structure of **3d** thereby confirms that both formerly doubly bonded units (vinylidene C=C ca. 130 pm,[10] ylide P=C ca. 170 pm[16]) have turned into singly bonded units upon formation of the new C–C bond, that the vinylidene ligand has turned into an alkylidyne ligand, and that the phosphorus ylide has turned into a phosphonium group. The structure, in accord with the electron-counting rules, thus implies the above-mentioned zwitterionic formulation. The complexes **3** are thereby homologous to the complexes $FeCo_2(CO)_9(\mu_3\text{-}\eta^1\text{-}CCH_2PR_3)$ which were obtained from 1 and PR_3.[11] They are also homologous to Shriver's complexes $[Fe_2Co(CO)_9(\mu_3\text{-}\eta^1\text{-}CPR_3)]^-$, which have yet another CH_2 group less between the trimetal unit and the phosphonium center.[17]

While C–C bond formation by combination of electrophilic and nucleophilic carbon centers is one of the most basic reactions in organic chemistry, it has, to our knowledge, never been performed in the way described here, namely, as an adduct formation between uncharged methylene units of nonpolar compounds. The reagents are either charged species like enolates or onium compounds or the primary adducts quickly undergo rearrangement reactions.[4,5] The ease of formation of the adducts **3** results from the fact that in the starting materials **1** and **2** the methylene units are in an unusual electronic situation due to their attachment to inorganic centers. Likewise the stability of the adducts rests on the efficient charge separation brought about by the cationic phosphonium group and the anionic $FeCo_2$ cluster unit at both ends of the CH_2–CHR chain. It therefore seems to us that the charge separation drives the C–C bond formation and not vice versa.

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Registry No. 1, 85249-99-6; **2a**, 3487-44-3; **2b**, 3739-97-7; **2c**, 859-65-4; **2d**, 1099-45-2; **3a**, 126156-16-9; **3b**, 126156-17-0; **3c**, 126156-18-1; **3d**, 126156-19-2.

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[16] Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350.

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Facile Synthesis and Structural Characterization of $[(Ph_2PCHCH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCHCH_2)Pd^I]_2(BF_4)_2$: Unprecedented Formation of a Structurally Unusual Palladium(I) Complex

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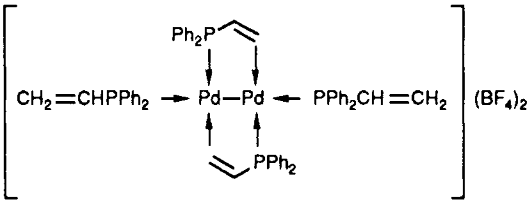
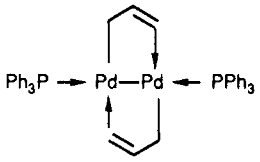
Summary: Photochemical reaction of $(Ph_2PCH{=}CH_2)_2PdCl_2$ with $AgBF_4$ produces the novel palladium(I) phosphaallyl complex $[(Ph_2PCH{=}CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH{=}CH_2)Pd^I]_2(BF_4)_2$ in high yield. This compound is fluxional in solution.

In light of current interest[1] in the coordination chemistry of heteroatom compounds that are isolobal[2] with classical unsaturated hydrocarbon fragments, we wish to report the facile synthesis[3] of the novel compound [(vinyldiphenylphosphine)(μ-η^3-diphenylphosphaallyl)palladium(I)]$_2$(BF_4)$_2$, 1. Compound 1 is the first example of a neutral vinylphosphine acting as a bridging μ-η^3 four-electron donor to two metals. As such it is a neutral phosphaallyl analogue of the Pd(I) compound[4] $[(Ph_3P)(\mu\text{-}\eta^3\text{-}C_3H_5)Pd^I]_2$, 2, and of the anionic phosphaallyl compound[1] $(CO)_5W(\mu\text{-}\eta^3\text{-}PhPCH{=}CH_2)(C_5H_5)FeCO$, 3. In 3 the anionic phosphaallyl moiety is a two-electron donor to W(0) and a three-electron donor to Fe(I). Alternatively, compound 1 could be considered to contain a bridging η^1-P, η^2-(C=C) vinylphosphine, but in light of the structural similarities of compounds 1 and 2 we prefer the μ-η^3-phosphaallyl bonding description.



1



2

Reaction of dichlorobis(vinyldiphenylphosphine)palladium(II)[5] with slightly more than 2 equiv of silver fluoroborate in dichloromethane in the presence of light produces 1, which is isolated in 70% yield as a bright yellow crystalline compound after slow addition of diethyl ether to the filtered dichloromethane reaction mixture. The unexpected formation of 1 is yet another example of an unusual result[6] of an anticipated simple silver salt metathesis[7] of a noble-metal halide complex.

In contrast to the formation of 1, similar reactions with $[PhP(C_2H_3)_2]_2MCl_2$, M = Pd[5] or Pt,[8] or $(Ph_2PC_2H_3)_2PtCl_2$[9]

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[1] Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. Mercier, F.; Hugel-LeGoff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955.

[2] Mathey, F. *Nouv. J. Chim.* **1987**, *11*, 585.

[3] Under a purge of N_2 gas, 2.14 g of $AgBF_4$ (0.0110 mol) was added to a solution of 3.0 g of $(Ph_2PCH{=}CH_2)_2PdCl_2$ (0.0050 mol) in 125 mL of CH_2Cl_2 in a 500-mL round-bottom flask. White AgCl precipitate began to form immediately. The flask was closed with a rubber septum and stirred with a magnetic stirrer under ambient light. During this time the precipitate became black and BF_3 gas was evolved. The gas was released periodically by using a hypodermic needle. After 1 week the reaction was complete as evidenced by cessation of gas evolution. The reaction mixture was gravity filtered, and the resulting bright yellow solution was reduced to an orange yellow solid by rotary evaporation. This solid was recrystallized by diffusion of diethyl ether into a saturated 3:1 CH_2Cl_2:Et_2O solution of the compound at −20 °C, yielding 2.12 g (0.00175 mol) of $[(Ph_2PCH{=}CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH{=}CH_2)Pd^I]_2(BF_4)_2$ (70.0%) as yellow crystals, mp 204 °C. Anal. Calcd for $C_{56}H_{52}B_2F_8P_4Pd_2$: C, 58.04; H, 4.49; P, 10.69; Pd, 18.36. Found: C, 57.79; H, 4.52; P, 10.51; Pd, 18.20.

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[6] Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

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[8] Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288.

[9] Rahn, J. A.; Holt, M. S.; Gray, G. A.; Alcock, N. W.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 217.

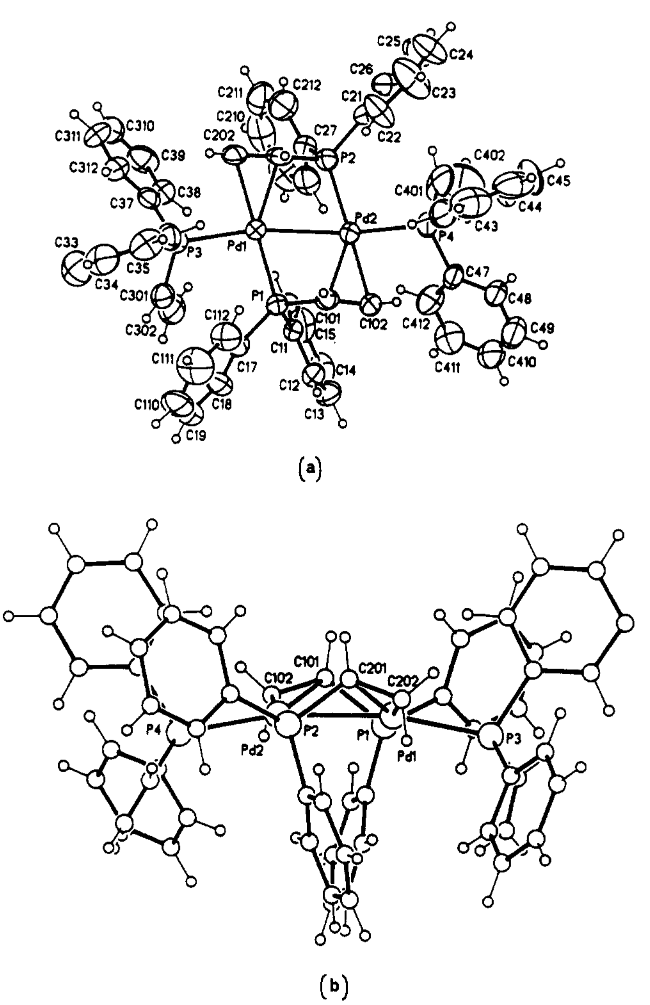

Figure 1. Structure of the cation of bis[(vinyldiphenylphosphine)(μ-η^3-diphenylphosphaallyl)palladium(I)] fluoroborate, 1: (a) showing the 50% probability ellipsoids and atom-labeling scheme; (b) showing the conformation of its central portion. Selected bond distances (Å) are as follows: Pd(1)-Pd(2), 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.

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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.

0276-7333/90/2309-1700$02.50/0