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Synthesis, Structure and Reactivity of η^3-Allenyl/Propargyl Dinuclear Palladium Complexes

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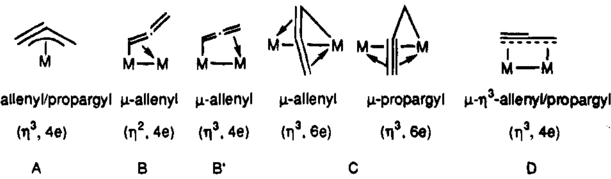
Recently, much attention has been paid to transition metal complexes of polyhapto allenyl/propargyl ligands because of their unique bonding mode and reactivity. Typical examples include mononuclear η^3-allenyl/propargyl complexes[1] [type A (η^3, 4e)[2]] and dinuclear μ-allenyl/propargyl complexes [type B (η^2, 4e)[3] or type C (η^3, 6e)[4]] (Chart 1). Geometrically, the inherently linear unsaturated hydrocarbon framework might match a linear dinuclear moiety better than a mononuclear moiety, but only one such example has been reported in Ru_2 and Os_2 systems (B').[5] On the other hand, there has been no example of a type D complex having such a more delocalized structure through resonance of η^3-allenyl and η^3-propargyl forms, as is found in type A complex. We report here the synthesis, structure, and reactivity of type D complexes of Pd.

Chart 1



The reaction of η^1-allenyl- or η^1-propargylbis(triphenylphosphine)palladium chloride complexes **1a−d**[6] with $Pd_2(dba)_3\cdot CHCl_3$ in $CDCl_3$ at room temperature gave μ-η^3-allenyl/propargyldipalladium complexes **2a−d** (eq 1).[7] The analogous reaction of **1b** in the presence of NaI and NaSPh gave the iodide and phenyl thiolate analogues, respectively (**2b**-I, 63%; **2b**-SPh, 78%). Addition of PPh_3 to **2a−d** led to regeneration of **1a−d** as well as generation of $Pd(PPh_3)_2$.

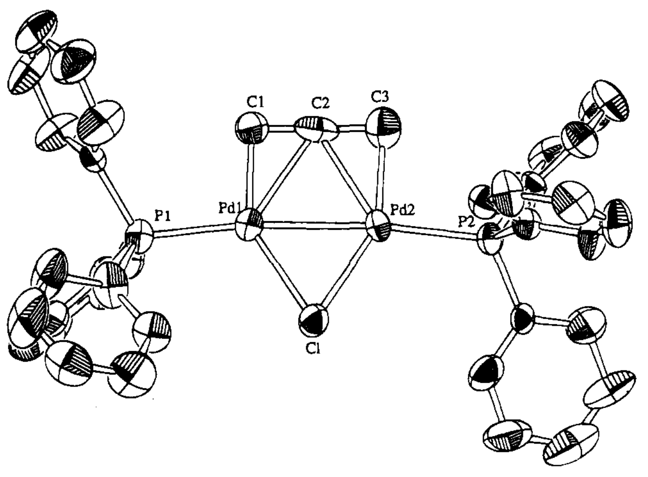
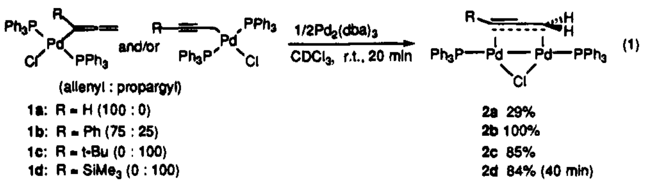


Figure 1. Molecular structure of **2a**. Selected bond distances (Å): Pd1−Pd2 = 2.642(2), Pd1−Cl = 2.405(6), Pd2−Cl = 2.397(6), Pd1−P1 = 2.252(6), Pd2−P(2) = 2.282(6), Pd1−C1 = 2.06(2), Pd1−C2 = 2.47(3), Pd2−C2 = 2.42(3), Pd2−C3 = 2.08(2), C1−C2 = 1.33(3), C2−C3 = 1.36(3). Selected angle (deg): C1−C2−C3 = 178(2).



The structures of dinuclear complexes **2a**[8] and **2b**-SPh[9] are presented in Figures 1 and 2. The μ-η^3-allenyl/propargyl group is almost linear (C1−C2−C3 = 178° in **2a**, 173° in **2b**-SPh), in contrast to that of η^3-allenyl/propargyl mononuclear complexes (Pd,[1h] Pt,[1f,g] Mo[1a]) and other μ-allenyl or μ-propargyl dinuclear complexes (types B and C) having bent C−C−C units, and parallels the Pd−Pd bond. Thus, the Pd1−C1 distance (2.06, 2.066 Å) is almost equal to the Pd2−C3 distance (2.08, 2.096 Å). Moreover, the Pd−Pd distance (2.642, 2.6291 Å) is almost equal to the C1−C3 distance (2.69, 2.659 Å). Two palladiums, η^3-allenyl/propargyl carbons, a chlorine or sulfur atom, and two phosphorus atoms are located on the same plane.

The dinuclear complexes **2b** and **2b**-I reacted with HCl (generated from a reaction of H_2O with Me_3SiCl in situ) to give unusual dinuclear complexes **3b** (89%)[10] and **3b**-I (76%) (eq 2). The structure of **3b** was determined by X-ray diffraction (Figure 3).[11] The structure reveals the first example of μ-vinylcarbene (or μ-η^1,η^3-allyl) complex of palladium, which

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(1) (a) Mo: Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, 103. (b) W: McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (c) Zr: Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994. (d) Re: Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597. (e) Pt: Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170. (f) Pt: Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. (g) Pt: Stang, P. J.; Crittell, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799. (h) Pd: Ogoshi, S.; Tsutsumi, K.; Kurosawa, H. *J. Organomet. Chem.* **1995**, *493*, C19. (i) Reviews: Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. Wojcicki, A. *New. J. Chem.* **1994**, *18*, 61.

(2) In Chart 1, each allenyl or propargyl group is formally regarded as an anion.

(3) (a) Fe: Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (b) Ru: Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1986**, *5*, 1179.

(4) (a) Mo: Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491. (b) Fe−Mo, Fe−W: Young, G. H.; Wojcicki, A. *J. Am. Chem. Soc.* **1989**, *111*, 6890. (c) Fe−Mo, Fe−W: Young, G. H.; Raphael, M. V.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *Organometallics* **1991**, *10*, 1934.

(5) (a) Synthesis and reactions: Breckenridge, S. M.; Taylor, N. J.; Carty, A. J. *Organometallics* **1991**, *10*, 837. (b) X-ray: Carleton, N.; Corrigan, J. F.; Doherty, S.; Pixner, R.; Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1994**, *13*, 4179.

(6) (a) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716. Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Häming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586.

(7) Selected spectral data for **2a**: mp 129−131 °C dec; IR (KBr) 2180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (ddd, J_{HH} = 2.3 Hz, J_{PH} = 6.4, 0.7 Hz, 2H), 5.64 (tdd, J_{HH} = 2.3 Hz, J_{PH} = 32.1, 1.0 Hz, 1H), 7.40 (m, 20H), 7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.49 (s, CCH_2), 79.23 (t, J_{CP} = 5.7 Hz, CCH_2), 108.49 (d, J_{CP} = 4.9 Hz, HCC); ^{31}P NMR δ 27.4 (d, J_{PP} = 98.2 Hz), 22.7 (d, J_{PP} = 98.2 Hz); Anal. Calcd for $C_{39}H_{33}P_2Pd_2Cl$: C, 57.69; H, 4.10. Found: C, 57.52; H, 4.32.

(8) Crystal data for **2a**·THF: $C_{43}H_{41}ClP_2Pd_2O$, triclinic, $P1$ (No. 1); a = 10.090(2) Å, b = 11.768(2) Å, c = 8.747(1) Å, α = 94.16(1)°, β = 108.35(1)°, γ = 78.19(1)°, Z = 1, D_{calc} = 1.521 g/cm³. The data were collected at 23 °C with Mo Kα radiation: μ = 11.17 cm^{-1}, $2\theta_{max}$ = 55.0°, 440 variables refined with 3435 unique reflections with $I > 3.00\sigma(I)$ to $R(F)$ = 0.056 and $R_w(F)$ = 0.045.

(9) Crystal data for **2b**-SPh: $C_{51}H_{42}P_2Pd_2S$, monoclinic, $P2_1/n$ (No. 14); a = 16.809(2) Å, b = 16.608(3) Å, c = 17.238(2) Å, β = 114.871(8)°, Z = 4, D_{calc} = 1.463 g/cm³. The data were collected at 23 °C with Mo Kα radiation: μ = 9.64 cm^{-1}, $2\theta_{max}$ = 55.0°, 505 variables refined with 7988 unique reflections with $I > 3.00\sigma(I)$ to $R(F)$ = 0.036 and $R_w(F)$ = 0.029.

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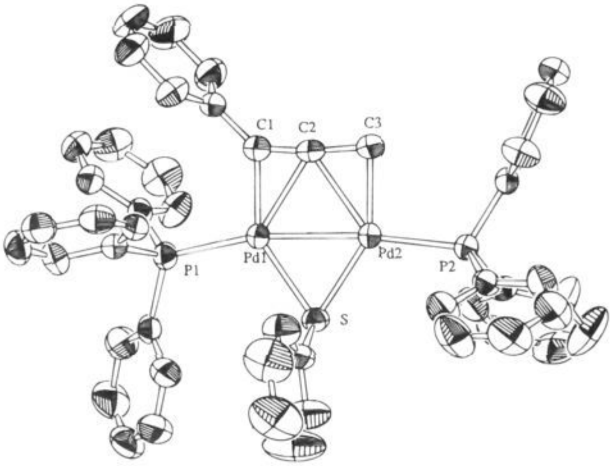


Figure 2. Molecular structure of **2b**-SPh. Selected bond distances (Å): Pd1−Pd2 = 2.6291(4), Pd1−S = 2.3621(8), Pd2−S = 2.3679(9), Pd1−P1 = 2.2595(9), Pd2−P2 = 2.2626(9), Pd1−C1 = 2.066(3), Pd1−C2 = 2.361(3), Pd2−C2 = 2.431(3), Pd2−C3 = 2.096(3), C1−C2 = 1.257(4), C2−C3 = 1.406(5). Selected angle (deg): C1−C2−C3 = 173.2(3).

is similar to μ-vinylcarbene complexes of other transition metals.[12] Intriguingly, in this reaction, a proton added to the center carbon of the η^3-allenyl/propargyl group, as confirmed by the reaction with DCl, which points out the occurrence of an unusual electrophilic attack at the center carbon of the η^3-allenyl/propargyl group. On the other hand, in both mononuclear[1c,e,f] and other dinuclear[5a] complexes, the η^3-allenyl/propargyl group is prone to attack by a nucleophile at the central carbon. The present unique reactivity might be due to high electron density at the central carbon (C2) in the allenyl/propargyl ligand bound on the Pd−Pd moiety, as explained below. Preliminary MO calculations on $Pd_2(\mu\text{-allyl})(\mu\text{-Cl})(PH_3)_2$[13] suggest that back-donation from two filled MOs of the fragment $Pd_2(\mu\text{-Cl})(PH_3)_2$ to empty π^* MO of the allyl ligand shown in Chart 2 plays a crucial role in combining the allyl ligand with the Pd−Pd fragment. The π^* MO of the μ-allenyl/propargyl ligand is equivalent to that of the μ-allyl ligand, so that a similar back-donation may be responsible for the unique structural and reactivity aspects revealed in this study. Such a strong back-bonding interaction cannot be expected in $M_2(\mu\text{-PhC}{=}C{=}CH_2)(\mu\text{-PPh}_2)(CO)_6$ (M = Ru and Os) (type B′)[5b] due to the presence of four strongly π-accepting carbon monoxide ligands which compete with the allenyl π^* MO for the $d\pi{-}d\pi$ MO of the M_2 fragment.

The treatment of **2b**-SPh with 2 equiv of HCl led to the formation of $Pd(\eta^3\text{-PhCHCHCH}_2)Cl(PPh_3)$, which is a formal hydrogenation product of starting complex **1b** (eq 3).[14] Thus, this reaction might be a model for a hydrogenation reaction on a metal surface.

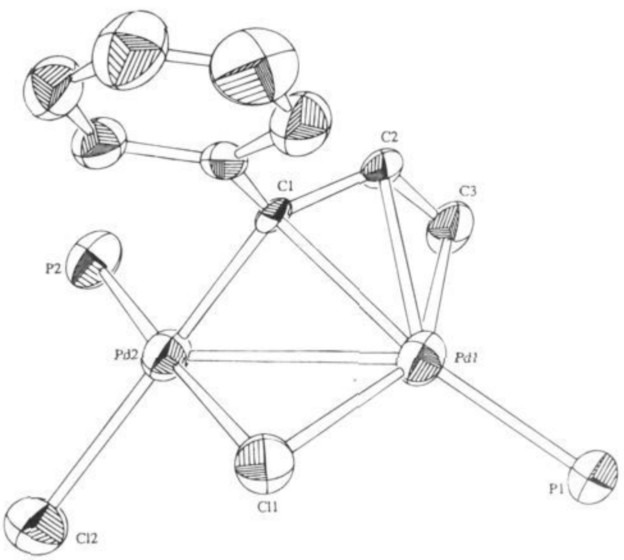
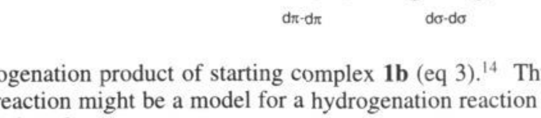
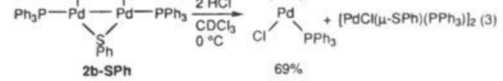


Figure 3. Molecular structure of **3b**. Selected bond distances (Å): Pd1−Pd2 = 2.868(1), Pd1−Cl1 = 2.425(2), Pd2−Cl1 = 2.489(2), Pd2−C1 = 2.374(3), Pd1−P1 = 2.298(2), Pd2−P2 = 2.243(2), Pd1−C1 = 2.260(8), Pd1−C2 = 2.224(9), Pd1−C3 = 2.113(10), Pd2−C1 = 2.031(9), C1−C2 = 1.40(1), C2−C3 = 1.39(1). Selected angle (deg): C1−C2−C3 = 121.9(9).

Chart 2





(3)

2b-SPh 69%

In summary, we prepared μ-η^3-allenyl/propargyldipalladium complexes of a novel structural type which reacted with HCl to give the first example of a μ-vinylcarbenepalladium complex or to undergo hydrogenation of the μ-η^3-allenyl/propargyl ligand. Further investigation is now in progress.

Acknowledgment. Partial support of this work by grants-in-aid from the Ministry of Education, Science, and Culture and Shorai Foundation for Science and Technology (S.O.) is acknowledged. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of JEOL JNM-GSX 400 and Bruker AM600 spectrometers.

Supporting Information Available: Typical experimental procedures and spectral data of products, and tables of atomic coordinates and anisotropic thermal parameters of all atoms, bond distances, and angles for **2a**, **2b**-SPh, and **3b** (83 pages). This material is contained in many libraries on microfiche, immediately follows in the microfilm version of the journal, can be ordered frin the ACS, and can be downloaded from the Internet; see any current masthead pages for ordering information and Internet access instructions.

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(10) To a solution of 29.9 mg (0.034 mmol) of **2b** in 0.5 mL of CH_2Cl_2 were added 0.1 mL of H_2O and 4.6 mg (0.042 mmol) of $(CH_3)_3SiCl$ at room temperature. The mixture changed to a yellow suspension within 10 min. After 45 min, addition of 0.35 mL of hexane to the suspension yielded yellow solids (24.4 mg, 78%). ^1H NMR spectra of **3b** showed the presence of two isomers, which we tentatively assume to arise from different disposition of P2 and Cl2 on Pd2 (see Figure 3). Selected spectral data for **3b** (major:minor = 67:33) follow. Major isomer: ^1H NMR ($CDCl_3$) δ 3.28 (dd, J_{HH} = 7.5 Hz, J_{HP} = 1.2 Hz, 1H), 3.62 (d, J_{HH} = 10.7 Hz, 1H), 5.31 (ddd, J_{HH} = 7.5, 10.7 Hz, J_{HP} = 6.3 Hz, 1H); ^{31}P NMR δ 28.9 (d, J_{PP} = 4.0 Hz), 24.7 (d, J_{PP} = 4.0 Hz). Minor isomer: ^1H NMR ($CDCl_3$) δ 2.58 (dd, J_{HH} = 13.0 Hz, J_{HP} = 1.6 Hz, 1H), 3.04 (d, J_{HH} = 6.7 Hz, J_{HP} = 1.0 Hz, 1H), 5.52 (ddd, J_{HH} = 13.0, 6.7 Hz, J_{HP} = 3.4 Hz, 1H); ^{31}P NMR δ 26.6 (br s), 21.2 (br s). Anal. Calcd for $C_{45}H_{38}P_2Pd_2Cl_2{\cdot}(CH_2Cl_2)_{1.5}$: C, 53.10; H, 3.93. Found: C, 53.03; H, 4.02.

(11) Crystal data for $\mathbf{3b}{\cdot}(H_2O)_3$: $C_{45}H_{44}P_2Cl_2Pd_2O_3$, triclinic, $P\bar{1}$ (No. 2); $a = 10.233(2)$ Å, $b = 24.617(7)$ Å, $c = 9.028(2)$ Å, $\alpha = 97.69(2)°$, $\beta = 108.69(1)°$, $\gamma = 87.23(2)°$, $Z = 2$, $D_{calc} = 1.522$ g/cm^3. The data were collected at 23 °C with Mo Kα radiation: $\mu = 10.81$ cm^{-1}, $2\theta_{max} = 55.0°$, 488 variables refined with 7851 unique reflections with $I > 3.00\sigma(I)$ to $R(F) = 0.065$ and $R_w(F) = 0.082$.

(12) Macomber, D. W.; Liang, M.; Rogers, R. D. *Organometallics* **1988**, *7*, 416 and references therein.

(13) Ab initio MP2 level calculations explaining the stronger Pd_2−allyl interaction for an allyl ligand having the more electron withdrawing substituent: Kurosawa, H.; Ogoshi, S.; Sakaki, S. Manuscript in preparation

(14) The reaction employing 1 equiv of HCl gave 28% of $Pd(\eta^3\text{-PhCHCHCH}_2)Cl(PPh_3)$, with 0.5 equiv of **2b**-SPh remaining unchanged, while **3b** and **3b**-I were stable to the attack of HCl. The Pd(II) complex $[PdCl(\mu\text{-SPh})(PPh_3)]_2$ was identified by comparison of ^{31}P NMR spectra of the reaction mixture with that of an authentic sample. (a) Boschi, T.; Crociani, B.; Toniolo, L.; Belluco, V. *Inorg. Chem.* **1970**, *9*, 532. (b) Jain, V. K. *Inorg. Chim. Acta* **1987**, *133*, 261.