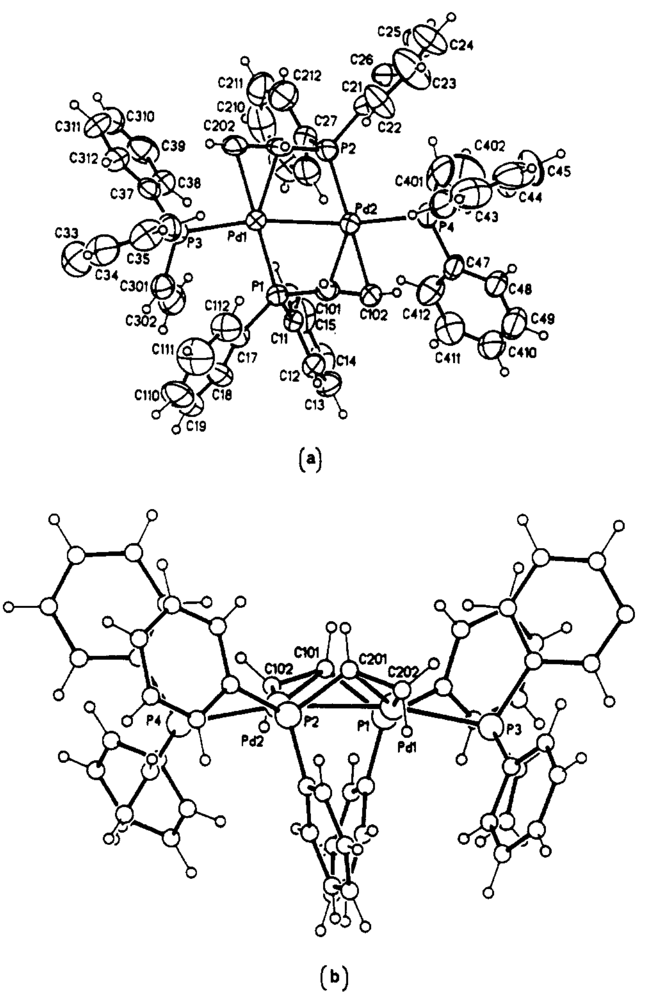

Figure 1. Structure of the cation of bis[(vinyldiphenylphosphine)(μ-η^3-diphenylphosphaallyl)palladium(I)] fluoroborate, 1: (a) showing the 50% probability ellipsoids and atom-labeling scheme; (b) showing the conformation of its central portion. Selected bond distances (Å) are as follows: Pd(1)-Pd(2), 2.748 (2); Pd(1)-P(1), 2.254 (3); Pd(1)-P(2), 2.923 (3); Pd(1)-P(3), 2.324 (3); Pd(1)-C(201), 2.284 (8); Pd(1)-C(202), 2.252 (8); Pd(2)-P(1), 2.956 (3); Pd(2)-P(2), 2.257 (3); Pd(2)-P(4), 2.333 (3); Pd(2)-C(101), 2.297 (8); Pd(2)-C(102), 2.258 (9); P(1)-C(101), 1.781 (10); P(2)-C(201), 1.775 (9); P(3)-C(301), 1.793 (9); P(4)-C(401), 1.765 (12); C(101)-C(102), 1.350 (11); C(201)-C(202), 1.362 (14); C(301)-C(302), 1.263 (14); C(401)-C(402), 1.144 (19). Selected bond angles (deg) are as follows: Pd(2)-Pd(1)-P(1), 71.7 (1); Pd(2)-Pd(1)-P(3), 165.3 (1); P(1)-Pd(1)-P(3), 97.2 (1); Pd(1)-Pd(2)-P(2), 70.7 (1); Pd(1)-Pd(2)-P(4), 165.7 (1); P(2)-Pd(2)-P(4), 98.8 (1); P(1)-C(101)-C(102), 125.8 (7); P(2)-C(201)-C(202), 124.5 (8); P(3)-C(301)-C(302), 127.5 (8); P(4)-C(401)-C(402), 129.9 (12).

each produced the expected[10] $(R_3P)_2M(BF_4)_2$ in which neither reduction to the univalent metal nor phosphaallyl formation occurred.

The $^{31}P\{^1H\}$ NMR spectrum of 1 in $CDCl_3$ consists of two temperature-dependent second-order $[AB]_2$ multiplets centered at δ 27.3 (terminal phosphine) and δ 9.7 (phosphaallyl). Both the $^{13}C\{^1H\}$ and ^1H NMR spectra[11] exhibit sharp second-order resonances for the terminal phosphine nuclei and broad temperature-dependent second-order resonances for the phosphaallyl nuclei. The dynamic behavior of 1 in solution is akin to the fluxional processes observed[12] for analogous η^3-allyl compounds.

The structure of 1 was determined by X-ray crystallography[13] (Figure 1). Compounds 1 and 2 are structural analogues in several aspects. Their Pd-Pd distances are similar (1, 2.748 (2) Å; 2, 2.720 (1) Å), and the two allyl groups in both compounds are syn and unsymmetrically bound to the two palladium atoms. For 1, the Pd-P distances to the terminal phosphines (2.333 (3) and 2.324 (3) Å) are longer than those to the phosphaallyls (2.257 (3) and 2.254 (3) Å), the $P-C_{vinyl}$ distances (1.775 (9) and 1.781 (10) Å) of the phosphaallyls are not significantly shorter than those of the terminal phosphines (1.793 (9) and 1.765 (12) Å), and the vinyl C-C distances of the phosphaallyls (1.362 (14) and 1.350 (11) Å) are significantly longer than those of the terminal phosphines (1.263 (14) and 1.144 (19) Å). The reaction chemistry of 1 is currently under investigation.

Acknowledgment. The financial assistance of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 1, 126217-52-5; $(Ph_2PCH{=}CH_2)_2PdCl_2$, 78629-73-9.

Supplementary Material Available: Listings of atomic positional and thermal parameters and interatomic distances and angles for 1 (7 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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[11] ^1H NMR ($CDCl_3$, −50 °C) δ 2.34 ($^3J_{PH}$ = 15.02 Hz, $^3J_{HH}$ = 16.23 Hz, $H_{c'}$, 2 H), 3.94 ($^2J_{PH}$ = 27.0 Hz, $^3J_{HH}$ = 10.22 Hz, $^3J_{HH}$ = 16.23 Hz, $H_{a'}$, 2 H), 4.52 ($^3J_{PH}$ = 33.1 Hz, $^3J_{HH}$ = 10.22 Hz, $H_{b'}$, 2 H), 5.09 ($^3J_{PH}$ = 22.5 Hz, $^3J_{HH}$ = 17.73 Hz, H_c, 2 H), 5.84 ($^3J_{PH}$ = 42.0 Hz, $^3J_{HH}$ = 12.02 Hz, H_b, 2 H), 6.03 ($^2J_{PH}$ = 24.0 Hz, $^3J_{HH}$ = 12.02 Hz, $^3J_{HH}$ = 17.73 Hz, H_a, 2 H), 6.5–8.1 (multiplets, Ar H, 40 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C) all resonances are broad second-order multiplets at the following δ: 64.3 (C_{101}, C_{201}), 79.1 (C_{102}, C_{202}), 120.0–126.4 (3 C_i), 127.7 (C_{301}, C_{401}), 128.9 (C_{302}, C_{402}), 129–135 (several resonances, C_{phenyl}'s).

[12] Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441–487.

[13] Crystal data: space group $P2_1/a$, a = 15.814 (8) Å, b = 18.020 (10) Å, c = 19.381 (10) Å, and β = 104.19 (4)°, Z = 4. Data were collected on a Syntex $P2_1$, four-circle diffractometer in ω–2θ mode with Mo Kα (0.71073 Å) radiation at 290 K on a 0.04 × 0.35 × 0.15 mm crystal. Maximum 2θ was 45° with scan range ±1.1° (2θ) around Kα1–Kα2 angles. hkl ranges were 0/17, −19/19, −20/20. Reflections were processed by using profile analysis to give 7033 unique reflections (R_{inf} = 0.030); 4772 were considered observed ($I/\sigma(I) \geq 2.0$) and used in refinement. They were corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.96 and 0.82. Systematic absences: $h0l$, $h \neq 2n$, $0k0$, $k = 2n$ indicate space group $P2_1/a$. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and the light atoms were then found on successive Fourier syntheses. One BF_4 group was found to be disordered with one full-occupancy and six half-occupancy F positions. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, U = 0.07 Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined. Final refinement was on F by least-squares methods refining 646 parameters. Final R = 0.061, R_w = 0.050. Computing was with SHELXTL PLUS on a DEC Microvax-II.

Preparation and Properties of the Paramagnetic Organometallic Oxide $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$ with an Adamantane-like Structure

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Summary: Green-black, paramagnetic $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$, obtained either from the reaction between $[(\eta\text{-}C_5Me_5)V(O)(\mu_2\text{-}O)]_3$ and PMe_2Ph or from $(\eta\text{-}C_5Me_5)_2V$ and N_2O, has an adamantane-like structure.

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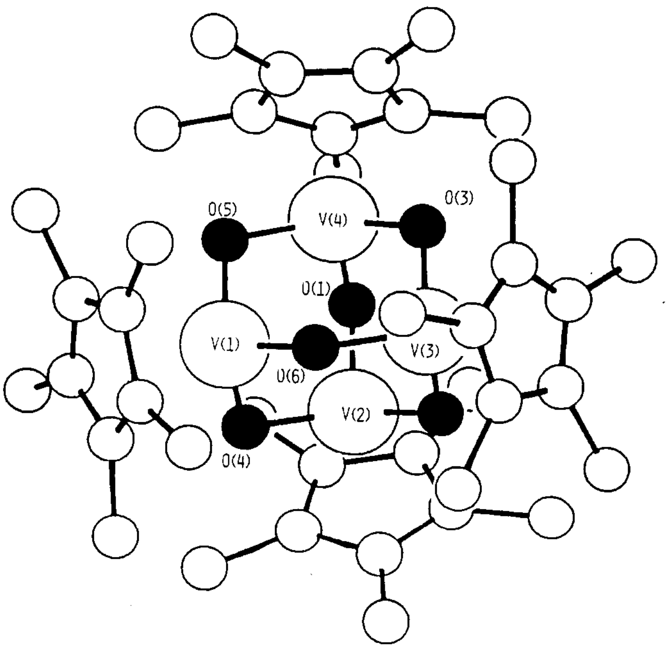

Figure 1. Molecular structure of $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$.

Cubane clusters with the general formula $[(\eta\text{-}C_5R_5)M(\mu_3\text{-}A)]_4$ are well established for metals (M) from groups 4–9 and atoms (A) from group 16 or, more rarely, 15 or 17.[1-4] Recently $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$, with an adamantane structure, has been described.[5,6] We report the preparation and properties of $[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6$ (1). This suggests that a large series of $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ clusters may be obtainable.

1 may be prepared in several ways.[7] The most rational is treatment of $[(\eta\text{-}C_5Me_5)V(O)(\mu_2\text{-}O)]_3$[8] with PMe_2Ph according to eq 1. Workup of the highly soluble 1 is

$$4[(\eta\text{-}C_5Me_5)V(O)(\mu\text{-}O)]_3 + 6PMe_2Ph \rightarrow 3[(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6 + 6OPMe_2Ph \quad (1)$$

complicated by the presence of PMe_2Ph and $OPMe_2Ph$.

Oxidation of $(\eta\text{-}C_5Me_5)_2V$ with N_2O gives 1 in yields greater than 60% according to eq 2. This is the most

$$4(\eta\text{-}C_5Me_5)_2V + 6N_2O \rightarrow [(\eta\text{-}C_5Me_5)V]_4(\mu_2\text{-}O)_6 + 6N_2 + 2(C_5Me_5)_2 \quad (2)$$

convenient preparation. Exposure of $(\eta\text{-}C_5Me_5)_2V$ to trace amounts of air also gives 1, though other products, including $[(\eta^3\text{-}C_5Me_5O_3)V(O)]_2$,[9] are present. This mixture appears to be the "$(C_5Me_5)_3V_4O_9$" referred to by Herberhold and co-workers.[10] However, 1 does not give a high yield of $(\eta\text{-}C_5Me_5)VCl_2(O)$ on reaction with HCl or $SOCl_2$, in contrast to the case for "$(C_5Me_5)_3V_4O_9$".[10,11]

Black-green 1 has a symmetrical adamantane-like (T_d) structure (see Figure 1).[12] The V–V distances average 3.003 (3, 3) Å and the V–O distances 1.808 (6, 17) Å; the O–V–O angles average 108.0 (3, 5)° and the V–O–V angles 112.3 (3, 8)°. This symmetrical structure is similar to that of $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$.[5] However, 1 is paramagnetic (Evans method, $\mu_{eff} = 2.15\ \mu_B$, independent of temperature between 210 and 298 K), whereas the titanium derivative is diamagnetic. Extended Hückel molecular orbital calculations[13] on $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}O)_6$ show that there are 12 cluster orbitals, as with the $[(\eta\text{-}C_5H_5)M(\mu_3\text{-}A)]_4$ cubanes.[14] Since $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ has no cluster electrons, it is diamagnetic; 1 has four cluster electrons which occupy an a_1 orbital at −10.68 eV and an e orbital at −9.08 eV. The electronic configuration is $a_1{}^2e^2$, and 1 is predicted to have two unpaired electrons. The observed spin-only magnetic moment is lower than expected. The reasons for this may become clear when other $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ clusters are prepared. The related cluster $\{[(\eta\text{-}C_5Me_5)Cr]_4(\mu_2\text{-}OH)_6\}^{2+}$ has 12 cluster electrons and is paramagnetic.[15]

Acknowledgment. We thank Dr. P. S. White for assistance with the X-ray diffraction studies and the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Imperial Oil (Canada) Research Fund for financial support.

Supplementary Material Available: A discussion of how a monoclinic space group was ruled out, a figure showing the numbering scheme, and tables of positional and anisotropic thermal parameters and supplemental bond distances and angles (16 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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(7) Characterization of 1. Anal. Calcd for $C_{40}H_{60}O_6V_4$: C, 57.1; H, 7.1; V, 24.2. Found: C, 58.0, 56.1; H, 7.5, 7.2; V (as V_2O_5), 23.4, 22.9. Mass spectrum (FAB): *m/e* 840 ($(C_5Me_5)_4V_4O_6{}^+$), 570 ($(C_5Me_5)_2V_4O_6{}^+$). Mass spectrum (EI): *m/e* 840 ($(C_5Me_5)_4V_4O_6{}^+$), 706 (base peak) ($(C_5Me_5)_3V_4O_6H^+$), 689 ($(C_5Me_5)_3V_4O_5{}^+$), 571 ($(C_5Me_5)_2V_4O_6H^+$), 554 ($(C_5Me_5)_2V_4O_5{}^+$), 435 ($(C_5Me_5)V_4O_6{}^+$), 419 ($(C_5Me_5)V_4O_5{}^+$), 403 ($(C_5Me_5)V_4O_4{}^+$), 355 ($(C_5Me_5)V_4O^+$), 300 ($V_4O_6{}^+$). NMR (^1H, 200 MHz, C_6D_6 solution): s, 2.00 ppm. Infrared (Nujol mull, KBr plates): 635, 615 cm^{-1} (ν(V–O–V)); 375 cm^{-1} (δ(V–O–V)). ESR: no signal at room temperature; extremely broad, featureless, signal at 4 K.

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