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Carbonyl and Phosphine Adducts of Open Titanocenes and Open Vanadocenes: Syntheses, Spectroscopic Studies, and Solid-State Structures

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The syntheses of a variety of 17-electron open vanadocene adducts are reported, incorporating a variety of pentadienyl (Pdl = C_5H_7, 1-, 2-, or 3-C_6H_9, 2,3-C_7H_{11}, 2,4-C_7H_{11}) and additional ligands (CO, dmpe, PX_3; X = F, OCH_3, CH_3, C_2H_5). Also prepared for comparison are the carbonyl adducts of $Ti(C_5H_7)_2$ and $Ti(3\text{-}C_6H_9)_2$. Spectroscopic and structural data are in accord with the adoption of symmetric syn-eclipsed structures in all cases. Single-crystal structure determinations have been carried out for several $V(Pdl)_2CO$ complexes. For Pdl = 1-C_6H_9, the space group is $P\bar{4}2_1c$, with $a = b = 19.173$ (8) Å, $c = 6.753$ (2) Å, and $Z = 8$. For Pdl = 2,4-C_7H_{11}, the space group is $P2_12_12_1$, with $a = 9.933$ (6), $b = 10.013$ (5), and $c = 14.612$ (7) Å for $Z = 4$, while, for Pdl = 3-C_6H_9, the space group is *Pbca*, with $a = 11.179$ (4), $b = 14.016$ (5), and $c = 15.797$ (5) Å for $Z = 8$. A variety of infrared and ESR spectral studies have been carried out to help probe the electronic natures of these compounds.

While open metallocenes of titanium and vanadium have been prepared by utilizing the 2,4-dimethylpentadienyl ligand,[3] similar attempts with pentadienyl ligands having fewer methyl groups have not succeeded.[4] However, it has been found that the presence of an additional 1 equiv of a Lewis base such as $P(C_2H_5)_3$ can allow isolation of adducts such as $Ti(Pdl)_2P(C_2H_5)_3$ (Pdl = C_5H_7, 3-C_6H_9).[5] Herein we report the syntheses of analogous carbonyl and phosphine adducts of a variety of open vanadocenes (Pdl = C_5H_7, 1-C_6H_9, 2-C_6H_9, 3-C_6H_9, 2,3-C_7H_{11}, 2,4-C_7H_{11}), as well as some related titanium carbonyls. In addition to several solid-state structural determinations, infrared and ESR spectroscopy has been used as probes of the electronic natures of these complexes, especially with regard to the influences of the pentadienyl ligands' methyl substitution patterns and, for the phosphine complexes, to the nature of the phosphine substituents.

Experimental Section

The compounds reported below are all air sensitive to some extent, and hence all syntheses were carried out with due precautions to exclude the presence of air and moisture. Solvent purification methods and most spectroscopic studies were carried out as previously described.[5,6] UV–visible spectra were recorded with a Cary 17D spectrophotometer. Extinction coefficients are estimated to have uncertainties of ±10%. Variable-temperature UV–visible spectroscopic studies (185–295 K) of hexane solutions utilized an optical Dewar flask flushed continuously with cold, dry (blowoff) nitrogen, whose rate of introduction was determined by the temperature indicated by a thermocouple. Temperatures within the Dewar flask were measured by thermometer and are estimated to be accurate to ±2 °C. Spectra at 80 K were obtained for frozen-solution (glass) samples in 3-methylpentane using the same optical Dewar flask with a modified quartz cell submerged in liquid nitrogen. Spectra at 20 K were obtained using a closed-cycle refrigerator (Air Products 202 cryostat) mated to a stainless steel vacuum vessel with CaF_2 optical ports. Transparent films of the sample were deposited onto a CaF_2 window at 20 K by heating the crystalline compound to 45 °C in a Schlenk tube opened to the evacuated vessel. The temperature was estimated (±2 °C) by an electronic thermocouple.

ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with a Bruker ER 042 MRH microwave bridge. Sample solutions having concentrations of ca. 10^{-6}–10^{-5} M were prepared in toluene or hexane solutions. For the phosphine and phosphite adducts, an excess of the ligands was added to minimize dissociation in solution. Spectral shifts were referenced to that of DPPH. Microwave frequency modulations of ca. 24–40 MHz were employed for the vanadium compounds, and an 8-MHz frequency was used for DPPH. The *g* values and hyperfine splittings have been calculated using Breit–Rabi second-order corrections and have estimated uncertainties of ±0.005 and 0.2 G, respectively. Magnetic susceptibilities were obtained by the Evans method at room temperature with a Varian EM-390 CW spectrometer.

Phosphines and phosphites were either obtained commercially or prepared by standard methods. $TiCl_4$, CO, and PF_3 were also obtained commercially, while $VCl_3(THF)_3$ was prepared by a published procedure.[7] Various methyl-substituted pentadienyl anions were prepared as potassium salts by the Schlosser method or by a slight modification thereof.[8] K(2,4-C_7H_{11}) and K(3-C_6H_9) were prepared exactly as described by Schlosser,[9] while K(C_5H_7), K(1-C_6H_9), K(2-C_6H_9), and K(2,3-C_7H_{11}) were synthesized by stirring a suspension of potassium *tert*-butoxide (KO-*t*-C_4H_9) in hexanes cooled to −78 °C before adding the diene, followed by *n*-butyllithium. The mixture was allowed to warm slowly to room temperature, after which time stirring was continued for 2–6 h before the KPdl salt was filtered away from the solvent and washed with two portions of benzene and then dried in vacuo. When dried and free from impurities, all of these KPdl salts appear as slightly varied shades of yellow and are pyrophoric when exposed to air. Solubility in THF increases with increasing methyl substitution.

V(2,4-C_7H_{11})$_2$,[8] V(2,4-C_7H_{11})$_2$(CO),[10] and the $Ti(Pdl)_2(PEt_3)$[5] (Pdl = C_5H_7, 3-C_6H_9) complexes were prepared by published procedures. The other ligand adducts were prepared by one of the four following methods.

Method A. Ligand adducts of the isolable V(2,4-C_7H_{11})$_2$ could be prepared by the direct addition of an excess of the ligand (1.5–2 equiv) to V(2,4-C_7H_{11})$_2$ in several times the minimum volume of hexane or pentane required for dissolution. After 15 min, the

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(3) (a) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. (b) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737.

(4) (a) Ti(2,3-C_7H_{11})$_2$ (two isomers) may be prepared by a procedure similar to that used for Ti(2,4-C_7H_{11})$_2$.[4b] Attempts to prepare $V(C_5H_7)_2$ or V(3-C_6H_9)$_2$ lead only to very pale green solutions which apparently contain traces of these species, as indicated by ESR spectra of the solutions (Table VII). (b) Newbound, T. D.; Ernst, R. D. Unpublished results.

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

(6) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1990**, *9*, 2962.

(7) (a) Kurras, E. *Naturwissenschaften* **1959**, *46*, 171. (b) Alternatively, anhydrous VCl_3 may be placed in a Soxhlet extractor thimble with a small quantity of zinc dust and extracted as $VCl_3(THF)_3$ using THF.

(8) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organomet. Synth.* **1986**, *3*, 136.

(9) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453.

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

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solution was filtered through Celite, concentrated, and stored for at least 4–6 h at −20 to −90 °C. High-quality crystals were usually obtained by slowly cooling the solution to −20 °C; however, more complete crystallization and better yields were often afforded by cooling to −90 °C. PF_3 and CO adducts were prepared by simply bubbling the gas into a solution of the open metallocene for 5–10 s before filtering and cooling as described above. Crystals were well-drained before the supernatant was syringed away. For all Lewis base adducts except the triethylphosphine complex, the crystals were vacuum dried. Since triethylphosphine is easily removed from $V(2,4\text{-}C_7H_{11})_2P(C_2H_5)_3$ by evacuation, these crystals were dried in a stream of nitrogen. Yields were nearly quantitative.

Method B. $TiCl_4(THF)_2$ or $VCl_3(THF)_3$ was reduced in THF by the procedure appropriate to "MCl_2" in THF.[3,8] Typically, these reactions were run on a 5–10 mmol scale using 20–30 mL of THF. After reduction was complete, 2 equiv of phosphine was added via syringe and the mixture allowed to stir at room temperature for 5 min. The resulting solution was then cooled to −78 °C followed by dropwise addition of 2.2 equiv of the desired pentadienylpotassium solution in THF. Stirring was continued as the reaction mixture warmed to ambient temperature over ca. 5 h. After being stirred at room temperature for at least an additional 1 h, the solvent was removed in vacuo and the residue extracted into several portions of pentane or hexane, after which the mixture was filtered through Celite. The volume of the extract solution was reduced in vacuo until nearly saturated, after which cooling to −90 °C led to precipitation of the product. Recrystallization was almost always necessary in order to obtain a product that was free of excess phosphine and oils. Yields ranged from 20 to 70% depending mostly upon the quality of the starting materials.

Method C. In general, replacement of triethylphosphine from its complexes by other phosphines, phosphites, or CO is possible, provided that they have smaller cone angles. The replacement was accomplished by stirring a solution of the triethylphosphine complex in hexane or THF for 15 min at ambient temperature with at least a 2-fold excess of the desired ligand followed by filtration and crystallization from hexane as described in method A. Gaseous ligands such as CO or PF_3 were either bubbled through or passed over hexane solutions of the phosphine adducts for as long as necessary to produce a color change indicative of ligand replacement (usually 10–30 s). The CO and PF_3 adducts sublime at reduced pressure between 20 and 70 °C, thus providing a convenient method to purify these compounds. The sublimates were then recrystallized from hexane at −90 °C. Yields range from 80 to 95%.

Method D. Carbonyl adducts can be produced without first making the phosphine adduct for all of the carbonylbis(pentadienyl)metal complexes of vanadium and titanium by exposing the reaction mixture of the divalent metal chloride complex to CO subsequent to the addition of the pentadienyl anion. The product yields were typically quite low (10–30%); however, this method was particularly useful for producing carbonyl adducts with unsymmetric pentadienyl ligands for which the phosphine adduct precursors were difficult to purify. Thus, a THF solution of the desired pentadienylpotassium was added dropwise to a suspension of "MCl_2" in THF cooled to −78 °C. After the reaction mixture was allowed to warm slowly to ca. −20 °C, CO was leaked into the reaction flask while the reaction mixture was allowed to continue warming until it reached ambient temperature. After the mixture had been stirred for at least an additional 1 h, the solvent was removed in vacuo and the product was extracted with hexane and then transferred to a clean flask. The solution was evaporated to dryness in vacuo and the product(s) (the unsymmetric pentadienyl ligands usually yielded more than one isomer) sublimed in vacuo onto a dry-ice-cooled cold finger, which was then transferred to a clean flask with the product(s) dissolved into pentane or hexane. The volume was reduced until the solution was near saturation at room temperature, and the product was crystallized by cooling to −20 or −90 °C.

Physical and Spectroscopic Data. Carbonylbis(pentadienyl)titanium(II), $Ti(C_5H_7)_2CO$. Lime-green feathers (decomposition >105 °C) were isolated in 92% yield from the sublimed product upon cooling a concentrated hexane solution to −20 °C (method C). The crystals were drained for 3 h and then dried in vacuo for 5 min. Anal. Calcd for $C_{11}H_{14}OTi$: C, 62.88; H, 6.88. Found: C, 61.78; H, 6.83. ^1H NMR (C_6D_6): δ 4.54 (1 H, t of m, $J = 9$ Hz), 4.29 (2 H, d of d of d, $J = 14, 12, 9$ Hz), 2.73 (2 H, d of d of d, $J = 12, 4, 2$ Hz), 0.67 (2 H, d of d, $J = 14, 4$ Hz) ppm. ^{13}C NMR (C_6H_6, solvent reference δ 128.0): δ 254.3 (CO, s), 106.2 (CH, d of d, $J = 159, 9$ Hz), 100.3 (CH, d of m, $J = 163$ Hz), 59.7 (CH_2, t of d, $J = 158, 9$ Hz) ppm. IR (hexane solution): $\nu_{CO} = 1964.2$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (295 K): 388 nm, 2700 M^{-1} cm^{-1}; 717 nm, 200 M^{-1} cm^{-1}.

Carbonylbis(3-methylpentadienyl)titanium(II), $Ti(3\text{-}C_6H_9)_2CO$. Green feathers (decomposition >118 °C) were isolated in 90% yield upon cooling a concentrated hexane solution of the sublimed product to −20 °C (method C). The crystals were drained and then dried in vacuo for 5 min. Anal. Calcd for $C_{13}H_{18}OTi$: C, 65.56; H, 7.67. Found: C, 65.82; H, 7.93. ^1H NMR (C_6D_6, C_6D_5H reference δ 7.15): δ 4.12 (4 H, d of d, $J = 12, 13$ Hz), 2.67 (4 H, d of d, $J = 12, 4$ Hz), 1.66 (6 H, s), 0.76 (4 H, d of d, $J = 13, 4$ Hz) ppm. ^{13}C NMR (C_6D_6, solvent reference 128.0 ppm): δ 255.4 (CO, s), 113.2 (C, s), 104.6 (CH, d of m, $J = 156$ Hz), 57.9 (CH_2, t, $J = 158$ Hz), 26.3 (CH_3, q of t, $J = 127, 5$ (from $H_{2,4}$) Hz) ppm. IR (hexane solution): $\nu_{CO} = 1957.4$ cm^{-1}. UV–vis data (λ, ϵ_{max}) (295 K): 392 nm, 3000 M^{-1} cm^{-1}; 692 nm, 200 M^{-1} cm^{-1}.

Carbonylbis(pentadienyl)vanadium(II), $V(C_5H_7)_2CO$. Thin violet flakes (decomposition >150 °C) were isolated in 90% yield by crystallization of the sublimed product from a concentrated hexane solution cooled to −20 °C (method C). After draining and removing of the supernatant, the crystals were dried in vacuo for 5 min. Upon being warmed to ambient temperature, the crystals turned a dull dark purple color. This thermochromic behavior was observed to be reversible even under vacuum. Anal. Calcd for $C_{11}H_{14}OV$: C, 61.98; H, 6.62. Found: 61.66; H, 7.05. IR (hexane solution): $\nu_{CO} = 1961.9$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (hexane, 295 K): 388 nm, 2300 M^{-1} cm^{-1}; 570 nm, 185 M^{-1} cm^{-1}. UV–vis data (λ, ϵ_{max}) (3-methylpentane, 80 K): 388 nm, 3650 M^{-1} cm^{-1}; 555 nm, 280 M^{-1} cm^{-1}. UV–visible solid state (λ) (20 K): 552 nm. EPR (toluene, 20 °C): $g = 1.987$; $A_V = 79.1$ G. Magnetic susceptibility (Evans method, THF): 1.6 μ_B.

Carbonylbis(1-methylpentadienyl)vanadium(II), $V(1\text{-}C_6H_9)_2CO$. Dark-green crystals (mp 116–118 °C) were isolated in 15% yield by cooling a concentrated solution of the sublimed product in hexane to −90 °C (method D). After being drained overnight, the crystals were dried in vacuo for 5 min. Two successive crystallizations were necessary to remove another product that melted just below room temperature. The low-melting product appeared to have the same color and was presumed to be another isomer of the higher melting product; however, the lower melting product was not further characterized. X-ray-quality crystals in the form of long rectangular-shaped rods were grown from a concentrated hexane solution by slow-cooling to −20 °C. Anal. Calcd for $C_{13}H_{18}OV$: C, 64.73; H, 7.52. Found: C, 64.42; H, 7.46. IR (hexane solution): $\nu_{CO} = 1943.8$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (295 K): 396 nm, 2500 M^{-1} cm^{-1}; 587 nm, 240 M^{-1} cm^{-1}. EPR (hexane, 20 °C): $g = 1.986$; $A_V = 79.2$ G.

Carbonylbis(2-methylpentadienyl)vanadium(II), $V(2\text{-}C_6H_9)_2CO$. Dark crystals (mp 122–124 °C) were isolated in 15% yield upon cooling a concentrated blue-green hexane solution of the sublimed product to −90 °C (method D). Two successive crystallizations were necessary to remove a product that melted just below room temperature. The low-melting product appeared to have the same color and was presumed to be another isomer of the higher melting product. The crystals were drained overnight and then dried in vacuo for 5 min. Anal. Calcd for $C_{13}H_{18}OV$: C, 64.73; H, 7.52. Found: C, 64.92; H, 7.51. IR (hexane solution): $\nu_{CO} = 1958.0$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (295 K): 392 nm, 2900 M^{-1} cm^{-1}; 595 nm, 180 M^{-1} cm^{-1}. EPR (hexane, 20 °C): $g = 1.986$; $A_V = 78.4$ G.

Carbonylbis(3-methylpentadienyl)vanadium(II), $V(3\text{-}C_6H_9)_2CO$. Red plates (decomposition >100 °C) were isolated in 90% yield from cooling a concentrated hexane solution of the sublimed product to −90 °C (method C). After being drained, the crystals were dried in vacuo for 5 min. X-ray-quality crystals were grown from a concentrated hexane solution by slow cooling to −20 °C. Anal. Calcd for $C_{13}H_{18}OV$: C, 64.73; H, 7.52. Found: C, 65.10; H, 7.68. IR (hexane solution): $\nu_{CO} = 1952.0$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (295 K): 393 nm, 2700 M^{-1} cm^{-1}; 551

nm, 200 M^{-1} cm^{-1}. EPR (hexane, 20 °C): $g = 1.987$, $A_V = 78.4$ G.

Carbonylbis(2,3-dimethylpentadienyl)vanadium(II), V-(2,3-C_7H_{11})$_2$CO. Dull-red crystals (decomposition >120 °C) were isolated in 10% yield upon cooling a blue-green hexane solution of the sublimed product to −90 °C (method D). Two crystallizations were necessary to remove a low-melting product, which was presumed to be another isomer of the higher melting product. Both compounds appear to be thermochromic and can be redissolved in hexane at room temperature to give the original blue-green solutions. After being drained, the crystals were dried in vacuo for 5 min without decomposition or loss of CO. Anal. Calcd for $C_{15}H_{22}OV$: C, 66.91; H, 8.23. Found: C, 67.14; H, 8.30. IR (hexane solution): $\nu_{CO} = 1945.9$ cm^{-1}. UV–visible data (λ, ϵ_{max}) (hexane, 23 °C): 403 nm, 2200 M^{-1} cm^{-1}; 576 nm, 230 M^{-1} cm^{-1}. EPR (toluene, 20 °C): $g = 1.987$, $A_V = 76.9$ G.

(Triethylphosphine)bis(pentadienyl)vanadium(II), V-(C_5H_7)$_2$P(C_2H_5)$_3$. Dark-green prisms (mp 114–115 °C) were isolated in 40% yield following two crystallizations from a saturated hexane solution cooled to −20 °C (method B). The crystals were drained and the supernatant removed before drying in vacuo for 5 min. Anal. Calcd for $C_{16}H_{29}PV$: C, 63.36; H, 9.64. Found: C, 63.28; H, 9.79. EPR (toluene, 20 °C): $g = 1.985$; $A_V = 78.4$ G; $A_P = 26.4$ G. Magnetic susceptibility (Evans method, THF): 1.6 μ_B.

(Trimethylphosphine)bis(pentadienyl)vanadium(II), V(C_5H_7)$_2$P(CH_3)$_3$. Green needles (mp 121–123 °C) were isolated in 50% yield from a concentrated hexane solution after slow-cooling to −20 °C (method B). After draining and removing of the supernatant, the crystals were dried in vacuo for 5 min. Anal. Calcd for $C_{13}H_{23}PV$: C, 59.77; H, 8.87. Found: C, 59.89; H, 8.78. EPR (toluene, 20 °C): $g = 1.975$; $A_V = 77.7$ G; $A_P = 29.7$ G.

(Trimethyl phosphite)bis(pentadienyl)vanadium(II), V(C_5H_7)$_2$P(OCH_3)$_3$. Green bar-shaped crystals (mp 113–114 °C) were isolated in 85% yield from a saturated hexane solution after slow cooling to −20 °C (method C). The crystals were drained and the supernatant removed before drying in vacuo for 5 min. Anal. Calcd for $C_{13}H_{23}O_3PV$: C, 56.11; H, 8.33. Found: C, 55.89; H, 7.86. EPR (toluene, 20 °C): $g = 1.986$; $A_V = 78.0$ G; $A_P = 38.8$ G. Magnetic susceptibility (Evans method, THF): 1.4 μ_B.

(Trifluorophosphine)bis(pentadienyl)vanadium(II), V-(C_5H_7)$_2$PF_3. Violet needles (decomposition >180 °C) were isolated in 95% yield from the sublimed product following recrystallization from a concentrated hexane solution cooled to −20 °C (method C). The crystals were drained, and the supernatant was removed before drying in vacuo for 5 min. Anal. Calcd for $C_{10}H_{14}F_3PV$: C, 43.97; H, 5.17. Found: C, 44.14; H, 5.39. EPR (toluene, 20 °C): $g = 1.987$; $A_V = 77.7$ G; $A_P = 47.6$ G.

(Triethylphosphine)bis(3-methylpentadienyl)vanadium(II), V(3-C_6H_9)$_2$P(C_2H_5)$_3$. Dark-green prisms (mp 90–91 °C) were isolated in 40% yield from a saturated hexane solution cooled to −20 °C following two crystallizations of the product (method B). The crystals were drained, and the supernatant was removed before drying in vacuo for 5 min. Anal. Calcd for $C_{13}H_{18}OV$: C, 65.24; H, 10.04. Found: C, 65.39; H, 10.14. EPR (toluene, 20 °C): $g = 1.985$; $A_V = 77.3$ G; $A_P = 28.8$ G.

(Trimethyl phosphite)bis(3-methylpentadienyl)vanadium(II), V(3-C_6H_9)$_2$P(OCH_3)$_3$. Dark-green feathers (mp 125–126 °C) were isolated in 85% yield from a concentrated pentane solution cooled to −20 °C (method C). The crystals were drained and dried in vacuo for 5 min. Anal. Calcd for $C_{15}H_{27}O_3PV$: C, 53.42; H, 8.07. Found: C, 52.81; H, 8.40. EPR (toluene, 20 °C): $g = 1.986$, $A_V = 77.5$ G; $A_P = 41.8$ G.

(Trifluorophosphine)bis(3-methylpentadienyl)vanadium(II), V(3-C_6H_9)$_2$PF_3. Red plates (decomposition >160 °C) were isolated in 95% yield after cooling a filtered hexane solution of the sublimed product to −90 °C (method C). The crystals were drained, and the supernatant was removed before drying in vacuo for 5 min. Anal. Calcd for $C_{12}H_{18}F_3PV$: C, 47.85; H, 6.02. Found: C, 48.55; H, 6.27. EPR (hexane, 20 °C): $g = 1.987$; $A_V = 76.7$ G; $A_P = 51.4$ G.

(Triethylphosphine)bis(2,4-dimethylpentadienyl)vanadium(II), V(2,4-C_7H_{11})$_2$P(C_2H_5)$_3$. Orange needles (mp 41–43 °C) were isolated in 60% yield from a pentane solution cooled to −90 °C after direct addition of triethylphosphine to V(2,4-C_7H_{11})$_2$ (method A). The crystals were drained for at least 4 h, after which time the supernatant was removed and the crystals were allowed to dry under a stream of nitrogen. Evacuation resulted in rapid loss of triethylphosphine as evident from the formation of a green oil. Anal. Calcd for $C_{20}H_{37}PV$: C, 66.83; H, 10.37. Found: C, 66.87; H, 9.98. EPR (toluene, 20 °C): $g = 1.984$; $A_V = 77.8$ G; $A_P = 32.7$ G.

(Trimethylphosphine)bis(2,4-dimethylpentadienyl)vanadium(II), V(2,4-C_7H_{11})$_2$P(CH_3)$_3$. Large black plates (mp 113–115 °C) were prepared by the direct addition method (method A) and isolated in 90% yield from a hexane solution cooled to −20 °C. After being drained for 20 min, the supernatant was removed and the crystals were dried in vacuo for 3–5 min. Anal. Calcd for $C_{17}H_{31}PV$: C, 64.34; H, 9.85. Found: C, 64.48; H, 9.59. EPR (toluene, 20 °C): $g = 1.985$; $A_V = 77.6$ G; $A_P = 32.5$ G. Magnetic susceptibility (Evans method, THF): 1.4 μ_B.

(Trimethyl phosphite)bis(2,4-dimethylpentadienyl)vanadium(II), V(2,4-C_7H_{11})$_2$P(OCH_3)$_3$. Fine, dark-green needles (mp 69–70 °C) were prepared by the direct addition method (method A) and isolated in 85% yield from a saturated pentane solution cooled to −20 °C. After being drained for 4 h, the supernatant was removed and the crystals were dried in vacuo for 3–5 min. Anal. Calcd for $C_{17}H_{31}O_3PV$: C, 55.89; H, 8.55. Found: C, 55.96; H, 8.79.

EPR (toluene, 20 °C): $g = 1.985$; $A_V = 77.9$ G; $A_P = 41.2$ G. Magnetic susceptibility (Evans method, THF): 1.5 μ_B.

[1,2-Bis(dimethylphosphino)ethane]bis(2,4-dimethylpentadienyl)vanadium(II), V(2,4-C_7H_{11})$_2$(dmpe). Golden microcrystals were prepared by the direct addition method (method A) and isolated in 90% yield from a hexane solution cooled to −90 °C. After being drained 4 h, the crystals were dried in vacuo for 5 min. Larger crystals with a dark-brown appearance (mp 139–140 °C) were grown by slow cooling a 60/40 hexane/toluene solution of the compound to 0 °C. The compound appeared to be only sparingly soluble in hexane. Anal. Calcd for $C_{20}H_{38}P_2V$: C, 64.55; H, 9.56. Found: C, 64.56; H, 9.72. EPR (toluene, 20 °C): $g = 1.985$; $A_V = 78.3$ G; $A_P = 29.5$ G.

Collection of X-ray Data. Crystal data for structures 1–3 are collected in Table I. Crystals were mounted in glass capillaries due to their instability in air. Exact cell constants and orientation matrices were determined by the least-squares refinement of 25 high-angle reflections ($20 \leq 2\theta \leq 25$). Data were collected on a Nicolet R3m diffractometer with a graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections (XEMP, 6 reflections, 216 data, ψ scan) were applied to 1 and 2, but no correction for 3 was required from the low ratio of maximum/minimum transmission.

Solution and Structure Refinement. 1–3 were solved by direct methods (SOLV) which located the V atom in each structure. Locations of the remaining non-hydrogen atoms were determined through subsequent Fourier syntheses and least-squares refinement. Hydrogen atoms in 1–3 were calculated and fixed ($U_H = 1.2U$ of adjacent C; d(C–H) = 0.96 Å). All non-hydrogen atoms were refined anisotropically. All computer programs used for data collection and structure refinement are from the Nicolet P3 (Nicolet XRD, Madison, WI) and SHELXTL (Sheldrick, 1984) program libraries.

Figures 1–3 depict the structures and numbering schemes of 1–3, respectively. Tables II–IV contain the atomic coordinates for 1–3, respectively. Selected bond distances and angles are given in Table V.

Results and Discussion

Several routes have been developed for the preparations of 16-electron ligand adducts of open titanocenes and 17-electron ligand adducts of open vanadocenes. In cases for which the free open metallocene is isolable, e.g., M(2,4-C_7H_{11})$_2$ (M = Ti, V), its direct combination with the ligand may be most convenient, as has already been reported for a variety of Ti(2,4-C_7H_{11})$_2$(L) (L = CO, PF_3, PMe$_3$, PEt$_3$, P(OMe)$_3$, P(OEt)$_3$)[5,10] and V(2,4-C_7H_{11})$_2$(L) (L = CO, PF_3)[10] compounds. Thus, through this approach a number of new open vanadocene adducts may be obtained (eq 1).

$$\mathrm{V(2,4\text{-}C_7H_{11})_2 + L \rightarrow V(2,4\text{-}C_7H_{11})_2(L)} \qquad (1)$$

$$\mathrm{L = PMe_3,\ PEt_3,\ P(OMe)_3,\ dmpe}$$

Table I. Crystal Data

	1	2	3
formula	$C_{12}H_{18}V(CO)$	$C_{14}H_{22}V(CO)$	$C_{12}H_{18}V(CO)$
mol wt	241.23	269.28	241.23
cryst system	tetragonal	orthorhombic	orthorhombic
space group	$P\bar{4}2_1c$	$P2_12_12_1$	$Pbca$
a, Å	19.173 (8)	9.933 (6)	11.179 (4)
b, Å	19.173 (8)	10.013 (5)	14.016 (5)
c, Å	6.753 (2)	14.612 (7)	15.797 (5)
V, Å^3	2483 (1)	1453 (1)	2475 (2)
Z	8	4	8
ρ_{calc}, g cm^{-3}	1.28	1.23	1.29
μ, cm^{-1}	8.07	6.96	8.10
temp, °C	23	23	23
cryst dimens, mm	0.20 × 0.20 × 0.42	0.23 × 0.23 × 0.45	0.25 × 0.22 × 0.40
scan speed, deg/min	variable 5–20	variable 7–20	variable 6–20
scan range, deg	$4 \leq 2\theta \leq 50°$	$4 \leq 2\theta \leq 50°$	$4 \leq 2\theta \leq 48°$
scan type	θ–2θ	θ–2θ	Ω
octants collcd (h,k,l)	+23,+23,+9	+12,+12,+18	+13,+17,+19
no. of data collcd	1354	1533	2079
no. of indpdnt data	1256	1187	1764
no. of observed data	824 ($F_o \geq 5\sigma$)	1137	1096 ($F_o \geq 4\sigma$)
std rflns	3 std/197 rflns (940, 190, 243)	3 std/197 reflns (118, 054, 501)	3 std/197 reflns (512, 273, 218)
R_F, %	5.72	7.70	6.95
R_{wF}, %	5.80	10.84	6.96
GOF	1.323	1.946	1.647
N_o/N_v	824/136	1137/154	1096/136
Δ/σ	0.024	0.007	0.011
min, max $\Delta(\rho)$, e Å^{-3}	−0.327, 0.332	−0.478, 0.713	−0.637, 0.555

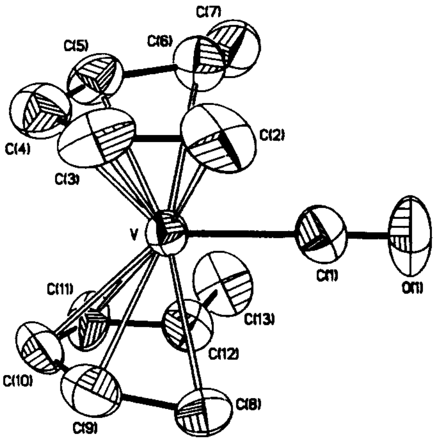


Figure 1. $V(1\text{-}C_6H_9)_2CO$ (1) molecular structure and numbering scheme with thermal ellipsoids drawn at the 40% level.

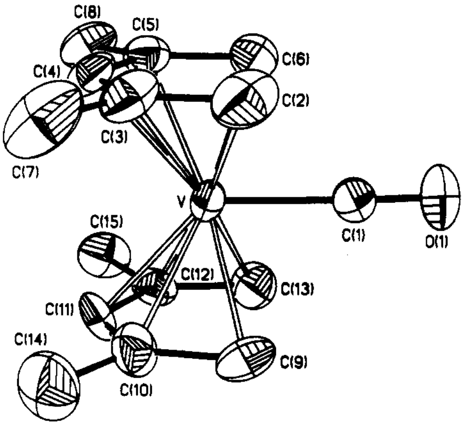


Figure 2. $V(2,4\text{-}C_7H_{11})_2CO$ (2) molecular structure and numbering scheme with thermal ellipsoids drawn at the 40% level.

However, as with the related $Ti(2,4\text{-}C_7H_{11})_2(L)$ complexes,[5] this reaction is reversible, in large part due to the CH_3-CH_3 interactions which result from a syn-eclipsed structure (vide infra).

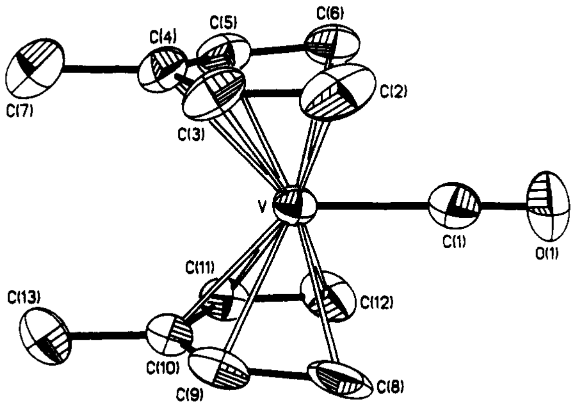


Figure 3. $V(3\text{-}C_6H_9)_2CO$ (3) molecular structure and numbering scheme with thermal ellipsoids drawn at the 40% level.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 1

	x	y	z	U^a
V	307.2 (6)	2264.2 (6)	2461 (4)	40.2 (4)
C(1)	−87 (6)	2823 (6)	4572 (16)	58 (4)
O(1)	−314 (4)	3156 (4)	5815 (11)	93 (4)
C(2)	−121 (8)	1384 (8)	4361 (20)	74 (6)
C(3)	127 (5)	1121 (4)	2616 (23)	65 (4)
C(4)	−29 (8)	1369 (8)	687 (21)	65 (5)
C(5)	−496 (5)	1928 (5)	261 (16)	60 (4)
C(6)	−890 (5)	2314 (5)	1537 (15)	57 (4)
C(7)	−1282 (6)	2949 (6)	833 (17)	85 (5)
C(8)	1307 (7)	2375 (7)	4401 (18)	75 (6)
C(9)	1440 (4)	2064 (4)	2647 (20)	62 (3)
C(10)	1264 (7)	2310 (6)	735 (20)	56 (4)
C(11)	908 (5)	2915 (5)	290 (16)	65 (4)
C(12)	651 (5)	3410 (5)	1578 (15)	60 (4)
C(13)	173 (6)	3995 (5)	947 (18)	84 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The corresponding complexes of otherwise unisolable open vanadocenes[4] may be prepared by the reaction of a divalent vanadium(II) complex with 2 equiv of pentadienyl anions in the presence of a phosphine, as has been reported for $V(C_5H_7)_2(PEt_3)$.[11] Thus, $V(C_5H_7)_2(PMe_3)$ and V(3-

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	*y*	*z*	*U*[a]
V	7267 (2)	82 (2)	661 (1)	43 (1)
O(1)	6128 (15)	−665 (12)	−1195 (6)	135 (6)
C(1)	6593 (14)	−398 (14)	−521 (8)	83 (5)
C(2)	4981 (11)	−21 (16)	859 (9)	86 (5)
C(3)	5561 (11)	213 (13)	1726 (7)	68 (4)
C(4)	6639 (12)	−592 (12)	2070 (7)	62 (4)
C(5)	7311 (12)	−1712 (10)	1649 (7)	57 (4)
C(6)	7005 (17)	−2198 (11)	724 (8)	83 (5)
C(7)	5123 (18)	1282 (16)	2298 (10)	107 (6)
C(8)	8487 (15)	−2303 (13)	2173 (9)	78 (5)
C(9)	7235 (15)	2062 (10)	−98 (8)	77 (5)
C(10)	7774 (13)	2272 (11)	788 (8)	68 (4)
C(11)	8912 (11)	1462 (10)	1120 (7)	54 (4)
C(12)	9540 (11)	361 (10)	670 (7)	61 (4)
C(13)	9182 (12)	−89 (13)	−214 (7)	70 (4)
C(14)	7308 (18)	3386 (12)	1390 (11)	103 (7)
C(15)	10625 (12)	−397 (12)	1180 (10)	76 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 3

	x	*y*	*z*	*U*[a]
V	728 (1)	2062 (1)	1261 91)	33 (1)
C(1)	1038 (9)	743 (8)	998 (6)	58 (4)
O(1)	1221 (8)	−40 (5)	848 (5)	106 (4)
C(2)	761 (8)	2088 (8)	−189 (5)	63 (4)
C(3)	423 (8)	2969 (8)	130 (6)	53 (3)
C(4)	−499 (8)	3183 (6)	691 (5)	49 (3)
C(5)	−1174 (8)	2480 (7)	1119 (6)	49 (3)
C(6)	−1170 (8)	1495 (7)	992 (6)	57 (4)
C(7)	−769 (10)	4212 (7)	912 (7)	85 (5)
C(8)	2748 (8)	1946 (7)	1391 (6)	66 (4)
C(9)	2356 (8)	2863 (7)	1637 (5)	50 (3)
C(10)	1480 (8)	3076 (6)	2236 (6)	49 (3)
C(11)	752 (9)	2405 (6)	2633 (6)	46 (3)
C(12)	819 (9)	1411 (6)	2587 (5)	59 (4)
C(13)	1252 (11)	4129 (6)	2449 (7)	80 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$C_6H_9)_2(PEt_3)$ may also be prepared in a similar manner (eq 2). Once isolated, these compounds serve as useful

$$\tfrac{1}{2}V_2Cl_6Zn(THF) + 2KPdl + L \rightarrow V(Pdl)_2(L) \quad (2)$$

$$Pdl = C_5H_7,\ L = PMe_3;\ Pdl = 3\text{-}C_6H_9,\ L = PEt_3$$

starting materials for the preparations of adducts with more strongly bound ligands (eq 3). Similar reactions can be used to prepare analogous titanium carbonyls from the known PEt_3 adducts[5] (eq 4).

$$V(Pdl)_2(PEt_3) + L \rightarrow V(Pdl)_2(L) + PEt_3 \quad (3)$$

$$Pdl = C_5H_7,\ 3\text{-}C_6H_9;\ L = CO,\ PF_3,\ P(OMe)_3$$

$$Ti(Pdl)_2(PEt_3) + CO \rightarrow Ti(Pdl)_2(CO) \quad (4)$$

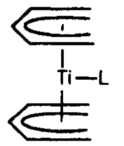
$$Pdl = C_5H_7,\ 3\text{-}C_6H_9$$

Related attempts to prepare phosphine adducts of open vanadocenes possessing unsymmetric pentadienyl ligands ($1\text{-}C_6H_9$, $2\text{-}C_6H_9$, $2,3\text{-}C_7H_{11}$) encountered difficulties due to the oily nature of the products. However, carbonyl adducts of these species can be isolated, although generally in low yields, by a more direct route (eq 5).

$$V_2Cl_6Zn(THF) + 2KPdl + CO \rightarrow V(Pdl)_2(CO) \quad (5)$$

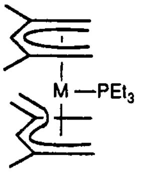
$$Pdl = 1\text{-}C_6H_9,\ 2\text{-}C_6H_9,\ 2,3\text{-}C_7H_{11}$$

The 16-electron titanium compounds $Ti(Pdl)_2(CO)$ (Pdl = C_5H_7, $3\text{-}C_6H_9$) are diamagnetic, and their ^1H and ^{13}C NMR spectra reflect the high (C_{2v}) symmetry expected for the syn-eclipsed conformation (I) and demonstrated by



I

structural studies on several $Ti(2,4\text{-}C_7H_{11})_2(PX_3)$ (X = F, CH_3, OCH_3) compounds.[12] The analogous 17-electron vanadium compounds, however, are paramagnetic, and hence structural studies were required to reveal that they too adopted the expected structural pattern of I (vide infra), rather than the less symmetric alternative II, which

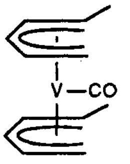


II

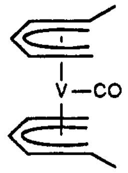
is adopted by $M(2,4\text{-}C_7H_{11})_2(PEt_3)$ (M = Mo, W) complexes.[12b,13] As the ESR spectrum of $V(2,4\text{-}C_7H_{11})_2(dmpe)$ revealed coupling of the unpaired electron to only one phosphorus nucleus, the general structure I may again be assigned, rather than an alternative such as $V(\eta^5\text{-}2,4\text{-}C_7H_{11})(\eta^3\text{-}2,4\text{-}C_7H_{11})(\eta^2\text{-dmpe})$.

Structural Studies

The solid-state structures of the $V(Pdl)_2CO$ (Pdl = $1\text{-}C_6H_9$, $2,4\text{-}C_7H_{11}$, $3\text{-}C_6H_9$) compounds, **1**–**3**, are presented in Figures 1–3, while various bonding parameters are contained in Tables II–V. It can be seen that all three complexes adopt the syn-eclipsed structural pattern (I) observed for various titanium and zirconium analogues, rather than the less symmetric alternative (II), which characterizes molybdenum and tungsten.[12,13] While none of the compounds possess any crystallographically imposed symmetry, the structural parameters for **1**–**3** correspond in general fairly closely to that expected (C_s, C_{2v}, and C_{2v}, respectively). Interestingly, the isolated isomer of the $1\text{-}C_6H_9$ compound corresponds to the ideal C_s form (III),



III



IV

rather than the C_2 form (IV). However, the V–C bonding parameters for the pentadienyl fragments in **1** exhibit essentially C_{2v} symmetry within experimental error and will therefore be considered as such. For purposes of discussion, bonding parameters involving the terminal carbon atoms will have these atoms cited as C[1,5], while those for the formally uncharged and central carbon atoms will be cited as C[2,4] and C[3], respectively.

The bonding parameters for the ligands themselves are not unusual. The external C–C bonds range from 1.35 to

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(11) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860.

(12) (a) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Ziegler, M. L. Manuscript in preparation. (b) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.

(13) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016.

Table V. Selected Bond Distances (Å) and Angles (deg) for 1–3

1		2		3	
		(a) V-CO			
V–C(1)	1.937 (11)	V–C(1)	1.927 (12)	V–C(1)	1.926 (11)
C(1)–O(1)	1.141 (13)	C(1)–O(1)	1.107 (16)	C(1)–O(1)	1.141 (13)
V–C(1)–O(1)	179.4 (10)	V–C(1)–O(1)	177.0 (14)	V–C(1)–O(1)	179.5 (10)
		(b) V-Pdl			
V–C(2)	2.274 (15)	V–C(2)	2.295 (11)	V–C(2)	2.291 (8)
V–C(3)	2.221 (8)	V–C(3)	2.286 (11)	V–C(3)	2.219 (10)
V–C(4)	2.189 (15)	V–C(4)	2.256 (10)	V–C(4)	2.272 (9)
V–C(5)	2.234 (10)	V–C(5)	2.317 (10)	V–C(5)	2.217 (9)
V–C(6)	2.238 (9)	V–C(6)	2.300 (11)	V–C(6)	2.304 (9)
V–C(8)	2.332 (14)	V–C(9)	2.258 (11)	V–C(8)	2.274 (9)
V–C(9)	2.209 (8)	V–C(10)	2.271 (12)	V–C(9)	2.220 (9)
V–C(10)	2.175 (13)	V–C(11)	2.244 (11)	V–C(10)	2.258 (9)
V–C(11)	2.244 (10)	V–C(12)	2.277 (11)	V–C(11)	2.220 (9)
V–C(12)	2.369 (9)	V–C(13)	2.288 (11)	V–C(12)	2.287 (9)
		(c) Pdl			
C(2)–C(3)	1.37 (2)	C(2)–C(3)	1.38 (2)	C(2)–C(3)	1.39 (1)
C(3)–C(4)	1.42 (2)	C(3)–C(4)	1.42 (2)	C(3)–C(4)	1.39 (1)
C(4)–C(5)	1.43 (2)	C(4)–C(5)	1.43 (2)	C(4)–C(5)	1.41 (1)
C(5)–C(6)	1.36 (1)	C(5)–C(6)	1.45 (2)	C(5)–C(6)	1.40 (1)
C(8)–C(9)	1.35 (2)	C(9)–C(10)	1.40 (2)	C(8)–C(9)	1.41 (1)
C(9)–C(10)	1.42 (2)	C(10)–C(11)	1.48 (2)	C(9)–C(10)	1.39 (1)
C(10)–C(11)	1.38 (1)	C(11)–C(12)	1.40 (1)	C(10)–C(11)	1.39 (1)
C(11)–C(12)	1.38 (1)	C(12)–C(13)	1.41 (1)	C(11)–C(12)	1.40 (1)
C(2)–C(3)–C(4)	127 (1)	C(2)–C(3)–C(4)	122 (1)	C(2)–C(3)–C(4)	128.7 (9)
C(3)–C(4)–C(5)	125 (1)	C(3)–C(4)–C(5)	130 (1)	C(3)–C(4)–C(5)	123.4 (8)
C(4)–C(5)–C(6)	129 (1)	C(4)–C(5)–C(6)	124 (1)	C(4)–C(5)–C(6)	128.2 (8)
C(8)–C(9)–C(10)	127 (1)	C(9)–C(10)–C(11)	119 (1)	C(8)–C(9)–C(10)	126.9 (9)
C(9)–C(10)–C(11)	127 (1)	C(10)–C(11)–C(12)	129 (1)	C(9)–C(10)–C(11)	124.8 (9)
C(10)–C(11)–C(12)	128 (1)	C(11)–C(12)–C(13)	124 (1)	C(10)–C(11)–C(12)	128.2 (9)
		(d) Pdl-Me			
C(6)–C(7)	1.51 (1)	C(3)–C(7)	1.44 (2)	C(4)–C(7)	1.52 (1)
C(12)–C(13)	1.51 (1)	C(5)–C(8)	1.51 (2)	C(10)–C(13)	1.53 (1)
		C(10)–C(14)	1.46 (2)		
		C(12)–C(15)	1.51 (2)		

1.45 Å, averaging 1.392 (8) Å, and appear slightly shorter than the internal C–C bonds, which range from 1.38 to 1.48 Å, averaging 1.413 (8) Å. This is the usual situation,[14] in accord with a contribution from resonance hybrid V. For

V

V(1-C_6H_9)$_2$(CO), the three C–C–C bond angles are reasonably similar to one another (Table V). It is generally observed that methyl substituents will lead to contractions of the angles about the atoms to which they are attached.[14] However, the effect for V(3-C_6H_9)$_2$(CO) appears small, whereas, for V(2,4-C_7H_{11})$_2$(CO), contractions of ca. 5.5° are observed and actually seem somewhat offset by an expansion about the central carbon atom (Table V). It is interesting to note that substituent tilts (vida infra) follow a similar pattern, the effect for the 3-position being smaller than those for the 2- and 4-positions. The relative degrees of contraction for the ligands are also illustrated well by the C1- -C5 separations and again correlate with the total number of methyl groups, being 3.00, 2.97, and 2.94 Å for 0–2 internal methyl groups, respectively. Despite the eclipsing orientation of the methyl groups in V(2,4-C_7H_{11})$_2$(CO), they still are bent slightly (average 1.8°) out of the dienyl plane toward the metal atom. However, in noneclipsing situations, tilts of ca. 6–12° are more normal and have been ascribed to an attempt by the ligand to point its p orbitals more toward the metal atom.[12b,14] An even greater tilt is generally experienced by the exo substituents on the terminal carbon atoms, and that is observed for the methyl groups in 1 (average 7.9°), although only to perhaps half the usual degree. However, tilts for the 3-position tend to be the smallest, and for 3 their eclipsing orientation leads to an average 3.1° tilt *away from* the metal.[15]

While V(2,4-C_7H_{11})$_2$ experiences a significant tilt between the two dienyl ligand planes (13.9°),[16] its carbonyl adduct does not (0.1°), although the tilt becomes larger for the 3-methyl and 1-methyl analogues, 3.0 vs. 13.0°, respectively. The relatively large tilt for the latter compound entails an increased separation of the terminal carbon atoms (especially those bearing a methyl substituent) away from one another, which for the other two compounds would probably be opposed by unfavorable methyl–methyl interactions.

In comparing the M–C parameters for the three compounds (Table V), one observes several general trends. First, the V–C and C–O bonds are all reasonably similar, averaging[17] 1.930 (7) and 1.130 (8) Å, respectively, for the

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[14] Ernst, R. D. *Struct. Bonding* (*Berlin*) **1984**, *57*, 1.

[15] (a) The relative tendencies to tilt toward the metal plane may have a geometric origin, as the most internal (central) atoms' substituents tilt the least, while the exo substituents on the outermost (C[1,5]) atoms tilt the most. In cases for which the substituents are methyl groups, occasionally the attached dienyl carbon atom(s) also appear to be pulled slightly beneath the dienyl plane. The actual CH_3- -CH_3 nonbonded contact distances are 3.437 (28) Å for 1, 3.203 (33) and 3.303 (39) Å for 2, and 3.319 (26) Å for 3, all less than the 4.0-Å sum of their van der Waals radii.[15b] (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[16] Campana, C. F.; Ernst, R. D.; Wilson, D. R.; Liu, J.-Z. *Inorg. Chem.* **1984**, *23*, 2732.

[17] Except for the C–C bonding parameters, the esd's accompanying average values reflect the uncertainties in the averages themselves but not necessarily the distributions of the individual data.

Table VI. C–O Stretching Frequencies (cm^{-1}) for the Monocarbonyl Adducts of Open Titanocenes and Open Vanadocenes (Hexane Solution)

methylated positions	Ti	V	methylated positions	Ti	V
	1964.2	1961.9	3	1957.4	1952.0
1		1943.8	2, 3		1945.9
2		1958.0	2, 4	1951.7	1948.3

three compounds. For the dienyl ligands, the longest bond(s) in a given position occur for the sites which are methylated. Such influences have been observed before, although not invariably,[12b,14] and have counterparts in metal diene chemistry.[6,18] Overall, however, the V–C[1,5] bonds, ranging from 2.285 to 2.303 Å, are longest, while the V–C[3] ones (2.182–2.265 Å) are shortest. In contrast, for $V(2,4\text{-}C_7H_{11})_2$ the V–C[1,5] bonds are shortest. The lengthening in the carbonyl adducts may readily be attributed to the close proximity of the carbonyl ligand to the C[1,5] atoms. Interestingly, the range of V–C[1,5] distances is notably smaller than those for the other positions, perhaps an indication that these distances are determined primarily by the nonbonded repulsions occurring between the C[1,5] and carbonyl carbon atoms (i.e., the contacts prevent an otherwise possible closer approach).

For $V(1\text{-}C_6H_9)_2(CO)$, the V–C[1,5] bonds are significantly longer than those for the internal carbon atoms (Table V). This could arise from two somewhat related factors. First, the terminal carbon atoms are situated near the carbonyl ligand, which could inhibit a close approach to the metal as well as leading to the observed tilt between dienyl planes (vida supra). The central carbon atom is closest to the metal, quite likely as a result of this tilt between planes. Notably, for the other methyl-substituted compounds the V–C[3] bonds are significantly lengthened, a possible consequence of the differences in tilts between the dienyl ligand planes. Additionally, significant lengthenings of the internal V–C bonds are observed upon methylation,[19] by ca. 0.061 (8) and 0.083 (12) Å for the [3]- and [2,4]-positions, respectively. Such lengthenings are also observed in metal diene complexes[18] but not invariably in dienyl compounds.[20]

Infrared Spectral Studies. Just as methylation of a cyclopentadienyl ligand in a metal carbonyl complex brings about a decrease in the C–O stretching frequency,[21] brought about by the partial transfer of electrons into the C–O π^* orbitals through π back-bonding interactions, one would expect methylation of pentadienyl ligands to bring about similar results. However, pentadienyl ligands possess three types of carbon atoms, one unchanged (2,4), the other two (1,5 and 3) charged. Hence, the situation is clearly more complicated and one could expect to observe a useful correlation between the position of substitution and the relative decrease in C–O frequency.

From the data in Table VI, one can see some apparent differences in the relative frequency decreases as a function of the position of methylation. Methylation of the 1-position clearly produces the greatest decrease, 9.0 cm^{-1} per substituent. Methylations of the formally uncharged 2-positions (0 → 2, 3 → 2,3, 0 → 2,4, 2 → 2,4) bring about decreases of 2.0, 3.0, 3.4, and 4.8 cm^{-1} per substituent, averaging 2.9 cm^{-1}, the lowest effect. For the 3-position, an intermediate average (5.5 cm^{-1}) is observed, derived from values of 5.0 and 6.0 cm^{-1} per substituent (0 → 3, 2 → 2,3). One therefore observes that methylations of the formally charged 1-, 3-, and 5-positions are more effective in transferring electron density to the VCO fragment than are methylations of the formally uncharged positions. The greater effect of the 1,5-positions could be attributed to the greater tilts of these substituents below the dienyl planes (vida supra), which appear to lead to greater overlap of the metal and C(1,5) orbitals (see VI). It is also interesting to compare these decreases to that observed on methylation of a cyclopentadienyl ligand. As the C–O stretching frequency for $V(C_5Me_5)_2CO$ is ca. 39 cm^{-1} lower than that of $V(C_5H_5)_2CO$, an average decrease of 3.9 cm^{-1} per substituent is obtained,[11,22] a little less than the weighted average of 5.9 cm^{-1} for the dienyl ligands and nominally falling between the open dienyl ligand values for the formally charged and uncharged positions, as might be expected on the basis of idealized relative charges.

Table VII. Isotropic ESR Data for Open Vanadocenes and Their Mono(ligand) Adducts, $V(Pdl)_2(L)$[a]

L	parm	Pdl		
		C_5H_7	$3\text{-}C_6H_9$	$2,4\text{-}C_7H_{11}$
	g	1.976	1.977	1.974
	A_V	77.0	75.4	76.5
CO[b]	g	1.987	1.987	1.986
	A_V	79.1	78.4	78.4
PF_3	g	1.987	1.987	1.987
	A_V	77.7	76.7	76.7
	A_P	47.6	51.4	53.6
$P(OMe)_3$	g	1.986	1.986	1.985
	A_V	78.0	77.5	77.9
	A_P	38.7	41.8	41.2
PMe_3	g	1.985		1.985
	A_V	77.7		77.6
	A_P	29.7		32.5
PEt_3	g	1.985	1.985	1.984
	A_V	78.4	77.3	77.8
	A_P	26.4	28.8	32.7

[a] Hyperfine couplings are given in Gauss units. [b] For the unsymmetric complexes having Pdl = $1\text{-}C_6H_9$, $2\text{-}C_6H_9$, and $2,3\text{-}C_7H_{11}$, the g values are all 1.986, while the A_V values are 79.2, 78.4, and 76.9 G, respectively.

EPR Spectroscopic Studies. As the vanadium complexes possess 17-electron configurations, additional characterization by EPR spectroscopy has been obtained. Selected data appear in Table VII and provide further insight into the electronic structures of these compounds. For the most part, the g values are relatively uninformative, although the values for the CO and various phosphine adducts (1.984–1.987) are greater than those for the free $V(Pdl)_2$ (Pdl = C_5H_7, $3\text{-}C_6H_9$, $2,4\text{-}C_7H_{11}$) complexes (1.974–1.977) and less than those for $V(C_5H_5)_2CO$ and $V(C_5Me_5)_2CO$ (2.004–2.005).[23] The A_V values for the $V(Pdl)_2CO$ compounds fall in the range 77–79 G, significantly greater than those for $V(C_5H_5)(C_5H_7)CO$ or $V(C_5H_5)_2CO$ (63 and 28 G, respectively).[11,23] The trend in A_V

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(18) Ernst, R. D.; Melendez, E.; Stahl, L.; Ziegler, M. L. *Organometallics* **1991**, *10*, 3635.

(19) While the V–C[1,5] bond lengths are longer for $V(1\text{-}C_6H_9)_2CO$ than those for the other two compounds, this does not seem to arise from a geometric or electronic effect on the dienyl ligands, as there is no obvious trend involving the bond distances for the methylated (C6, C12) and unmethylated (C2, C8) ends of the $1\text{-}C_6H_9$ ligand.

(20) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.

(21) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 167.

(22) (a) Calderazzo, F.; Fachinetti, G.; Florinani, C. *J. Am. Chem. Soc.* **1974**, *96*, 3695. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739. (c) Facinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046. (d) The smaller decrease for the C_5Me_5 ligand might derive from the fact that its methyl groups are tilted away from the metal.

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

parallels the trend in C–O stretching frequencies for the $V(C_5H_5)_x(C_5H_7)_{2-x}(CO)$ (x = 0–2) compounds (1962, 1938,[11] and 1893 cm^{-1}). In each case, the increase on replacement of the first C_5H_5 ligand in vanadocene carbonyl by a pentadienyl ligand is generally greater than that brought about by a second replacement, which could be understood on the basis of the greater accepting ability of the pentadienyl ligand.[12b,23] While $V(C_5H_5)_2CO$ is relatively electron rich, replacement of C_5H_5 by C_5H_7 leads to a significantly less electron-rich vanadium center, which then is less cooperative in releasing electron density once the second open ligand is incorporated. This readily could explain the various A_V values, as replacement of C_5H_5 ligands by C_5H_7 will lead to a more positively charged metal center, which then will exert a greater attraction for the unpaired electron, and result in the observed increases in A_V values. However, the vanadium hyperfine couplings are also dependent upon the relative 4s orbital contribution to the singly occupied molecular orbital, and molecular orbital studies, while supporting the proposal that pentadienyl ligands are better acceptors in these compounds than cyclopentadienyl, also have been interpreted as indicating a correlation between the 4s contribution and the vanadium hyperfine splittings.[23]

Additional comparisons may be made for the various phosphine ligands (Table VII). It can be seen that for a given Pdl ligand, the values of A_P increase for L = $PEt_3 \leq PMe_3 < P(OEt)_3 < PF_3$. This would seem reasonable in that a better accepting ligand might be better able to attract the unpaired electron spin density. However, it also needs to be kept in mind that the V–P bond distances in these compounds should follow the opposite trend,[24] increasing from PF_3 to PEt_3, and this could play a role in these considerations.[12a] Notably, the rather significant increases in A_P values with phosphorus substituent electronegativity are accompanied by only much smaller decreases in the A_V value, so that relatively small delocalizations of the unpaired electron from vanadium may really be involved. Not surprisingly, perhaps, these general trends have also been observed for a variety of analogous half-open vanadocene complexes.[26]

An additional, but smaller trend occurs upon methylation of the pentadienyl ligands (Table VII). With the addition of methyl groups, the values of A_V and A_P decrease and increase, respectively. While this could be explained as an electronic effect, in which electron donation by the methyl groups renders the metal centers more electron-releasing themselves, a similar trend is also exhibited by the carbonyl adducts (see Experimental Section), except for $V(1\text{-}C_6H_9)_2CO$, whose A_V value is essentially unchanged from that of the C_5H_7 counterpart. As IR spectral results demonstrate that methylation at the 1-position actually leads to the greatest decrease in ν_{C-O}; however, this explanation does not seem entirely correct. It would seem more likely that the effect is somehow brought about by the contraction of the pentadienyl ligand which results from methylation at the 2,4- or 3-positions (but not 1,5-positions). In fact, the effect is once again also operative for analogous half-open vanadocenes.[26] While possible correlations between Pdl ligand size and A_V and A_P values could be proposed, the effect is nonetheless relatively small and additional speculation would be unwarranted.

Visible Absorption Spectra. The titanium and vanadium compounds exhibit metal-dependent absorptions in the visible range. With relatively low extinction coefficients (~200 M^{-1} cm^{-1}), these transitions would appear to be primarily d–d in nature. Interestingly, the position of this absorption shifts dramatically with temperature for at least three of these compounds, $V(C_5H_7)_2CO$, $V(2\text{-}C_6H_9)_2CO$, and $V(2,3\text{-}C_7H_{11})_2CO$, accompanied by a change in sample color. Thus, while $V(C_5H_7)_2CO$ appears blue-green at room temperature either in solution or the solid state, at −80 °C it becomes a bright red. A plot of the wavelength for the absorption maximum as a function of temperature (20–295 K, supplementary material) reveals a nearly linear relationship. A similar shift of ca. 15 nm has been observed for $V(2\text{-}C_6H_9)_2CO$ (295 vs 77 K) by Trogler.[27] Shifts of these types can readily be caused by thermal population of relatively low-lying excited vibrational states of the electronic ground state.[28]

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Supplementary Material Available: Tables of IR and mass spectral data, anisotropic thermal parameters, hydrogen atom parameters, and least-squares planes and a figure illustrating the temperature dependence of λ_{max} for the midrange visible band of $V(C_5H_7)_2CO$ (15 pages); tables of structure factors (24 pages). Ordering information is given on any current masthead page.

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(24) Structural studies of $Ti(2,4\text{-}C_7H_{11})_2(PX_3)$ (X = F, OEt, CH_3) compounds demonstrate that the Ti–P distance correlate well with the electronegativity of X but not with the Ti–P bond strength.[12a]

(25) (a) ESR studies on $VCl_4(PX_3)_2$ compounds can also be interpreted in a consistent fashion, as the greatest A_V value was observed for the phosphorus ligand having the most electronegative substituents ($P(C_6H_5)(OEt)_2$), while the smallest values of A_V were found for bulky alkylphosphines.[25b] (b) Zah-Letho, J.; Samuel, E.; Livage, J. *Inorg. Chem.* **1988**, *27*, 2233.

(26) Gedridge, R. W. Ph.D. Dissertation, University of Utah, 1987.

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