

# Syntheses, Characterization, and Structural Studies of Lewis Base Adducts of Half-Open Vanadocenes, $V(C_5H_5)(Pdl)(L)$

Robert W. Gedridge,<sup>1</sup> John P. Hutchinson,<sup>1</sup> Arnold L. Rheingold,<sup>\*2</sup> and Richard D. Ernst<sup>\*1</sup>

Departments of Chemistry, University of Utah, Salt Lake City, Utah 84112, and the University of Delaware, Newark, Delaware 19716

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A variety of mono(ligand) adducts of half-open vanadocenes,  $V(C_5H_5)(Pdl)(L)$ , have been prepared from  $V(C_5H_5)Cl_2(PEt_3)_2$  or  $V(C_5H_5)I_2$  and various pentadienyl anions ( $Pdl = C_5H_7$ ,  $3-C_6H_9$ ,  $2,4-C_7H_{11}$ ;  $L = PEt_3$ ,  $PMe_3$ ,  $P(C_6H_5)_3$ ,  $dmpe/2$ ). Other ligand adducts ( $L = CO$ ,  $PF_3$ ,  $P(OMe)_3$ ,  $P(OC_6H_5)_3$ ,  $P(OCH_2)_3CCH_3$ ,  $CN(t-C_4H_9)$ ) may also be prepared, by a replacement of  $PEt_3$  from the appropriate  $V(C_5H_5)(Pdl)(PEt_3)$  complex. These species have been characterized by infrared and ESR spectroscopic studies, as well as magnetic susceptibility measurements and single-crystal structural determinations. Crystals of  $V(C_5H_5)(C_5H_7)(CO)$  are monoclinic, space group  $P2_1/n$ , with  $a = 11.821(4)$  Å,  $b = 8.109(2)$  Å,  $c = 20.309(5)$  Å,  $\beta = 93.96(2)^\circ$ , and  $V = 1942.0(9)$  Å<sup>3</sup> for  $Z = 8$ , while crystals of  $V(C_5H_5)(C_5H_7)(PEt_3)$  are also monoclinic, space group  $P2_1/c$ , with  $a = 14.999(5)$  Å,  $b = 7.710(2)$  Å,  $c = 14.290(7)$  Å,  $\beta = 101.59(3)^\circ$ , and  $V = 1618.9(11)$  Å<sup>3</sup> for  $Z = 4$ .

In previous studies of open-metallocene complexes,  $M(Pdl)_2$ , a number of complications prevented straightforward comparisons being made with their analogous metallocenes  $M(C_5H_5)_2$ . First of all, pentadienyl ligands are more sterically demanding,<sup>3</sup> and hence the open metallocenes are subject to much greater steric crowding. Additionally, the high symmetry of the metallocenes could greatly retard the extent of metal-ligand orbital mixing relative to that in the low-symmetry open metallocenes.<sup>4</sup> A third complication arose for the open titanocenes and open vanadocenes, which adopt low-spin configurations relative to their metallocene analogs (zero and one vs two and three unpaired electrons, respectively).<sup>5</sup> This complication seemed potentially the most significant of all, as structural data for the open vanadocene  $V(2,4-C_7H_{11})_2$  ( $C_7H_{11}$  = dimethylpentadienyl) revealed a much shorter average V-C bond distance relative to  $V(C_5H_5)_2$  itself, 2.211(2) vs 2.280(5) Å, which might be either a reflection of stronger V-pentadienyl bonding or simply an artifact of the low-spin configuration for the former complex (cf. manganocenes<sup>6</sup>). In order to circumvent these problems and allow for clearer comparisons to be made between cyclopentadienyl and pentadienyl ligands, we have begun to investigate complexes simultaneously containing both ligands, i.e., half-open metallocenes. Initial results on some such vanadium complexes have already been published,<sup>7</sup> and we now present a more complete report.

## Experimental Section

All operations were carried out under a nitrogen atmosphere, either in a Schlenk apparatus or in a glovebox. Organic solvents were predried and distilled from Na/benzophenone under nitrogen prior to use. Magnetic and spectroscopic data were obtained as previously described.<sup>8</sup> IR and mass spectral data are included as supplementary materials. Elemental analyses were obtained from Analytische Laboratorien (Gummersbach, Germany) Dornis and Kolbe (Mülheim, Germany) and Desert Analytics (Tucson, AZ) Laboratories.

Organic dienes,<sup>9</sup> phosphines,<sup>10</sup> and phosphites<sup>11</sup> were either prepared by standard procedures or purchased from commercial sources. Pentadienyl anions were prepared by published procedures,<sup>12</sup> as were  $V(C_5H_5)I_2$ ,<sup>13</sup>  $V(C_5H_5)Cl_2(PEt_3)_2$ ,<sup>14</sup>  $V(C_5H_5)(C_5H_7)(L)$ , and  $V(C_5H_5)(2,4-C_7H_{11})(L)$  ( $L = CO, PEt_3$ )<sup>7a</sup> complexes ( $C_5H_7$  = pentadienyl).

**$V(C_5H_5)(3-C_6H_9)(PEt_3)$  ( $C_6H_9$  = Methylpentadienyl). Procedure A.** This compound was synthesized in manners analogous to those for the  $V(C_5H_5)(C_5H_7)(PEt_3)$  complex. In one route 0.56 g (1.3 mmol) of  $(C_5H_5)VCl_2(PEt_3)_2$  dissolved in 30 mL of THF was refluxed for 2 h with 0.0952 g (1.46 mmol) of Zn dust. The purple solution was cooled to  $-78^\circ C$ , and 0.27 g (1.4 mmol) of  $K(3-C_6H_9)(THF)$  in 30 mL of THF was added dropwise with stirring. After the addition was complete, the mixture was slowly warmed to room temperature and stirred overnight to give a golden green solution. Workup followed in an entirely analogous fashion,<sup>7a</sup> yielding 0.38 g (ca. 90%).

**Procedure B.** 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  $-78$

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°C. To this solution was added dropwise 0.31 g (2.6 mmol) of  $K(3-C_6H_9)$  in 40 mL of THF. Workup was carried out as before, yielding 0.25 g (ca. 67%). The very air-sensitive golden green crystals (mp 67–70 °C) were purified by either sublimation in vacuo (ca. 50 °C) or recrystallization from hexane at –86 °C. Anal. Calcd for  $C_{17}H_{29}PV$ : C, 64.75; H, 9.27. Found: C, 64.78; H, 8.96. Magnetic susceptibility (THF, 23.3 °C): 1.64  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.989 \pm 0.001$ ,  $A_V = 68.1 \pm 0.2$  G,  $A_P = 27.5 \pm 0.2$  G.

$V(C_5H_5)(2,4-C_7H_{11})(PMe_3)$ . To a solution of 2.54 g (7.49 mmol) of  $(C_5H_5)VCl_2(PMe_3)_2$  in 100 mL of THF was added 0.2449 g (3.746 mmol) of Zn dust. The blue solution was refluxed for 2 h, producing a deep purple solution of  $[(C_5H_5)VCl(PMe_3)]_2$ . After this solution was cooled to –78 °C, a solution of 1.20 g (8.96 mmol) of  $K(2,4-C_7H_{11})$  in 50 mL of THF was added dropwise with stirring. After the addition was complete, the solution was warmed to room temperature slowly and stirred overnight, producing a brown solution. Workup followed in an entirely analogous fashion, yielding 1.33 g (ca. 62%) of dark green crystals. The product (mp 101–103 °C) was purified by recrystallization in hexane at –86 °C or sublimation in vacuo (ca. 70 °C). Anal. Calcd for  $C_{15}H_{25}PV$ : C, 62.71; H, 8.77. Found: C, 62.65; H, 8.49. Magnetic susceptibility (THF, 23.3 °C): 1.70  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.989 \pm 0.001$ ,  $A_V = 66.8 \pm 0.1$  G,  $A_P = 30.1 \pm 0.3$  G.

$V(C_5H_5)(2,4-C_7H_{11})(PPh_3)$ . To the deep red solution produced by dissolving 0.50 g (1.4 mmol) of  $(C_5H_5)VI_2$  in 30 mL of THF was added 0.0557 g (0.852 mmol) of Zn dust. Stirring this solution at room temperature for 3 h produced a violet solution of  $(C_5H_5)VI(THF)$ . The violet solution was cooled to –78 °C, and 0.3541 g (1.350 mmol) of  $P(C_6H_5)_3$  was added with stirring. To this solution was added dropwise 0.19 g (1.4 mmol) of  $K(2,4-C_7H_{11})$  dissolved in 30 mL of THF. The mixture was warmed to room temperature slowly and stirred overnight to produce a dark orange solution. After the solvent was removed in vacuo, the residue was extracted into three 25-mL portions of hexane. The dark orange extracts were filtered under nitrogen and the solution volume was reduced in vacuo to approximately 20 mL. Moderately air-sensitive red-orange crystals (mp 144–146 °C) were isolated and purified by cooling to –25 °C, yielding 0.55 g (ca. 86%). Anal. Calcd for  $C_{30}H_{31}PV$ : C, 76.10; H, 6.60. Found: C, 76.19; H, 6.83. Magnetic susceptibility (THF, 26.5 °C): 1.64  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.989 \pm 0.001$ ,  $A_V = 65.8 \pm 0.1$  G,  $A_P = 26.4 \pm 0.2$  G.

$V(C_5H_5)(2,4-C_7H_{11})(PF_3)$ . A variable quantity of  $V(C_5H_5)[2,4-(CH_3)_2C_6H_5](PEt_3)$  dissolved in hexane was exposed to an excess of gaseous  $PF_3$ . 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 68–69 °C) was purified by either sublimation in vacuo (ca. 55 °C) or recrystallization from hexane at –86 °C, yielding dark green crystals. Anal. Calcd for  $C_{12}H_{16}F_3PV$ : C, 48.18; H, 5.39. Found: C, 48.55; H, 5.48. Magnetic susceptibility (THF, 26.5 °C): 1.53  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 2.009$ ,  $A_V = A_P = 59$  G.

$[V(C_5H_5)(2,4-C_7H_{11})]_2[\mu-PMe_2(CH_2)_2PMe_2]$ . To a solution of 0.2141 g (0.6500 mmol) of  $V(C_5H_5)[2,4-(CH_3)_2C_6H_5](PEt_3)$  in 10 mL of toluene was added 0.22 mL (1.3 mmol) of dmpe with stirring. The dark brown solution was stirred at room temperature for 1 h and then filtered, and the solution volume was reduced to 5 mL in vacuo. Cooling to –86 °C produced a light green microcrystalline product. The product (mp 215–217 °C) was purified by recrystallization from hot toluene, yielding 0.16 g (ca. 86% based on vanadium). Anal. Calcd for  $C_{30}H_{48}P_2V_2$ : C, 62.94; H, 8.45. Found: C, 63.43; H, 8.68. ESR data (toluene, ambient temperature):  $g = 1.989 \pm 0.001$ ,  $A_V = 66.3 \pm 0.2$  G,  $A_P = 29.0 \pm 0.3$  G.

$V(C_5H_5)(3-C_6H_9)(CO)$ . This compound was prepared in a manner analogous to that used for the  $V(C_5H_5)(C_6H_7)(CO)$  complex. The product (mp 106–109 °C) was purified by either sublimation in vacuo (ca. 30 °C) or recrystallization from hexane

at –86 °C to yield dark green crystals. Anal. Calcd for  $C_{12}H_{14}OV$ : C, 64.01; H, 6.27. Found: C, 63.47; H, 6.23. Magnetic susceptibility (THF, 23.3 °C): 1.57  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.991 \pm 0.001$ ,  $A_V = 62.0 \pm 0.1$  G.

$V(C_5H_5)(C_6H_7)[P(OMe)_3]$ . To a stirred solution of 0.14 g (0.47 mmol) of  $V(C_5H_5)(C_6H_7)(PEt_3)$  in 30 mL of hexane was added 0.11 mL (0.93 mmol) of  $P(OCH_3)_3$  at room temperature. The solution changed color from golden brown to green instantly, indicating the formation of the product. The solution was filtered under nitrogen and the solution volume reduced in vacuo to approximately 10 mL. Very air-sensitive green crystals (mp 80–84 °C) were isolated and purified by cooling to –86 °C, yielding 0.13 g (ca. 91%). Anal. Calcd for  $C_{13}H_{21}O_3PV$ : C, 50.82; H, 6.89. Found: C, 50.19; H, 6.53. Magnetic susceptibility (THF, 28.9 °C): 1.57  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.990 \pm 0.001$ ,  $A_V = 67.3 \pm 0.1$  G,  $A_P = 41.0 \pm 0.1$  G.

$V(C_5H_5)(3-C_6H_9)[P(OMe)_3]$ . To a stirred solution of 0.31 g (0.98 mmol) of  $V(C_5H_5)(3-C_6H_9)(PEt_3)$  in 40 mL of hexane was added 0.23 mL (1.9 mmol) of  $P(OCH_3)_3$  at room temperature. The solution turned green instantly, and the workup was carried out in a manner analogous to that for the complex above. Very air-sensitive green crystals (mp 107–109 °C) were isolated and purified by cooling to –25 °C, yielding 0.31 g (ca. 97%). Anal. Calcd for  $C_{14}H_{23}O_3PV$ : C, 52.34; H, 7.22. Found: C, 52.64; H, 6.82. Magnetic susceptibility (THF, 23.3 °C): 1.60  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.990 \pm 0.001$ ,  $A_V = 66.6 \pm 0.1$  G,  $A_P = 41.7 \pm 0.3$  G.

$V(C_5H_5)(2,4-C_7H_{11})[P(OMe)_3]$ . To a stirring solution of 0.3659 g (1.111 mmol) of  $V(C_5H_5)[2,4-(CH_3)_2C_6H_5](PEt_3)$  in 30 mL of hexane was added 0.26 mL (2.2 mmol) of  $P(OCH_3)_3$  at room temperature. The solution turned from golden to green instantly, indicating the formation of the product, and the workup was carried out in a manner analogous to that above. Very air-sensitive green crystals were isolated and purified by cooling to –86 °C, yielding 0.33 g (ca. 89%). Anal. Calcd for  $C_{15}H_{25}O_3PV$ : C, 53.74; H, 7.51. Found: C, 53.74; H, 6.94. Magnetic susceptibility (THF, 23.3 °C): 1.58  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.990 \pm 0.001$ ,  $A_V = 65.8 \pm 0.2$  G,  $A_P = 40.6 \pm 0.1$  G.

$V(C_5H_5)(2,4-C_7H_{11})[P(OCH_2)_3CCH_3]$ . To a stirred solution of 0.3532 g (1.072 mmol) of  $V(C_5H_5)[2,4-(CH_3)_2C_6H_5](PEt_3)$  in 30 mL of hexane was added a solution of 0.24 g (1.6 mmol) of  $P(OCH_2)_3CCH_3$  (Caution! highly toxic) in 25 mL of hexane and 15 mL of THF at room temperature. The solution turned green instantly, indicating the formation of the product. The solution was filtered under nitrogen, and the volume was reduced in vacuo to approximately 40 mL. Air-sensitive dark green crystals (mp 204–208 °C) were isolated and purified by cooling to –25 °C, yielding 0.27 g (ca. 70%). Anal. Calcd for  $C_{17}H_{25}O_3PV$ : C, 56.83; H, 7.01. Found: C, 56.96; H, 7.12. Magnetic susceptibility (THF, 21.5 °C): 1.54  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.991 \pm 0.001$ ,  $A_V = 63.4 \pm 0.1$  G,  $A_P = 44.6 \pm 0.1$  G.

$V(C_5H_5)(2,4-C_7H_{11})[P(OPh)_3]$ . To a stirred solution of 0.2229 g (0.6768 mmol) of  $V(C_5H_5)[2,4-(CH_3)_2C_6H_5](PEt_3)$  in 15 mL of hexane was added 0.35 mL (1.3 mmol) of  $P(OC_6H_5)_3$  at room temperature. The solution changed color from golden brown to green instantly, indicating the formation of the product. The solution was filtered under nitrogen and the solution volume reduced in vacuo to approximately 5 mL. Very air-sensitive green crystals (mp 80–86 °C) were isolated and purified by cooling to –25 °C, yielding 0.31 g (ca. 89%). Anal. Calcd for  $C_{30}H_{31}O_3PV$ : C, 69.10; H, 5.99. Found: C, 68.60; H, 5.95. Magnetic susceptibility (THF, 21.5 °C): 1.58  $\mu_B$ . ESR data (toluene, ambient temperature):  $g = 1.991 \pm 0.001$ ,  $A_V = 63.6 \pm 0.1$  G,  $A_P = 42.8 \pm 0.2$  G.

$V(C_5H_5)(2,4-C_7H_{11})(CNCMe_3)$ . A solution of 0.4013 g (1.218 mmol) of purified  $V(C_5H_5)(2,4-C_7H_{11})(PEt_3)$  in 50 mL of hexane was cooled to –78 °C. To this slurry was added dropwise with stirring 0.15 mL (1.3 mmol) of  $CNCMe_3$ . The solution was warmed slowly to room temperature and turned bright green at approximately 0 °C. The solution was stirred at room temper-

**Table I. Crystallographic Data for V(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>7</sub>)(PEt<sub>3</sub>) (A) and V(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>7</sub>)(CO) (B)**

	A	B
formula	C <sub>16</sub> H <sub>27</sub> PV	C <sub>11</sub> H <sub>12</sub> OV
fw	301.3	211.2
cryst syst	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
a, Å	14.999(5)	11.821(4)
b, Å	7.710(2)	8.109(2)
c, Å	14.290(7)	20.309(5)
β, deg	101.59(3)	93.96(2)
V, Å <sup>3</sup>	1618.9(11)	1942.0(9)
Z	4	8
cryst dimens, mm	0.09 × 0.32 × 0.72	0.22 × 0.34 × 0.47
d(calc), g/cm <sup>3</sup>	1.24	1.44
μ(Mo Kα), cm <sup>-1</sup>	6.44	10.22
temp, °C	20	25
λ, Å	0.710 73	0.710 73
scan range, deg	3–50	4–50
data collected (hkl)	±17,+9,+16	±15,+10,+25
no. of indpt obs rflns	1293 (2.5σ)	2270 (5σ)
R(F)	0.0637	0.0371
R <sub>w</sub> (F)	0.0701	0.0410
Δ(ρ), e Å <sup>-3</sup>	0.47	0.25

ature for 2 h, and the volume was reduced in vacuo to 20 mL. Cooling this solution to -86 °C produced 0.25 g (ca. 70%) of dark green crystals. The product (mp 74–75 °C) was purified by recrystallization from hexane. Anal. Calcd for C<sub>17</sub>H<sub>25</sub>NV: C, 69.37; H, 8.56; N, 4.76. Found: C, 69.37; H, 8.27; N, 4.68. Magnetic susceptibility (THF, 26.0 °C): 1.61 μ<sub>B</sub>. ESR data (toluene, ambient temperature): *g* = 1.990 ± 0.001, *A<sub>v</sub>* = 66.7 ± 0.2 G.

V(2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>(CNCMe<sub>3</sub>). To a solution of 0.60 g (2.5 mmol) of purified V[2,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sub>2</sub> in 25 mL was added 0.31 mL (2.7 mmol) of CNCMe<sub>3</sub> at -78 °C with stirring. The solution changed color from dark green to bright green, indicating the formation of the product. After the solution was warmed to room temperature, the solution was filtered and the volume reduced in half. Green crystals were isolated and purified by cooling the hexane solution to -86 °C, yielding 0.62 g (ca. 77%). Anal. Calcd for C<sub>15</sub>H<sub>31</sub>NV: C, 70.35; H, 9.63; N, 4.32. Found: C, 69.40; H, 8.96; N, 4.53. Magnetic susceptibility (THF, 27.0 °C): 1.59 μ<sub>B</sub>. ESR data (toluene, ambient temperature): *g* = 1.986 ± 0.001, *A<sub>v</sub>* = 79.6 ± 0.3 G.

**X-ray Crystallography.** A crystal of V(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>7</sub>)(CO) suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table I. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data uniquely established the space group as P2<sub>1</sub>/n. No correction factor for absorption was required (low μ).

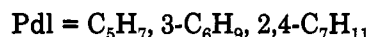
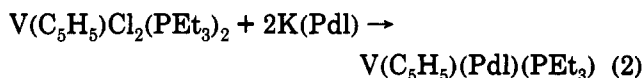
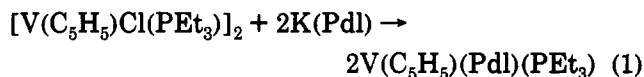
The structure was solved by direct methods, which located the V atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (*d<sub>CH</sub>* = 0.960 Å, *U* = 1.2*U* for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The asymmetric unit contains two chemically similar but crystallographically independent molecules. Pertinent information relating to data collection and structure solution may be found in Table I. All software and the sources of the scattering factors are contained in the SHELXTL(5.1) program library.<sup>15</sup>

A crystal of V(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>7</sub>)(PEt<sub>3</sub>) was mounted in a glass capillary under nitrogen for data collection. Unit cell parameters and systematic absences uniquely identified the space group as P2<sub>1</sub>/c. A numerical absorption correction was applied (μ = 6.44 cm<sup>-1</sup>), leading to a range in transmission factors of 0.65–0.94. The vanadium atom position was determined from a Patterson map, after which the remaining non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were placed in

idealized positions with thermal parameters (*U*) equal to those of their attached carbon atoms plus 0.01. Calculations employed the SHELX-76 program package. All refinements proceeded routinely.

### Synthetic Results and Discussion

The reactions of either [V(C<sub>5</sub>H<sub>5</sub>)Cl(PEt<sub>3</sub>)<sub>2</sub>] or V(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> with 2 equiv of a given potassium pentadienide led to the formation of the appropriate half-open vanadocene complexes, which could be isolated in good yields following straightforward procedures (eqs 1 and 2). The

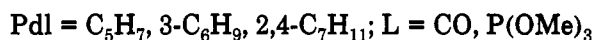
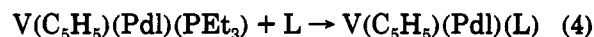


retention of a single phosphine ligand in these complexes even when sublimed is notable given that alkyl phosphines will not coordinate to vanadocene, while their coordination to open vanadocenes (and even titanocenes) is somewhat reversible.<sup>16</sup> A similar situation also applies to half-open chromocenes; however, they may at least be isolated without additional ligand incorporation.<sup>7b</sup> Only for Pdl = 1,5-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>5</sub>H<sub>5</sub> is there evidence that a half-open vanadocene may be isolated without additional coordinated ligands.<sup>7b</sup> Besides the PEt<sub>3</sub> complexes above, V(C<sub>5</sub>H<sub>5</sub>)(2,4-C<sub>7</sub>H<sub>11</sub>)(PMe<sub>3</sub>) may be isolated by a variation of eq 1.

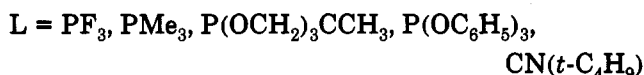
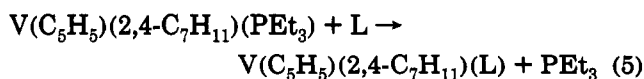
Although there is no direct spectroscopic evidence for phosphine dissociation (vide infra), the above complexes possess strong odors of PEt<sub>3</sub>, and it does appear that in solution these species exist in equilibrium with the expected 15-electron complexes (eq 3). Thus, although



these complexes are sterically crowded, CO or P(OMe)<sub>3</sub> react instantly with them to produce the expected adducts (eq 4). For V(C<sub>5</sub>H<sub>5</sub>)(2,4-C<sub>7</sub>H<sub>11</sub>)(PEt<sub>3</sub>) additional substi-



tution reactions were investigated and found generally to proceed readily when the added ligand was smaller and/or a stronger π-acid (eq 5). Notably, kinetic studies for



the L = CO species do indicate that CO exchange occurs at least predominantly by a dissociative pathway.<sup>7a</sup>

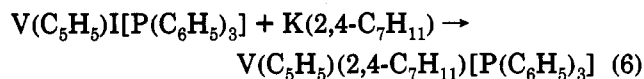
(15) Sheldrick, G. Siemens XRD Co., Madison, WI.

(16) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* 1987, 109, 5673.

**Table II. Selected Isotropic ESR Data for Selected Half-Open Vanadocene and Other Related Complexes**

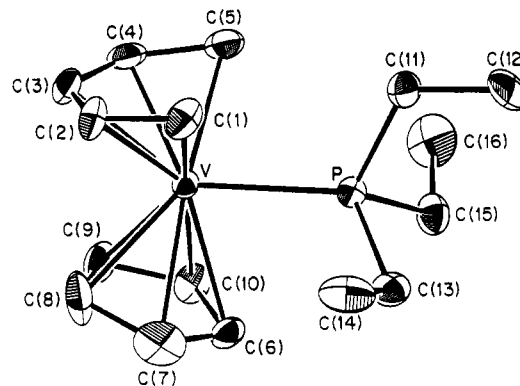
compd	$A_V$ , G	$A_P$ , G [ $\nu_{C-O}$ , $\text{cm}^{-1}$ ]
$V(C_5H_5)(C_5H_7)(PEt_3)$	68.7	26.8
$V(C_5H_5)(3-C_6H_9)(PEt_3)$	68.1	27.5
$V(C_5H_5)(2,4-C_7H_{11})(PEt_3)$	67.4	26.7
$V(C_5H_5)(2,4-C_7H_{11})(PMe_3)$	66.8	30.1
$V(C_5H_5)(2,4-C_7H_{11})(PPh_3)$	65.8	26.4
$V(C_5H_5)(2,4-C_7H_{11})(PF_3)$	(59)	(59)
$V(C_5H_5)(C_5H_7)[P(OMe)_3]$	67.3	41.0
$V(C_5H_5)(3-C_6H_9)[P(OMe)_3]$	66.6	41.7
$V(C_5H_5)(2,4-C_7H_{11})[P(OMe)_3]$	65.8	40.6
$V(C_5H_5)(2,4-C_7H_{11})[P(OPh)_3]$	63.6	42.8
$V(C_5H_5)(2,4-C_7H_{11})[P(OCH_2)_3CCH_3]$	63.4	44.6
$V(C_5H_5)(C_5H_7)(CO)$	62.9	[1938.0]
$V(C_5H_5)(3-C_6H_9)(CO)$	62.0	[1935.7]
$V(C_5H_5)(2,4-C_7H_{11})(CO)$	61.5	[1934.6]
$V(C_5H_5)(2,4-C_7H_{11})(CNMe_3)$	66.7	
$V(2,4-C_7H_{11})_2(CNMe_3)$	79.6	

To prepare a complex with a larger ligand such as  $P(C_6H_5)_3$ , resort was made to the phosphine-free  $V(C_5H_5)_2$ ; this was reduced and coordinated by  $P(C_6H_5)_3$  in situ, after which 1 equiv of  $K(2,4-C_7H_{11})$  was added, leading to the desired product (eq 6). The  $P(C_6H_5)_3$  ligand could readily be replaced by  $PEt_3$  or  $CO$ .



The above complexes should each possess a 17-electron configuration and hence have one unpaired electron. Solution-phase magnetic susceptibility measurements confirm this, yielding reasonable values of ca. 1.6–1.7  $\mu_B$ . With one unpaired electron these complexes also may be studied by ESR spectroscopy. The isocyanide and carbonyl adducts all exhibit eight-line patterns in the  $g = 2$  region due to coupling with the vanadium nucleus ( $I = 7/2$ ,  $A_V = \text{ca. } 61\text{--}63$  G for  $CO$ , 66.7 G for  $CN(t-C_4H_9)$ ). With the exception of the  $PF_3$  complex, all the phosphine and phosphite complexes exhibit 16-line patterns, due to additional coupling involving the phosphorus center ( $I = 1/2$ ). Similar or slightly higher  $A_V$  values of ca. 63–69 G were observed, with  $A_P$  values ranging from ca. 26 to 45 G. For the  $PF_3$  adduct, a nine-line pattern is observed, which presumably arises from a near-coincidence of the  $A_V$  and  $A_P$  values at ca. 59 G. The data for these complexes are summarized in Table II and generally parallel trends observed for their open-vanadocene analogs.<sup>17</sup> For example, there is a nearly linear decrease in the  $A_V$  value as methyl groups are added to the pentadienyl ligand, whether for the  $PEt_3$ ,  $P(OMe)_3$ , or  $CO$  adducts. As noted before, it seems possible that this is related to the contraction in size of the ligand which occurs as these groups are added to the 2-, 3-, and 4-positions. The contraction could either improve the ligand overlap with the SOMO (singly occupied molecular orbital), and thereby allow for more delocalization from the metal, or perhaps lead to better overlap for the  $\sigma$  and  $\pi L \rightarrow M$  interactions, adding electron density to the metal, thereby reducing its charge and allowing more delocalization. In fact, as in the case of the open vanadocene carbonyls, a very good correlation exists between the  $A_V$  and  $\nu_{C-O}$  values. However, there is also a possibility that the lower  $A_V$  values reflect greater orbital character in the SOMO.<sup>18</sup> Additionally, one can observe

(17) Newbound, T. D.; Rheingold, A. L.; Ernst, R. D. *Organometallics* 1992, 11, 1693.

**Figure 1. Solid-state structure of  $V(C_5H_5)(C_5H_7)(PEt_3)$ .****Table III. Positional Parameters for the Non-Hydrogen Atoms of  $V(C_5H_5)(C_5H_7)(PEt_3)$** 

atom	x	y	z
V	0.16971(7)	0.32079(12)	0.66350(7)
P	0.30763(11)	0.49385(21)	0.66103(11)
C1	0.2722(6)	0.1321(10)	0.7342(6)
C2	0.1836(5)	0.0567(8)	0.7199(5)
C3	0.1190(5)	0.0523(9)	0.6335(6)
C4	0.1257(5)	0.1338(9)	0.5479(5)
C5	0.2018(7)	0.2228(11)	0.5273(6)
C6	0.1314(5)	0.5938(9)	0.7127(5)
C7	0.1239(5)	0.4763(9)	0.7848(5)
C8	0.0574(4)	0.3562(10)	0.7469(6)
C9	0.0226(6)	0.4001(14)	0.6519(7)
C10	0.0691(7)	0.5487(12)	0.6311(5)
C11	0.4046(5)	0.3850(10)	0.6230(6)
C12	0.4925(6)	0.4852(13)	0.6281(7)
C15	0.2930(5)	0.6892(9)	0.5848(5)
C16	0.2548(7)	0.6602(12)	0.4793(6)
C13	0.3645(5)	0.6001(10)	0.7742(5)
C14	0.4002(8)	0.4803(13)	0.8570(6)

that the  $A_P$  values decrease significantly along the series  $PF_3 > P(OR)_3 > PR_3$ , accompanied by a smaller increase in the  $A_V$  values. This could reflect either the relative  $\pi$ -accepting abilities of the ligands directly or the fact that the better accepting ligands, having more electronegative substituents attached to phosphorus, will generally make closer approaches to the metal center.<sup>19</sup> The observation that greater  $A_P$  values are seen for  $P(OCH_2)_3CCH_3$  relative to  $P(OMe)_3$ , and for  $PMe_3$  relative to  $PEt_3$ , might be an indication of a bond length dependence due to steric interactions.

Further insight may be obtained from the infrared spectral data. It has already been noted that the C–O stretching frequencies of  $V(2,4-C_7H_{11})_2(CO)$  and  $V(C_5H_5)(2,4-C_7H_{11})(CO)$  are significantly higher than that of  $V(C_5H_5)_2(CO)$  (1942, 1935, and 1881  $\text{cm}^{-1}$ ),<sup>20</sup> indicating that the pentadienyl ligands are stronger acceptor ligands than  $C_5H_5$ . Also, as observed for the open-vanadocene carbonyls, the addition of methyl groups to a pentadienyl skeleton leads to a decrease in the C–O stretching frequency,<sup>17</sup> though not so dramatic as observed for substituted  $C_5H_5$  ligands. For the fully open carbonyl complexes, the greatest decrease in C–O stretching frequency was observed for methylation at the 1-position

(18) Kowaleski, R. M.; Basolo, F.; Osborne, J. H.; Troglor, W. C. *Organometallics* 1988, 7, 1425.

(19) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Ziegler, M. L., manuscript in preparation. Notably, an excellent correlation is observed between the  $A_P$  values for the  $PF_3$ ,  $PMe_3$ ,  $P(OR)_3$ , and cage phosphite complexes and the Ti–P distances in the  $Ti(2,4-C_7H_{11})_2(L)$  complexes ( $R^2 = 6000$ ).

(20) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* 1983, 250, 257.

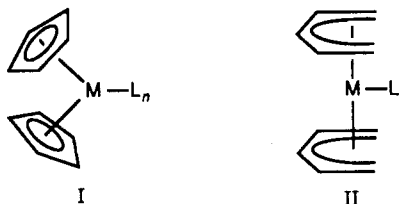
Table IV. Selected Bond Distances (Å) and Angles (deg) for  $V(C_5H_5)(C_5H_7)(PEt_3)$ 

Bond Distances							
V-C1	2.208(8)	V-C6	2.328(7)	P-C13	1.846(7)	C7-C8	1.389(10)
V-C2	2.184(7)	V-C7	2.323(7)	P-C15	1.860(7)	C8-C9	1.395(12)
V-C3	2.218(7)	V-C8	2.267(9)	C1-C2	1.427(11)	C9-C10	1.403(14)
V-C4	2.192(7)	V-C9	2.263(9)	C2-C3	1.408(10)	C10-C6	1.384(10)
V-C5	2.228(9)	V-C10	2.302(10)	C3-C4	1.396(11)	C11-C12	1.518(12)
V-P	2.468(2)	P-C11	1.853(8)	C4-C5	1.412(13)	C13-C14	1.518(10)
				C6-C7	1.393(11)	C15-C16	1.511(11)
Bond Angles							
V-P-C11	118.0(2)	P-C13-C14	116.1(6)	C6-C7-C8	107.6(6)		
V-P-C13	117.7(3)	P-C15-C16	116.3(5)	C7-C8-C9	108.5(7)		
V-P-C15	116.7(2)	C1-C2-C3	126.3(8)	C8-C9-C10	107.4(7)		
V-C11-C12	118.8(6)	C2-C3-C4	126.8(7)	C9-C10-C6	107.9(7)		
		C3-C4-C5	127.2(7)	C10-C6-C7	108.6(7)		

and the least at the formally uncharged 2-position. In this case one can see that, relative to  $\nu_{C-O}$  of  $V(C_5H_5)(C_5H_7)(CO)$ , the presence of a methyl group in the 3-position leads to a decrease in  $\nu_{C-O}$  of  $2.3\text{ cm}^{-1}$ , while the presence of methyl groups in the 2- and 4-positions leads to a decrease of  $3.4\text{ cm}^{-1}$ , or  $1.7\text{ cm}^{-1}$  per methyl group. Thus, these data are consistent with those for the fully open carbonyl compounds.

### Structural Results and Discussion

The structure of  $V(C_5H_5)(C_5H_7)(PEt_3)$  is presented in Figure 1, and pertinent bonding parameters are given in Tables III and IV. One can see that the structure is in essence a hybrid between the structure of mono(ligand) adducts of metallocenes (I) and of open metallocenes (II)



such that there is only a very small angle between the V-P vector and the open-dienyl ligand plane but a much larger one between this vector and the closed-dienyl plane. In this case the respective angles are  $4.7^\circ$  and  $19.5^\circ$ . Given the notable shortening of the V-C bonds in  $V(2,4-C_7H_{11})_2$  relative to  $V(C_5H_5)_2$ ,<sup>22</sup> of most interest are the V-C bond lengths for the two ligands. Those for the  $C_5H_5$  ligand range from 2.263(9) to 2.328(7) Å, averaging  $2.297(4)$  Å, while those for  $C_5H_7$  range from 2.184(7) to 2.228(9) Å, averaging  $2.206(4)$  Å. The significant shortening of the V-C( $C_5H_7$ ) bonds,  $0.091(6)$  Å, reveals that the similar shortening in  $V(2,4-C_7H_{11})_2$  relative to  $V(C_5H_5)_2$ ,  $2.211(2)$  vs  $2.280(5)$  Å, was not due simply to a difference in spin configuration. Notably, analogous observations have been made for both  $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ <sup>24</sup> and  $Cr(C_5Me_5)(C_5H_7)$ ,<sup>7b</sup> whereas for the later half-open metallocenes, the open and closed ligands have similar average M-C bond lengths.<sup>3a</sup> Thus, it appears that the relatively large

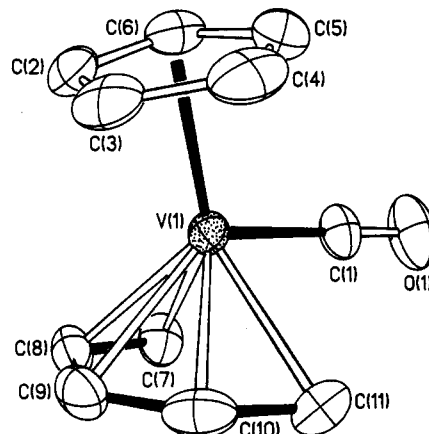


Figure 2. Solid-state structure of  $V(C_5H_5)(C_5H_7)(CO)$ .

size of the early metals allows for effective overlap with the pentadienyl orbitals, while also serving to reduce the interligand repulsions. As a result, for these metals one does find in the M-C bond lengths good evidence that the M-pentadienyl bonding is stronger than the M-cyclopentadienyl bonding, which should be otherwise expected given the greater  $\pi$  orbital stabilization (and aromaticity) in the cyclopentadienyl anion.<sup>3b,25</sup>

Several other ligand-related parameters are also of interest. The C-C-C bond angles in the  $C_5H_7$  ligand are all similar, averaging  $126.8(5)^\circ$ . The  $PEt_3$  ligand adopts a fairly common compact form in which one arm points back from the metal, with the other two going to the sides.<sup>16</sup> The V-P bond distance of  $2.468(2)$  Å is significantly longer than the analogous distance of  $2.246(1)$  Å in  $V(2,4-C_7H_{11})_2(PF_3)$ , but this is reasonable given the Ti-P bond distance of  $2.550(2)$  Å in  $Ti(2,4-C_7H_{11})_2(PMe_3)$ .<sup>19</sup>

The structure of  $V(C_5H_5)(C_5H_7)(CO)$  has also been determined and may be seen in Figure 2, while relevant bonding parameters are given in Tables V and VI. In this case there are two independent molecules in the unit cell, and they are probably essentially equivalent in their bonding. However, the  $C_5H_5$  ligand in the second molecule is very poorly defined as a result of high thermal libration. This can be seen in the average V-C and C-C distances for the two  $C_5H_5$  ligands,  $2.256(2)$  vs  $2.228(3)$  and  $1.390(3)$  vs  $1.323(5)$  Å (cf.  $1.391(5)$  Å in the  $PEt_3$  complex), respectively. In each case the second value is considered to be subject to significant systematic error and will not be included in further comparisons.

The orientation of the  $C_5H_5$  ligand appears slightly staggered relative to that for the  $PEt_3$  adduct. This could

(21) Campana, C. F.; Ernst, R. D.; Wilson, D. R.; Liu, J.-Z. *Inorg. Chem.* 1984, 23, 2732.

(22) (a) Haaland, A. *Acc. Chem. Res.* 1979, 12, 415. (b) Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* 1975, 88, 181.

(23) The esd's given for average values are obtained solely from the esd's of the individual values being averaged. Thus, these esd's reflect the uncertainties in the average values, but not the distributions of the individual values.

(24) Meléndez, E.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1099.

(25) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

**Table V. Positional Parameters for the Non-Hydrogen Atoms of  $V(C_5H_5)(C_5H_7)(CO)$** 

atom	x	y	z
V1	0.24528(4)	0.93065(7)	0.86871(3)
V2	0.25223(5)	1.07655(7)	0.38204(3)
O1	0.3138(3)	0.5705(3)	0.8495(2)
O2	0.5057(3)	1.0802(4)	0.4280(2)
C1	0.2876(3)	0.7060(5)	0.8570(2)
C2	0.0945(3)	1.0208(6)	0.9195(2)
C3	0.0916(3)	1.0943(5)	0.8573(2)
C4	0.0769(3)	0.9694(7)	0.8107(2)
C5	0.0717(3)	0.8214(6)	0.8435(2)
C6	0.0821(3)	0.8522(6)	0.9117(2)
C7	0.3972(3)	0.8875(5)	0.9401(2)
C8	0.3675(3)	1.0530(5)	0.9385(2)
C9	0.3526(3)	1.1524(5)	0.8817(2)
C10	0.3494(3)	1.0993(5)	0.8159(2)
C11	0.3760(3)	0.9414(5)	0.7939(2)
C12	0.4106(3)	1.0796(5)	0.4113(2)
C12	0.2568(6)	0.8751(10)	0.4577(4)
C14	0.1702(6)	0.9732(6)	0.4687(2)
C15	0.0955(4)	0.9631(9)	0.4163(4)
C16	0.1394(7)	0.8579(10)	0.3741(3)
C17	0.2357(8)	0.8063(7)	0.3988(5)
C18	0.2899(3)	1.3452(5)	0.4010(2)
C19	0.1822(3)	1.3251(5)	0.3688(2)
C20	0.1560(3)	1.2361(5)	0.3109(2)
C21	0.2288(4)	1.1355(6)	0.2772(2)
C22	0.3466(4)	1.1192(5)	0.2914(2)

**Table VI. Selected Bond Distances (Å) and Angles (deg) for  $V(C_5H_5)(C_5H_7)(CO)$** 

Bond Distances			
V1-C1	1.908(4)	V2-C12	1.925(4)
V1-C2	2.242(4)	V2-C13	2.241(8)
V1-C3	2.249(4)	V2-C14	2.232(5)
V1-C4	2.264(4)	V2-C15	2.222(6)
V1-C5	2.261(4)	V2-C16	2.218(8)
V1-C6	2.263(4)	V2-C17	2.228(6)
V1-C7	2.256(4)	V2-C18	2.252(4)
V1-C8	2.191(4)	V2-C19	2.188(4)
V1-C9	2.206(4)	V2-C20	2.197(4)
V1-C10	2.172(4)	V2-C21	2.180(4)
V1-C11	2.243(4)	V2-C22	2.244(4)
V1-CNT <sup>a</sup>	1.921(4)	V2-CNT <sup>b</sup>	1.923(4)
C1-O1	1.155(5)	C12-O2	1.152(5)
C7-C8	1.387(5)	C18-C19	1.400(5)
C8-C9	1.408(6)	C19-C20	1.397(5)
C9-C10	1.402(6)	C20-C21	1.398(6)
C10-C11	1.399(6)	C21-C22	1.408(6)
Bond Angles			
V1-C1-O1	179.3(3)	V2-C2-O2	178.9(3)
C7-C8-C9	126.2(4)	C18-C19-C20	126.5(4)
C8-C9-C10	126.8(4)	C19-C20-C21	127.2(3)
C9-C10-C11	126.4(4)	C20-C21-C22	126.1(4)
CNT <sup>a</sup> -V1-C1	110.7(2)	CNT <sup>b</sup> -V2-C12	109.3(2)

<sup>a</sup> CNT = centroid of atoms C2-C6. <sup>b</sup> CNT = centroid of atoms C13-C17.

either be a consequence of the much closer approach by the CO ligand, 1.916(3) vs 2.468(2) Å, or of the presence of the two lower ethyl groups in the latter structure. As in the  $PEt_3$  structure, the  $V-C_5H_7$  bonding appears

enhanced relative to the  $V-C_5H_5$  bonding, which is reflected by the average respective V-C distances of 2.213(2) vs 2.256(2) Å. The shortening of 0.043(3) Å, however, does not seem to be as much as in the  $PEt_3$  adduct, 0.091(6) Å. One can note that the difference arises from a change in  $M-C_5H_5$  bonding distances, but a clear explanation is not yet at hand.

Several other features may also be noted. The  $M-C_5H_7$  bonds vary somewhat, giving respective average  $V-C[1,5]$ ,<sup>26</sup>  $V-C[2,4]$ , and  $V-C[3]$  bond lengths of 2.249(2), 2.183(2), and 2.202(3) Å, whereas in the  $PEt_3$  adduct all values were more nearly similar. This might be a result of the close approach by the CO ligand (vide supra). The average  $C_5H_7$  C-C distance of 1.400(2) Å is similar to that of 1.411(6) Å for the  $PEt_3$  adduct, and one finds C-C-C angles around the  $C_5H_7$  2- and 4-positions averaging 126.3(2) vs 127.0(3)<sup>9</sup> for the 3-positions.

### Conclusions

The great size and steric demands of the pentadienyl ligands play a key role in much of their chemistry. For the smaller, later transition metals, the steric problems and poorer orbital overlap lead to relatively poor bonding. Structurally, it is only the larger, early transition metals which clearly have more favorable interactions with pentadienyl rather than cyclopentadienyl ligands. That the open ligand preference for the half-open vanadocene species  $V(C_5H_5)(C_5H_7)(L)$ , appears greater for  $L = PEt_3$  than for  $L = CO$  seems to be in line with other data which indicate that the open ligands are better acceptors than  $C_5H_5$ . It is lastly of interest to note that additional ligands coordinate to half-open metallocenes for vanadium and chromium better than they do to either the respective metallocenes or open metallocenes. As noted earlier, it would seem likely that the half-open metallocenes must undergo little reorganization to accommodate an additional ligand, whereas conversions of the other species to either bent metallocenes or syn-eclipsed open metallocenes are known to be unfavorable.<sup>7b</sup>

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**Supplementary Material Available:** Tables of infrared and mass spectral data for various compounds, tables of hydrogen atom and anisotropic thermal parameters for  $V(C_5H_5)(C_5H_7)(PEt_3)$ , and tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positional parameters for  $CpV(C_5H_7)(CO)$  (11 pages). Ordering information is given on any current masthead page.

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(26) The use of brackets indicates that average values of bonding parameters are being presented for all the carbon atoms in the 1- and 5-, 2- and 4-, or 3-positions of the pentadienyl groups.