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Synthesis, Characterization, and Reactivity of (η^5-C_5H_7)V(CO)$_4$ and Its Phosphine Derivatives

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Summary: Photolysis of NaV(CO)$_6$ with 1-chloropenta-2,4-diene in tetrahydrofuran at 20 °C produces (η^5-C_5H_7)V(CO)$_4$ (**1**). Compound **1** reacts with an equimolar amount of R_3P in pentane at 0 °C and spontaneously produces (η^5-C_5H_7)V(CO)$_3$(PR_3) (PR_3 = PMe_3 (**2**), PMe_2Ph (**3**)). Treatment of **2** with excess PMe_3 gives *trans*-(η^5-C_5H_7)V(CO)$_2$(PMe_3)$_2$ (**4**). The molecular structure of **3** has been determined by an X-ray diffraction study: orthorhombic $P2_12_12_1$, a = 7.1519 (2) Å, b = 13.172 (4) Å, c = 17.479 (4) Å, Z = 4, V = 1646.7 Å^3.

Transition-metal pentadienyl complex represents one class of compounds of considerable interest in both structural bonding and chemical reactivity.[1-3] One notable feature of these compounds is the variety of bonding modes by which the ligand is linked to the metal center, viz., η^1, η^3, and η^5-complexation. The ligand is also capable of undergoing coupling reactions with metal atoms or small molecules to form metallobenzene,[4] 1,3,7,9-decatetraaene,[5] and an interesting [5 + 1] acetylation adduct.[6] The (η^5-C_5H_5)V(CO)$_4$[7] complex has long been recognized as an indispensable reagent in organovanadium chemistry. In further development of versatile metal–pentadienyl complexes, we report here the synthesis, characterization, and molecular structure of (η^5-C_5H_7)V(CO)$_4$ and its phosphine derivatives.

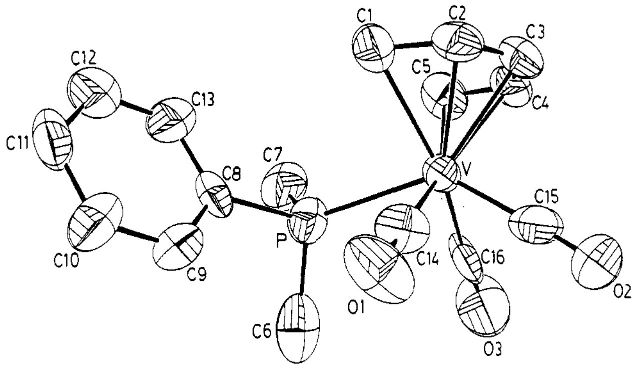


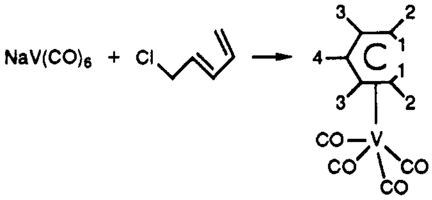
Figure 1. ORTEP drawing of complex **3**.

Table I. Selected Bond Distances and Bond Angles of 3

V–P	2.468 (3)	V–C(1)	2.337 (13)
V–C(2)	2.265 (13)	V–C(3)	2.261 (14)
V–C(4)	2.261 (14)	C(1)–C(2)	1.371 (19)
V–C(5)	2.359 (13)	C(2)–C(3)	1.393 (22)
V–C(14)	1.900 (13)	C(3)–C(4)	1.39 (3)
V–C(15)	1.870 (15)	C(4)–C(5)	1.379 (22)
V–C(16)	1.914 (14)		
P–V–C(14)	79.3 (4)	P–V–C(15)	135.7 (4)
P–V–C(16)	78.6 (4)	C(14)–V–C(15)	73.7 (6)
C(14)–V–C(16)	105.8 (6)	C(15)–V–C(16)	75.9 (6)
V–P–C(6)	114.8 (4)	V–P–C(7)	116.8 (5)
V–P–C(8)	117.1 (3)	C(1)–C(2)–C(3)	126.7 (13)
C(2)–C(3)–C(4)	126.9 (13)	C(3)–C(4)–C(5)	126.0 (13)

Results and Discussion

When a tetrahydrofuran solution of NaV(CO)$_6$ was UV-irradiated with 1-chloro-2,4-pentadiene (an equimolar amount, 20 °C, 2 h), a reaction occurred to yield (η^5-C_5H_7)V(CO)$_4$ (**1**).



No η^3-allyl species were detected during the course of reaction, monitored by IR spectroscopy. Further purification of this highly air-sensitive material was achieved by vacuum sublimation twice to give a dark red crystalline solid (37%). The ^1H NMR spectrum of **1** shows that the pentadienyl ligand adopts a symmetric U-shaped geometry. In cyclohexane, its IR spectrum shows three strong ν(C=O) lines at 2014 (s), 1964 (s), and 1906 (vs) cm^{-1}, which are assigned to the A_1 + B_1 + E modes for a local C_s symmetry.[8] The wavenumbers are comparable to those (2029 (A_1), 1954 (e), 1933 (B_1) cm^{-1}) of (η^5-C_5H_5)V(CO)$_4$[9] in Raman spectra.

Upon treatment of an equimolar amount of tertiary phosphine R_3P, complex **1** spontaneously loses one CO molecule to give (η^5-C_5H_7)V(CO)$_3$(PR_3) (PR_3 = PMe_3 (**2**), PMe_2Ph (**3**)) in 85–90% yield. Notably, a prolonged reaction period led to replacement of a second CO group by phosphine, giving bis(phosphine) complexes. According to in situ infrared spectroscopy, an optimum proper reaction period was 5 min at 0 °C, at which only **2** or **3** existed in the solution. Elemental analyses and mass and ^1H NMR spectra of **2** and **3** were consistent with the given formulas. The solution IR spectrum of **2** exhibits the ν(CO) stretching at 1943 (s) and 1849 (s) cm^{-1}, comparable to those reported for CpV(CO)$_3$(PMe_3)[10] (1947 (s), 1868 (s), 1840 (s) cm^{-1}).

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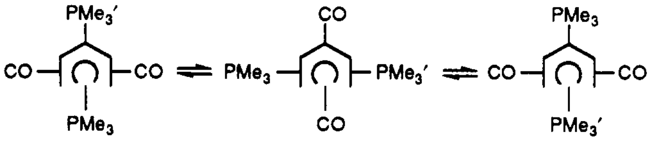
The molecular structure of **3** has been determined by X-ray diffraction. Its ORTEP drawing is provided in Figure 1, and the selected bond distances and angles are given in Table I. The coordination geometry around vanadium is square-pyramidal; the pentadienyl ligand is η^5-coordinated to the vanadium atom with V–C bond distances being 2.26 (1)–2.35 (1) Å and C–C bond lengths in the dienyl ligand being 1.37 (2) and 1.39 (3) Å. The former is close to the values 2.24–2.30 Å reported for the Cp–V(I) complexes. The pentadienyl group is reasonably planar within a maximum deviation of 0.07 Å. The alignment of P–V–C(15) atoms nearly bisects the pentadienyl group; in this manner, the local molecular symmetry is approximately C_s symmetry. The PMe_2Ph ligand lies beneath the open edge of the pentadienyl ligand, and this orientation is consistent with the ^1H NMR spectra, which indicate a coupling between the antiproton H^1 and phosphorus nuclei with a magnitude of J_{1p} = 5.6 Hz. The structure of **3** is essentially equivalent to that of Nb(2,4-dimethylpentadienyl)$(CO)_3(PMe_2Ph)$.[1c]

Complex **3** reacts further with additional PMe_3 in ether (0 °C, 5 days) in a vacuum-sealed Pyrex tube, resulting in replacement of CO and isolation of the highly air-sensitive *trans*-(η^5-C_5H_7)$V(CO)_2(PMe_3)_2$ (**4**). Attempts to prepare the bis(dimethylphenylphosphine) analogue were not successful because of its thermal instability. For **4**, the trans geometry is deduced primarily from the ^1H NMR spectrum (20 °C, $CD_3C_5D_5$), which exhibits an equivalent pattern for the resonances of both ends of the pentadienyl ligand. Moreover, the antiproton H^1 exhibits a doublet of triplets $J_{p+p'}$ = 3.2 Hz. This information indicates that one phosphine ligand is located at the open edge of the pentadienyl group whereas the other is located opposite it, being underneath the central pentadienyl carbon. The "equivalence" of the two phosphorus nuclei with respect to the H^1 proton implies rapid exchange of the two PMe_3 groups.

Like most η^5-pentadienyl complexes,[1c] rotation of the pentadienyl group with respect to the metal fragment proceeds with a low barrier. The ^1H NMR spectrum at −60 °C revealed inequivalent orientations of the two methyl groups that resonate at δ 1.42 and 1.08 ppm, respectively. However, with increasing temperatures, the rate of pentadienyl rotation with respect to the *trans*-$V(CO)_2(PMe_3)_2$ fragment increases; the two inequivalent PMe_3 proton resonances (Figure 2) broaden and eventually coalesce to one resonance at −40 °C (δ 1.28 ppm). ΔG^* of this process based on coalescence temperature is 45.2 kJ mol^{-1}.



This reaction clearly demonstrates the facile nature of the substitution reaction of (η^5-C_5H_7)$V(CO)_4$. In contrast, thermal substitution of $CpV(CO)_4$ with phosphine requires a high temperature (decalin, 110–130 °C); an S_N1 reaction with CO loss is the rate-determinating step.[11] For (η^5-C_5H_7)$V(CO)_4$, the substitution mechanism probably involves $\eta^5 \rightleftarrows \eta^3$ interconversion in which (η^3-C_5H_7)$V(CO)_4(PMe_3)$ is the intermediate. Theoretical studies have shown that the resonance energy of a η^5-pentadienyl ligand is smaller than that of its η^5-cyclopentadienyl analogue,[1a] and hence the $\eta^5 \rightleftarrows \eta^3$ interconversion is expected to be more facile for the metal–pentadienyl system. Interconversion between η^5 and η^3 modes of the latter has been observed by us and others.[12-14] Whether this facile $\eta^5 \rightleftarrows \eta^3$ interconversion further influences its reaction chemistry is under current study.

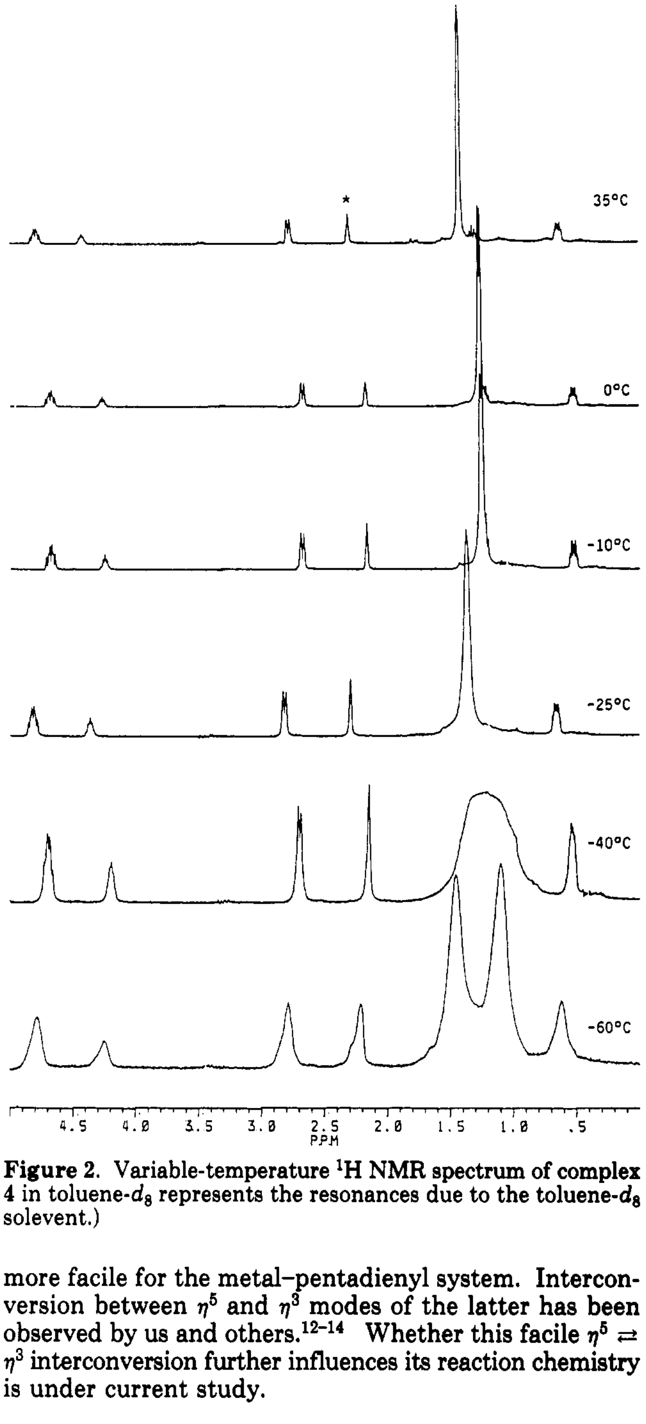


Figure 2. Variable-temperature ^1H NMR spectrum of complex **4** in toluene-d_8 represents the resonances due to the toluene-d_8 solevent.)

Experimental Section

All operations were performed under argon in a Schlenk apparatus or in a glovebox. The solvents diethyl ether, tetrahydrofuran, and pentane were dried with potassium/benzoquinone and distilled before use. PMe_3, PMe_2Ph, and $NaV(CO)_6$ (diglyme) (Strem Chemicals) were used without further purifications, 1-chloro-2,4-pentadiene was prepared according to the literature procedure.[15]

All ^1H (100 and 400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on either a JEOL FX-100 or a Bruker Am-400

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spectrometer. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. Mass spectra were recorded on a JEOL JMS-100 spectrometer.

Synthesis of (η^5-C_5H_7)V(CO)$_4$ (1). NaV(CO)$_6$(diglyme) (1.20 g, 2.36 mmol) was dissolved in THF (20 mL) and evaporated to dryness at 0 °C in vacuo (10^{-3} Torr) to remove diglyme. After evaluation for 6 h, 1-chloro-2,4-pentadiene (0.26 g, 2.56 mmol) in 20 mL of THF was added to the NaV(CO)$_6$ residue and the mixture was irradiated by a 400-W mercury lamp at 20 °C for 6 h. The solvent was removed, and the residues were sublimated twice under vacuum to give a dark red crystalline solid of 1 (0.20 g, 0.87 mmol). IR (cyclohexane): ν(CO) 2014 (s), 1965 (s), 1906 (vs) cm^{-1}. ^{1}H NMR (100 MHz, C_6D_6): δ 5.09 (1 H, t, H^4), 5.04 (2 H, ddd, H^3), 2.74 (2 H, d, H^2), 0.46 (2 H, d, H^1), J_{13} = 12.0 Hz, J_{23} = 9.0 Hz, J_{34} = 6.2 Hz. Mass (12 eV): *m/e* 230 (M$^+$), 202 (M$^+$ – CO), 174 (M$^+$ – 2CO). Anal. Calcd for $C_9H_7VO_4$: C, 46.97; H, 3.07. Found: C, 46.72; H, 3.21.

Synthesis of (η^5-C_5H_7)V(CO)$_3$PMe$_3$ (2). A 5-mL hexane solution of 1 (0.15 g, 0.65 mmol) was stirred with PMe$_3$ (50 mg, 0.66 mmol) at 0 °C for 5 min. After removal of the solvent in vacuo, the residues were recrystallized from pentane to give dark red crystals of **2** (0.16 g, 0.58 mmol). IR (hexane): ν(CO) 1943 (s), 1849 (s) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 5.02 (1 H, t, H^4), 4.45 (2 H, ddd, H^3), 2.56 (2 H, d, H^2), 1.05 (9 H, d, PMe$_3$), 0.37 (2 H, dd, H^1), J_{13} = 12.4 Hz, J_{1p} = 5.8 Hz, J_{23} = 8.8 Hz, J_{34} = 6.2 Hz, $J_{p\text{–}CH_3}$ = 7.0 Hz. ^{13}C NMR (400 MHz, C_6D_6): δ 19.8 (d, J = 92 Hz, PMe$_3$), 69.5 (CH^4), 89.9 (CH^{1}H^2), 105.7 (CH^3). Mass (12 eV): *m/e* 278 (M$^+$), 250 (M$^+$ – CO), 222 (M$^+$ – 2CO), 194 (M$^+$ – 3CO). Anal. Calcd for $C_{11}H_{16}VPO_3$: C, 47.88; H, 5.76. Found: C, 47.39; H, 5.81.

Synthesis of (η^5-C_5H_7)V(CO)$_3$(PMe$_2$Ph) (3). This complex was prepared similarly from the reaction between 1 and PMe$_2$Ph; the yield was 85%. IR (hexane): 1954 (s), 1882 (s), 1857 (s) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.01–7.26 (5 H, m, Ph), 5.01 (1 H, t, H^4), 4.47 (2 H, ddd, H^3), 2.48 (2 H, d, H^2), 1.52 (6 H, d, P*Me*$_2$Ph), 0.36 (2 H, dd, H^1), J_{13} = 12.3 Hz, J_{1p} = 6.0 Hz, J_{23} = 9.3 Hz, J_{34} = 6.7 Hz, $J_{p\text{–}CH_3}$ = 7.5 Hz. ^{13}C NMR (400 Mhz, C_6D_6): δ 17.5 (d, PCH_3), J = 97 Hz), 71.8 (CH^{1}H^2), 89.3 (CH^4), 105.9 (CH^3), 128.5, 128.6, 128.9 (Ph). Mass (12 eV): *m/e* 340 (M$^+$), 312 (M$^+$ ± CO), 284 (M$^+$ ± 2CO), 256 (M$^+$ ± 3CO). Anal. Calcd for $C_{16}H_{18}O_3VP$: C, 56.47; H, 5.29. Found: C, 56.41; H, 5.25.

Synthesis of *trans*-(η^5-C_5H_7)V(CO)$_2$(PMe$_3$)$_2$ (4). A vacuum-sealed Pyrex tube containing **2** (0.15 g, 0.54 mmol) and PMe$_3$ (0.20 g, 2.60 mmol) in 10 mL of ether was covered with aluminum foil and placed at 50 °C for 4 days. After removal of the solvent under reduced pressure, the residues were recrystallized from pentane to give a dark red crystalline solid (0.13 g, 0.40 mmol). IR (hexane): 1870 (s), 1780 (s) cm^{-1}. ^{1}H NMR (400 MHz, toluene-d_8): 23 °C δ 4.68 (2 H, ddd, H^3), 4.26 (1 H, t, H^4), 2.66 (2 H, d, H^2), 1.26 (18 H, d, 2 PMe$_3$), 0.52 (1 H, dt, H^1), J_{13} = 12.2 Hz, J_{23} = 9.7 Hz, J_{34} = 6.1 Hz, J_{1p} = 3.8 Hz, $J_{CH_3\text{–}P}$ = 7.2 Hz; –60 °C 1.42 (3 H, br s, PMe$_3$), 1.08 (3 H, br, s, PMe$_3$). ^{13}C NMR (400 MHz, toluene-d_8, 23 °C): δ 19.3 (d, J = 84 Hz, PCH$_3$), 66.8 (CH^4), 93.9 (CH^{1}H^2), 101.5 (CH^3). Mass (12 eV): *m/e* 326 (M$^+$), 298 (M$^+$ – CO), 270 (M$^+$ – 2CO). Anal. Calcd for $C_{13}H_{25}VP_2O_2$: C, 47.85; H, 7.67. Found: C, 47.78; H, 7.60.

X-ray Structure Determination of 3. Crystals of **3** were grown from a pentane solution at –20 °C. A crystal suitable for X-ray diffraction use was mounted in a sealed, thin-walled capillary tube. Data were collected at 23 °C on a CAD4 diffractometer by using graphite-monochromated Mo Kα radiation and a $\theta/2\theta$ scan.

Complex **3** crystallized in the orthorhombic space group $P2_12_12_1$ with a = 7.152 (2) Å, b = 13.172 (4) Å, c = 17.479 Å, V = 1646.7(8)Å^3, Z = 4. ψ scan absorption corrections were applied. All data reduction and structure refinement were performed by means of the NRCC-VAX package.[16] The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined with anisotropic thermal parameters; and the hydrogen atoms were added at the idealized positions and included in the structure factor calculation. The refinement was converged to R = 0.049 and R_w = 0.052 for 943 observed reflections ($I > 2\sigma(I)$) and 190 variables. Parameters from the crystal structure determination are given in the supplementary material.

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Supplementary Material Available: Tables of positional parameters of atoms, crystal data, anisotropic thermal parameters, and bond distances and angles (4 pages); a listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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