of this reaction is not known, and the reaction is not general, since other Cp_2VR and Cp^*_2VR complexes react with CO to give $Cp_2V(CO)R$ or the insertion product

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[78] Recent studies on the electrochemical reduction of the 18-electron complex $[Cp_2V(CO)_2]^+$ indicate that reduction leads to CO loss (to give Cp_2VCO) but not η^5–η^3 ring slippage. In contrast, $[(\eta^5\text{-indenyl})_2V(CO)_2]^+$ gives (η^3-indenyl)(η^5-indenyl)$V(CO)_2$ upon reduction. Miller, G. A.; Therien, M. J.; Trogler, W. C., submitted for publication.

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Table VI. Rate Constants for Associative Ligand Substitution Reactions of 17-Electron Complexes

complex[a]	nucleophile	k_2, M^{-1} s^{-1}	conditions	ref
$V(\mathit{CO})_6$	PMe_3	132	25 °C, hexane	4
$V(\mathit{CO})_6$	PPh_3	0.25	25 °C, hexane	4
$V(CO)_6$	py	1.22	25 °C, CH_2Cl_2–hexane	4
$V(\mathit{CO})_5[P(OMe)_3]$	$P(OMe)_3$	14.9	25 °C, hexane	4
$V(\mathit{CO})_5(PPh_3)$	PPh_3	2.81	25 °C, hexane	4
$Cp_2{}^*V\mathit{CO}$	$MeO_2C{\equiv}CCO_2Me$	7.7×10^{-3}	25 °C, toluene	28a
$Cp_2{}^*V\mathit{CO}$	CO	48^b	25 °C, toluene	d
$(pd)_2V\mathit{CO}$	CO	$5.2 \times 10^{-5\,c}$	25 °C, decalin	d
$CpW(\mathit{CO})_3$	$P(OPh)_3$	1.3×10^4	24 °C, benzene	11
$CpW(\mathit{CO})_3$	PPh_3	8.6×10^2	24 °C, benzene	11
$Mn(\mathit{CO})_5$	PPh_3	1.7×10^7	0 °C, hexane	5
$Mn(CO)_3\ [\mathit{P(i\text{-}Bu)_3}]_2$	CO	0.32	20 °C, hexane	6
$Mn(CO)_3[\mathit{P(n\text{-}Bu)_3}]_2$	CO	42	20 °C, hexane	6
$[Cp'Mn(CO)_2(\mathit{MeCN})]^+$	PPh_3	1.3×10^4	25 °C, MeCN	8b
$[P'Mn(CO)_2(\mathit{MeCn})]^+$	$P(OPh)_3$	12	25 °C, MeCN	8b
$[Cp'Mn(CO)_2(\mathit{py})]^+$	$P(OMe)Ph_2$	130	22 °C, CH_2Cl_2	8a
$[Cp'Mn(CO)_2(\mathit{4}\text{-MeOpy})]^+$	$P(OMe)Ph_2$	410	22 °C, CH_2Cl_2	8a
$[Cp'Mn(CO)_2(\mathit{4\text{-}NO_2py})]^+$	$P(OMe)Ph_2$	75	22 °C, CH_2Cl_2	8a
$[Fe(\mathit{CO})_3(PPh_3)_2]^+$	py	13.6	25 °C, CH_2Cl_2	9
$[Fe(\mathit{CO})_3(PPh_3)_2]^+$	3,4-Me_2py	100	25 °C, CH_2Cl_2	9
$[Fe(\mathit{CO})_3(PPh_3)_2]^+$	4-CNpy	0.33	25 °C, CH_2Cl_2	9

[a] Rates are for a single substitution of the underlined ligand; Cp′ = η^5-MeC_5H_4; py = pyridine. [b] Rate constant at 25 °C extrapolated from activation parameters. [c] Extrapolated from ligand-dependent activation parameters. [d] This work.

$Cp_2V(COR)(CO)$.[81a,82] No evidence for radical character in the Cp rings of Cp_2VCO or $Cp^*{}_2VCO$ was obtained from EPR studies,[29] and diene products were not detected in reactions of these complexes with CO in the presence of $HSnBu_3$.[83]

A third possibility (*C*) is formally a 19-electron complex that may be stabilized by delocalization of the "19th" electron over the $V(CO)_2$ fragment. The EPR spectra of $Cp_2V^{13}CO$ and of $Cp^*{}_2V^{13}CO$ show ^{13}C hyperfine interactions from delocalization of the unpaired spin on the CO ligand, although no evidence for a dicarbonyl complex such as *C* was obtained. Delocalization of the unpaired electron from the metal by the carbonyl ligands is believed to be important in promoting the associative reactions of $V(CO)_6$, $Mn(CO)_5$, and other 17-electron metal carbonyl complexes.[5] In $V(CO)_6$, an estimated 34% of the unpaired spin density resides on the CO ligands,[84] and the formally 19-electron complex $Fe(CO)_5^-$ contains a bent Fe–CO moiety with significant spin density localized on the carbon atom.[85] However, in 17-electron $[Fe(CO)_3L_2]^+$ complexes (L = PR_3), where the odd electron is more localized on the metal center[9] than in $V(CO)_6$, associative attack is rapid (Table VI) because of greater steric accessibility to the metal in a 5-coordinate complex.

A few formally 19-electron vanadocene adducts are known, including the complexes $Cp^*{}_2V(NR)$ (R = 2,6-$Me_2C_6H_3$, Ph, $SiMe_3$), which contain a vanadium–nitrogen triple bond,[86,87] and $Cp_2V(NO)I$, which is believed to contain a linear V–N–O moiety.[88] The reaction of $Cp^*{}_2V(CNR)$ with additional isocyanide[35] leads to formation of the 18-electron complex $Cp^*{}_2V(CN)(CNR)$, and analogous reactions of $Cp_2V(CNR)$ have been observed in our laboratory. These reactions may involve a transition state or intermediate similar to *C*; the subsequent homolytic cleavage of the R–CN bond also supports an intermediate with radical character localized on an isocyanide ligand.

The reaction profile for Cp_2VCO resembles that of $Cp^*{}_2VCO$, except the energy barriers for CO addition to Cp_2V and for CO exchange are both lower. The CO exchange reaction is only three times faster for Cp_2VCO compared to $Cp^*{}_2VCO$. On the basis of the steric arguments, this rate difference seems small for an associative reaction but is consistent with an enhanced CO exchange rate for $Cp^*{}_2VCO$ because of increased V–CO backbonding and delocalization of the unpaired spin from the metal center.

Associative substitution mechanisms have been implicated for the series of 17-electron complexes listed in Table VI. Although Cp_2VCO and $Cp^*{}_2VCO$ are labile in comparison to related 18-electron complexes ($(Cp_2Ti(CO)_2$,[89] $CpV(CO)_4$,[90] and Cp_2CrCO[74] react by dissociative pathways), their reactivity is typical among most other 17-electron complexes. In addition to the relatively inert pentadienyl vanadium carbonyls, a few other unreactive 17-electron complexes are known. The resistance of $Co[P(OMe)_3]_4$ to dimerization or to undergo hydrogen abstraction reactions has been attributed to steric crowding, although the substitution lability of this complex is not known.[91] The inertness of $(\eta^4$-butadiene$)_2MnL$ (L = CO, PR_3) has been attributed to the shielding of the singly occupied HOMO by the butadiene ligands,[92] and this explanation may also apply to the pentadienyl vanadium carbonyl complexes.[29]

Conclusions

The structural and electronic features of Cp_2VCO and $Cp^*{}_2VCO$ both predict that these complexes should be more likely to undergo associative attack at the metal as compared to $(pd)_2VCO$, and kinetic studies confirm this. The Cp–V–Cp angle is perturbed only slightly on addition of a second ligand, and the greater delocalization of the unpaired spin and increased V–CO π-back-bonding in these complexes may help stabilize a 19-electron transition state or intermediate. In contrast, the 17-electron complexes containing a pentadienyl ligand are relatively inert. The absence of a facile associative substitution pathway in these

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complexes may be attributed to the more rigid $(pd)_2V$ geometry, decreased V–CO π-back-bonding, or reduced spin delocalization, all of which make the metal center less susceptible to nucleophilic attack.

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The Oscillatory Landolt Reaction. Empirical Rate Law Model and Detailed Mechanism

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Abstract: The iodate oxidation of sulfite and ferrocyanide when carried out in a continuous flow stirred tank reactor exhibits large-amplitude oscillations in pH accompanied by an almost constant concentration of iodide. A description of the reaction in terms of component processes and associated empirical rate laws is used to model the dynamical behavior. Limitations and potential refinements of the empirical rate law model are discussed. A detailed mechanism consistent with the component process description is presented.

Just over one hundred years ago, Landolt reported on his studies of the iodate oxidation of sulfite.[2] His careful investigation yielded an empirical expression for the time of appearance of molecular iodine upon complete consumption of sulfite as a function of reactant concentrations and temperature, which is still used for the "Landolt clock reaction" classroom demonstration.[3] A detailed study published in 1921 by Eggert and Scharnow[4] extended Landolt's investigation of the oxidation of sulfite and also reported on the oxidations of ferrocyanide and arsenous acid. Their study was the first to recognize the autocatalytic nature of these reactions. More recently, the reaction with arsenite has served as a model system for the study of bistability[5-10] and propagating reaction–diffusion fronts.[11-14]

In a recent dramatic discovery, Edblom, Orbân, and Epstein[15] (EOE) found oscillatory behavior in the iodate oxidation of sulfite in a stirred flow reactor (CSTR) when ferrocyanide was also included as a reactant. Large-amplitude oscillations in pH and potential of a Pt electrode were measured. The highly temperature sensitive behavior is characterized by a cross-shaped phase diagram[16,17] showing the reactor residence times and feed concentrations of $Fe(CN)_6^{4-}$ where monostability, bistability, and oscillations are exhibited.

Table I. Reactant Stream Composition

$[KIO_3]_0{}^a = 7.5 \times 10^{-2}$ M	$[Na_2SO_3]_0 = 8.93 \times 10^{-2}$ M
$[K_4Fe(CN)_6]_0 = 2.5 \times 10^{-2}$ M	$[H_2SO_4]_0 = 3.5 \times 10^{-3}$ M

$^a[I^-]_0 = 7.5 \times 10^{-7}$ M, based on analysis of iodate reagent.

Oligo-oscillatory behavior in the batch reaction of iodate with sulfite and malonic acid has been reported by Beck et al.[18,19] Three damped extrema in the concentration of iodide are exhibited before the final approach to the equilibrium composition. The discovery by EOE[15] represents the first example of sustained oscillations in a Landolt type system. While bistability is exhibited in the related iodate oxidation of arsenous acid, no evidence of oscillatory behavior has been found in this system with buffered[15,20] or unbuffered solutions.[21] That oscillations are exhibited in the iodate oxidation of a mixture of sulfite and ferrocyanide points to subtle but important differences in the reaction of iodate with various reducing agents.

In this paper we report on additional experimental characterization and mechanism analysis of the oscillatory iodate oxidation of sulfite and ferrocyanide. Our analysis relies on reactions proposed by Landolt,[2] Eggert and Scharnow,[4] and EOE,[15] together with empirical rate laws and associated rate constants for the component processes. From these sources we develop a simple empirical rate law (ERL) model that reproduces the qualitative and in some cases nearly quantitative dynamical behavior of the system. The ERL model is tested by comparing experimental and

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