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[8] X-ray structure determination of **5**: Dark green crystals of **5** were obtained by slow crystallization from a saturated solution in hexane. The data were collected on an Enraf Nonius CAD4 diffractometer at room temperature. Intensity measurements were performed by $\omega/2\theta$ scans in the range $3^\circ < \theta < 27^\circ$ on a crystal of dimensions $0.35 \times 0.28 \times 0.23$ mm. Of the 4409 measured reflections, 4193 were independent; largest minimum and maximum in the final difference Fourier synthesis: -1.063 and $1.621\ \mathrm{e\,\AA^{-3}}$, $R1 = 0.107$ and $wR2 = 0.296$ (for 2496 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[9] Space groups $P2_1$ and $P2_1/m$ were used to solve and refine the structure, but only the former gave a sensible chemical structure due to disorder in the pentamethylcyclopentadienyl rings and the poor quality of the crystal (unfortunately, data could not be obtained at low temperature). However, this disorder did not affect the location of the core of the molecule. The hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[15] All DFT calculations were carried out with the ADF program[16] by using triple-ζ and polarization Slater basis sets to describe the valence electrons of C, N, and O. For titanium, a frozen core composed of the 1s, 2s, and 2p orbitals was described by double-ζ Slater functions, the 3d and 4s orbitals by triple-ζ functions, and the 4p orbital by a single orbital. Basis sets of the same quality were used for Cr, Mo, and W. Hydrogen atoms were described by triple-ζ and polarization functions. The geometries and binding energies were calculated with gradient corrections. We used the local spin density approximation, characterized by the electron gas exchange ($X\alpha$ with $\alpha = 2/3$) together with Vosko–Wilk–Nusair parametrization[17] for correlation. Becke's nonlocal corrections[18] to the exchange energy and Perdew's nonlocal corrections[19] to the correlation energy were added. Quasirelativistic corrections were employed by using the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC.[16] In the DFT calculations on complexes **4**–**8**, the methyl groups were replaced by hydrogen atoms.

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Coupling of Alkynes on a Pd–Pd Bond to Generate an Electrophilic μ-Butenediylidene Moiety[**]

Tetsuro Murahashi, Toshiaki Otani, Taketoshi Okuno, and Hideo Kurosawa[*]

In spite of its potential relevance to new palladium-catalyzed reactions, dipalladium(I)-mediated C–C bond-forming reactions have rarely been achieved in a well-defined manner.[1] This seems curious since the Pd^I–Pd^I complexes are readily accessible and the Pd^{II} and Pd^0 oxidation states also exist.[2] One reason could be that relatively nonlabile auxiliary ligands are used to support the Pd–Pd bond (for example, $Ph_2PCH_2PPh_2$, RNC)[2] so that only a single molecule of unsaturated compounds such as alkynes can be bound (Scheme 1).[3] We sought Pd–Pd complexes that can provide multiple coordination sites for substrate molecules. We report here a facile, regioselective coupling of a terminal alkyne onto the Pd–Pd bond of $[Pd_2(PPh_3)_2(CH_3CN)_4](PF_6)_2$ (**1**),[4] a dipalladium complex with more labile ligands, to generate an electrophilic μ-1κC1,4:2κC1,4-butenediylidene framework.

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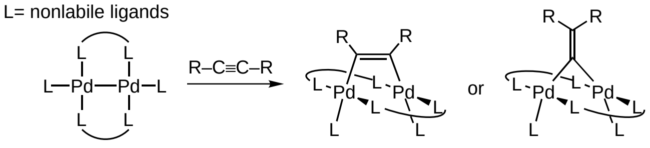
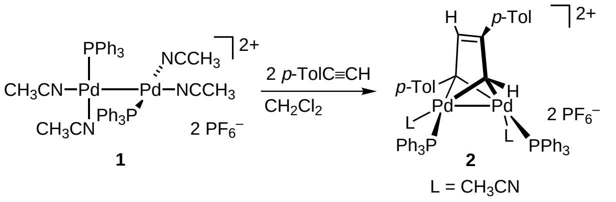
[**] We thank Prof. Y. Kai and E. Mochizuki (Osaka University) for use of X-ray crystallographic analysis facilities and collection of the data for **2** and **3**. Partial support of this work through Grant-in-Aid for Scientific Research, Ministry of Education, Science and Culture, and CREST of Japan Science and Technology Corporation is gratefully acknowledged. T.M. acknowledges the JSPS research fellowships for young scientists. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University for the use of NMR facilities.



Scheme 1. The known reaction patterns of Pd–Pd complexes with alkynes.

The dipalladium(I) complex **1** reacted with two equivalents of *p*-tolylacetylene (*p*-TolC≡CH) immediately at 0 °C in CH_2Cl_2 to give a single product **2** as red crystals in 60 % yield after recrystallization from CH_2Cl_2/*n*-hexane [Eq. (1)]. The reaction was quantitative according to ^1H and ^{31}P NMR spectroscopic analysis. The solid-state structure of **2** was determined by X-ray structure analysis (Figure 1) and showed that *p*-tolylacetylene was dimerized in a head-to-tail manner to form a slightly tilted[5] CHC(Tol)CHC(Tol) bridge across the Pd–Pd bond. The solution ^{31}P NMR spectrum of **2** showed only one sharp singlet at $\delta = 24.96$, even at -90 °C, which is consistent with the essentially symmetric bridge structure. Although a number of μ-1κC1,4:2κC1,2,3,4 and μ-1κC1,2,3,4:2κC1,2,3,4 bridging structures of similar C_4 units have been constructed on M–M bonds, the structural characteristics of **2** are rare[6] and may reflect the carbene-like nature of two terminal carbon atoms coordinated to a 4e acceptor $[L_2Pd{-}PdL_2]^{2+}$, as in $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$,[7] rather than a butadienediyl structure coordinated to a 6e acceptor without a Pd–Pd bond $[L_2PdPdL_2]^{2+}$.[8] The reaction shown in Equation (1) is in contrast to the oxidative coupling of alkynes to mononuclear Pd^0 to give palladacyclopentadienes, which is limited to disubstituted activated alkynes such as dimethylacetylene dicarboxylate (DMAD).[9] Moreover, terminal acetylenes usually undergo oxidative addition of an acetylenic C–H bond to Pd^0 to give a transient alkynyl palladium hydride complex.[10]



(1)

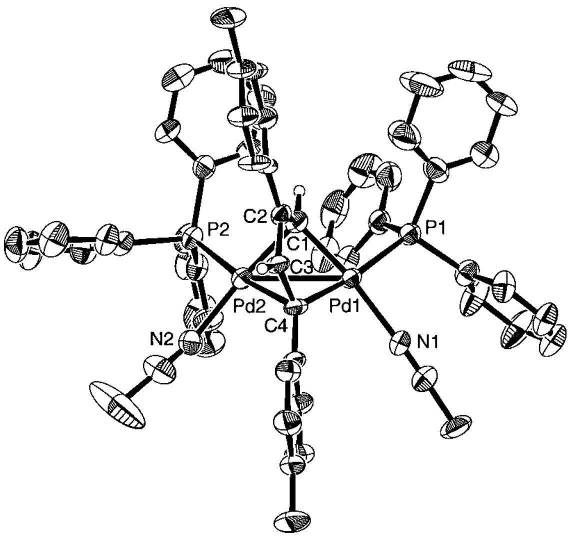
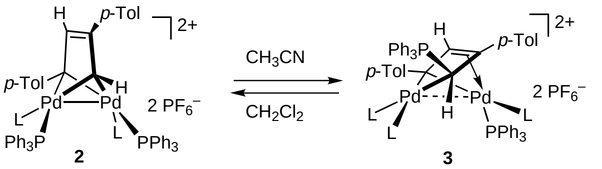


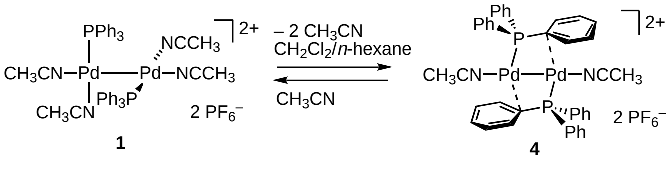
Figure 1. ORTEP plot of **2** (counteranions omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.798(1), Pd1–C1 2.01(1), Pd1–C4 2.06(1), Pd2–C1 2.02(1), Pd2–C4 2.18(1), C1–C2 1.40(2), C2–C3 1.43(2), C3–C4 1.38(2); Pd1-C1-Pd2 87.9(5), C1-C2-C3 109(1), C2-C3-C4 115(1), Pd1-C4-Pd2 82.4(4).

When **2** was dissolved in CD_3CN the new product **3** was immediately generated quantitatively [Eq. (2)]. A single crystal of **3** suitable for X-ray diffraction analysis was obtained from CH_3CN/Et_2O. One PPh_3 ligand of **2** migrated to the H-bearing bridging C atom to generate a phosphane ylide complex containing a palladacyclopentenyl moiety.[11] The ^{31}P NMR spectrum of **3** in CD_3CN at -45 °C showed two sets of pairs of doublets with a ratio of 2:1.[12] Both isomers of **3** were readily converted into **2** in CD_2Cl_2 by loss of a CH_3CN ligand, which means that formation of the ylide is reversible. To our knowledge, such nucleophilic addition at C4 of dinuclear μ-C_4R_4 complexes has not been reported so far in a well-defined manner.



(2)

This unique dimerization of an acetylene system may be attributable to the ability of **1** to generate at least two vacant sites on Pd–Pd in solution. This proposal is supported by the facile dissociation of acetonitrile from **1** to give the orange-yellow dipalladium complex **4**, which was isolated in 87 % yield on precipitation from a solution of **1** in CH_2Cl_2 [Eq. (3)]. The reverse reaction proceeded in CH_3CN solution.



(3)

The X-ray crystal structure of **4** (Figure 2) showed that the two vacant sites generated by loss of two CH_3CN ligands were occupied by η^1-bound[13] *ipso*-carbon atoms of the PPh_3 phenyl rings ($Pd{-}C_{ipso}$ 2.336(4) Å).[14] The distances between Pd1 and the *ortho*-C atoms adjacent to C1 (2.703(4), 2.974(4) Å) are outside the range for Pd–C interaction. No significant structural perturbation of the geometry at the η^1-phenyl or at the phosphorus atom was induced by the μ-1κP:2κC1 coordination,[15] except that the P–C bond of the coordinated phenyl group (P1–C1 1.832(4) Å) was somewhat longer than those of the uncoordinated phenyl groups (1.801(4), 1.806(4) Å). While triphenylphosphane is one of the most versatile ligands for Pd catalysts, there is no precedent in

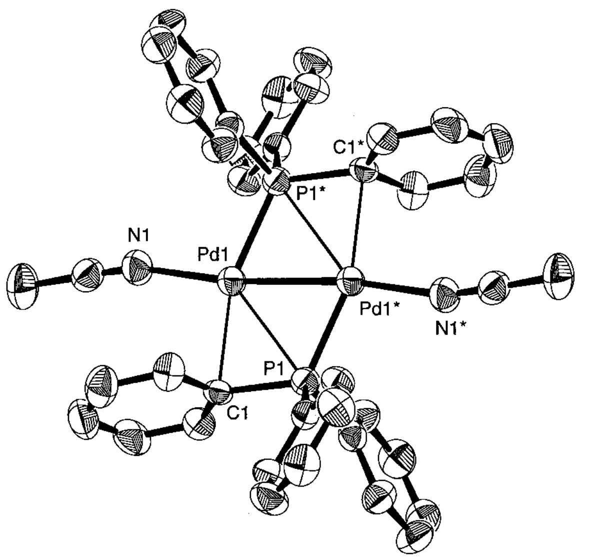
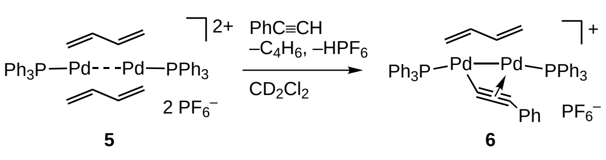


Figure 2. ORTEP plot of **4** (counteranions omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd1* 2.5833(7), Pd1*–P1 2.213(1), Pd1–P1 2.753(1), Pd1–C1 2.336(4), P1–C1 1.832(4); Pd1-Pd1*-P1 69.56(3), Pd1*-Pd1-P1 48.87(2), Pd1-P1-C1 57.1(1), P1-C1-Pd1 81.7(1).

which it bridges two Pd centers.[16] The lability of the PPh_3 bridge of **4** in solution was confirmed by variable-temperature NMR studies. A single set of phenyl carbon signals of the PPh_3 ligands at 23 °C split into two sets with relative intensities of 1:2 at −90 °C, consistent with the coordination and decoordination of the phenyl groups. The fluxional behavior at room temperature could arise from dissociation of *ipso*-C atoms from Pd followed by rotation about the P–Pd bond. Note that **4** reacted with two equivalents of tolylacetylene in CH_2Cl_2 to give **2** in 74 % yield after recrystallization; this represents a simple alkyne coupling on the metal–metal bond without any loss of the auxiliary ligands.

Finally, we also examined the reaction of phenylacetylene with another Pd–Pd complex containing labile bridging ligands, namely, $[(\mu\text{-1,3-butadiene})_2Pd_2(PPh_3)_2](PF_6)_2$ (**5**).[4] However, instead of an alkyne coupling taking place the quantitative formation of complex **6**, presumably having a μ-1κC1:2κC1,2-alkynyl ligand, occurred in CD_2Cl_2 after 30 min at room temperature with dissociation of one of the 1,3-butadiene ligands [Eq. (4)]. Presumably, the remaining μ-1,3-diene ligand, which would become rather tightly bound[17]



(4)

after the initial exchange between acetylene and the other butadiene ligand of **5**, prohibits either insertion of alkyne into the Pd–Pd bond,[3] which may represent the initial step of the alkyne coupling in Equation (1), or the coordination of a second molecule of the alkyne.

In summary, alkyne coupling on a Pd–Pd bond yielded an electrophilic butenediylidene species with complete regioselectivity (head-to-tail).[18] However, the presence of bridging ligands such as 1,3-butadiene prevented dimerization and allowed the formation of a μ-alkynyl ligand.

Experimental Section

2: To an orange solution of **4** (400.0 mg, 0.361 mmol) in CH_2Cl_2 (30 mL) was added dropwise a solution of *p*-tolylacetylene (100.4 µL, 0.721 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring the mixture for 20 min, the resultant red solution was poured into *n*-hexane. Red crystals of **2** (358.1 mg, 74 % yield) were obtained after recrystallization from CH_2Cl_2/*n*-hexane. ^1H NMR (270 MHz, CD_2Cl_2, 25 °C): $\delta = 8.75$ (d, $J = 3.5$ Hz, 1 H), 8.09 (d, $J = 8.4$ Hz, 2 H), 7.41 (d, $J = 8.4$ Hz, 2 H), 7.6–7.2 (m, PPh_3, 30 H), 7.04 (d, $J = 8.4$ Hz, 2 H), 6.85 (d, $J = 8.4$ Hz, 2 H), 5.61 (dt, $J = 7.80$ Hz, $J = 3.5$ Hz, 1 H), 2.42 (s, Me, 3 H), 2.38 (s, Me, 3 H), 1.74 (br s, CH_3CN, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2, −60 °C, CH COSY): $\delta = 196.99$ (t, $J = 60$ Hz, *C*(Tol)-CHC(Tol)CH), 172.84 (s, C(Tol)CH*C*(Tol)CH), 147.40 (s, C(Tol)-*C*HC(Tol)CH), 146.06 (s, *p*-Tol), 144.12 (s, *p*-Tol), 139.38 (s, *ipso*-Tol), 133.39 (d, $J = 13.5$ Hz, PPh_3), 131.60 (s, PPh_3), 130.39 (s, C(Tol)-CHC(Tol)*C*H), 130.10 (s, *m*-Tol), 129.86 (s, *o*-Tol), 129.04 (d, $J = 10.1$ Hz, PPh_3, *m*-Tol), 128.40 (s, *o*-Tol), 127.69 (d, $J = 47.2$ Hz, PPh_3), 126.88 (s, *ipso*-Tol), 123.17 (s, C≡N), 21.67 (s, Me), 21.62 (s, Me), 2.44 (CH_3CN); ^{31}P NMR (109 MHz, CD_2Cl_2, 25 °C): $\delta = 24.76$ (s); elemental analysis calcd for $C_{58}H_{52}N_2P_4F_{12}Pd_2$: C 51.92, H 3.91, N 2.09; found: C 51.71, H 3.84, N 2.12. Crystal data for $\mathbf{2}\cdot 2\,CH_2Cl_2\cdot 2\,H_2O$:[19] $C_{60}H_{60}N_2P_4O_2Cl_4F_{12}Pd_2$, $M_r = 1547.68$, space group $P\bar{1}$ (no. 2), $a = 14.458(4)$, $b = 20.078(4)$, $c = 13.703(5)$ Å, $\alpha = 106.49(2)$, $\beta = 108.28(3)$, $\gamma = 70.73(2)°$, $V = 3492.58$ Å^3, $Z = 2$, $F(000) = 1548$, $\rho_{calcd} = 1.468\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 8.31\ cm^{-1}$. The data were collected at 223 K on a Rigaku RAXIS CS imaging plate area detector up to $2\theta_{max} = 60.0°$. The structure was solved by direct methods; 775 variables were refined with 9167 reflections ($I > 3\sigma(I)$) by full-matrix least-squares methods to $R1 = 0.095$ and GOF = 2.32.

3: Orange crystals of **3** were obtained in 87 % yield by crystallization from a solution of **2** in CH_3CN/Et_2O. At ambient temperature all NMR signals were broadened, probably as a result of the interconversion between the isomers on the NMR timescale. Major isomer: ^1H NMR (270 MHz, CD_3CN, −45 °C): $\delta = 7.9$–7.2 (m, PPh_3, 30 H), 7.04 (d, $J = 4.86$ Hz, 2 H), 6.75 (d, $J = 7.83$ Hz, 2 H), 6.51 (d, $J = 7.83$ Hz, 2 H), 6.28 (br dd, 1 H), 4.54 (d, $J = 3.51$ Hz, 1 H); ^{31}P NMR (109 MHz, CD_3CN, −45 °C): $\delta = 31.39$ (d, $J = 25$ Hz), 26.37 (d, $J = 25$ Hz). Minor isomer: ^1H NMR (CD_3CN, −45 °C): $\delta = 3.45$ (s, 1 H), other signals could not be assigned; ^{31}P NMR (CD_3CN, −45 °C): $\delta = 24.19$ (d, $J = 22$ Hz), 20.41 (d, $J = 22$ Hz); elemental analysis calcd for $C_{60}H_{55}N_3P_4F_{12}Pd_2$: C 52.11, H 4.01, N 3.04; found: C 51.89, H 4.00, N 2.71. Crystal data for $\mathbf{3}\cdot 2\,Et_2O$:[19] $C_{68}H_{75}N_3O_2P_4F_{12}Pd_2$, $M_r = 1531.08$, space group $P\bar{1}$ (no. 2), $a = 18.72(3)$, $b = 18.723(7)$, $c = 10.580(4)$ Å, $\alpha = 96.43(3)$, $\beta = 105.51(6)$, $\gamma = 90.39(8)°$, $V = 3548(4)$ Å^3, $Z = 2$, $F(000) = 1560$, $\rho_{calcd} = 1.433\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 6.73\ cm^{-1}$. The data were collected at 223 K on a Rigaku RAXIS CS imaging plate area detector up to $2\theta_{max} = 60.4°$. The structure was solved by direct methods; 865 variables were refined with 12 340 reflections ($I > 3\sigma(I)$) by full-matrix least-squares methods to $R1 = 0.104$ and GOF = 5.19. The Pd-Pd distance was 2.811(4) Å.

4: Compound **1** (1.300 g, 1.09 mmol) was dissolved in CH_2Cl_2, and the solution poured into *n*-hexane to give orange crystals of **4** (1.052 g, 87 % yield). ^{13}C NMR (150 MHz, CD_2Cl_2, 23 °C): $\delta = 134.98$ (s, *p*-Ph), 133.08 (d, $J = 12.6$ Hz, *o*-Ph), 131.44 (d, $J = 11.6$ Hz, *m*-Ph), 119.90 (s, C≡N), 116.29 (br s, *ipso*-Ph), 2.96 (s, Me); ^{31}P NMR (162 MHz, CD_2Cl_2, 25 °C): $\delta = 23.13$ (s); elemental analysis calcd for $C_{40}H_{36}N_2P_4F_{12}Pd_2$: C 43.30, H 3.27, N 2.52; found: C 43.15, H 3.28, N 2.43; ESI-MS for $C_{40}H_{36}N_2P_3F_6Pd_2$: calcd: 964.49, found: 964.5; ^{13}C NMR (162 MHz, CD_2Cl_2, −90 °C, Ph* indicates coordinated Ph): $\delta = 136.83$ (s, *p*-Ph*), 133.90 (d, $J = 12.6$ Hz, *o*-Ph), 133.50 (s, *m*-Ph*), 132.83 (s, *p*-Ph), 129.04 (d, $J = 11.5$ Hz, *m*-Ph), 127.31 (s, *o*-Ph*), 126.02 (d, $J = 55.3$ Hz, *ipso*-Ph), 118.31 (s, C≡N), 92.11 (d, $J = 49.5$ Hz, *ipso*-Ph*), 2.94 (s, Me). Crystal data for **4**:[19] $C_{40}H_{36}N_2P_4F_{12}Pd_2$, $M_r = 1109.41$, space group $P\bar{1}$ (no. 2), $a = 11.045(2)$, $b = 12.434(2)$, $c = 8.354(2)$ Å, $\alpha = 90.92(2)$, $\beta = 92.94(2)$, $\gamma = 110.95(1)°$, $V = 1069.3(4)$ Å^3, $Z = 1$, $F(000) = 550$, $\rho_{calcd} = 1.723\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 10.60\ cm^{-1}$. The data were collected at 296 K on a Rigaku AFC5R diffractometer up to $2\theta_{max} = 55.1°$. The structure was solved by Patterson methods; 271 variables were

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refined with 4171 reflections ($I > 3\sigma(I)$) by full-matrix least-squares methods to $R1 = 0.049$, $R_w = 0.036$ and GOF = 3.03.

6: Phenylacetylene (14.5 µL, 0.132 mmol) was added to a yellow suspension of **5** (100.0 mg, 0.0881 mmol) in benzene and the solution stirred for 5 min at room temperature. Then pyridine (7.1 µL, 0.0881 mmol) was added, and the mixture was stirred for 10 min. The resultant orange solution was filtered, and the filtlate was poured into *n*-hexane to afford **6** as a yellow powder (63.7 mg, 70 % yield). The NMR spectra of the reaction mixture in CD_2Cl_2 confirmed quantitative formation of **6** without addition of pyridine. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 7.6-7.4$ (m, PPh_3, 30 H), 7.00 (t, $J =$ 7.6 Hz, 1 H), 6.80 (t, $J = 7.6$ Hz, 2 H), 6.59 (d, $J = 7.6$ Hz, 2 H), 3.67 (brs, 2 H), 3.02 (brs, 2 H), 2.79 (brd, 2 H); ^{31}P NMR (162 MHz, CD_2Cl_2, 25 °C): $\delta =$ 33.8 (s); elemental analysis calcd for $C_{48}H_{41}P_3F_6Pd_2$: C 55.56, H 3.98; found: C 55.35, H 4.03; Raman (solid): $\tilde{\nu}_{C\equiv C} = 2008$, 1975 cm^{-1}; the fluxional nature of **6** at 25 °C was confirmed by variable-temperature NMR analyses; ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C): $\delta = 7.6-7.4$ (m, 30 H), 6.94 (t, 1 H), 6.75 (t, 2 H), 6.48 (d, 2 H), 4.14 (brd, 1 H), 3.71 (brm, 1 H), 3.19 (brd, 1 H), 3.05 (brs, 1 H), 2.22 (brm, 2 H); ^{31}P NMR (162 MHz, CD_2Cl_2, −80 °C): $\delta =$ 35.2 (d, $J = 51.8$ Hz), 32.7 (d, $J = 51.8$ Hz).

Received: June 2, 1999 [Z13510]

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[5] The slight tilting of the C_4 framework results in an angle of 74.5° between the C1-C2-C3-C4 mean plane and the Pd1−Pd2 vector.

[6] Acetylene coupling on metal–metal bonds of middle transition metals has been reported; μ-1κC1,2,3,4:2κC1,2,3,4 type: a) Q. Feng, M. L. H. Green, P. Mountford, *J. Chem. Soc. Dalton Trans.* **1992**, 2171; μ-1κC1,4:2κC1,2,3,4-type: b) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, P. Woodward, *J. Chem. Soc. Dalton Trans.* **1982**, 173; c) M. H. Chisholm, K. Folting, J. C. Huffman, I. P. Rothwell, *J. Am. Chem. Soc.* **1982**, *104*, 4389, and references therein; d) Review: W. P. Fehlhammer, H. Stolzenberg in *Comprehensive Organometallic Chemistry, Vol. 4* (Eds.: G. Wilkinson, F. G. A. Stone, E. Abel), Pergamon, **1982**, chap. 31.4; A similar complex [(μ-1κC1,4:2κC1,4-CHC(Ph)C(Ph)CH)Ni_2(depe)$_2$]$(PF_6)_2$ (depe = 1,2-bis(diethylphosphanyl)ethane) was derived from a butadienediyl Ni^{II} complex without any evidence of acetylene coupling on the Ni−Ni bond: e) C. J. Lawrie, H. E. Dankosh, B. K. Carpenter, *J. Organomet. Chem.* **1991**, *411*, C7; [(μ-1κC1,4:2κC1,4-CHC(CH_2OH)C(CH_2OH)-CH)Ni_2(diimine)$_2$], which has a different formal valency of the metal centers from **3**, has also been structurally characterized: f) R. Diercks, L. Stamp, J. Kopf, H. tom Dieck, *Angew. Chem.* **1984**, *96*, 891; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 893.

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[16] The only example of a triphenylphosphane bridge across trinuclear Pd-Pd-Pd was recently found in $[Pd_3(\mu_3$-1κP:2κC1,2:3κC3,4-$PPh_3)_2(PPh_3)_2]^{2+}$: a) S. Kannan, A. J. James, P. R. Sharp, *J. Am. Chem. Soc.* **1998**, *120*, 215; μ-1κP:η^x-PPh_3 ($x = 2,4,6$) coordination was observed with other transition metals: b) G. B. Robertson, P. O. Whimp, *J. Organomet. Chem.* **1973**, *60*, C11; c) R. Luck, R. H. Morris, J. F. Sawyer, *Organometallics* **1984**, *3*, 1009; d) H.-F. Hsu, S. R. Wilson, J. R. Shapley, *Organometallics* **1997**, *16*, 4937; e) I. Ara, L. R. Falvello, J. Forniés, E. Lalinde, A. Martín, F. Martínez, M. T. Moreno, *Organometallics* **1997**, *16*, 5392.

[17] The μ-butadiene ligand in the monobutadiene complex $[Pd_2(\mu$-1,3-butadiene$)(\mu$-Cl$)(PPh_3)_2)]^{+[4]}$ is much less labile than that of **5**.

[18] Products analogous to **2** were obtained when *p*-X-$C_6H_4C\equiv CH$ (X = H, Cl) were used (36–56 % yield according to NMR spectroscopy; relatively low yields were partly a result of decomposition of the products). Inner alkynes such as $PhC\equiv CPh$ and $PhC\equiv CMe$ also reacted with **1** or **4**, but more complicated results were obtained under the reaction conditions of Equation (1).

[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-124471 (**2**), -124472 (**3**), and -124473 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).