Rational synthesis of anionic, neutral and cationic palladium(I) dinuclear complexes containing bridging conjugated dienes

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Addition of conjugated diene to an equimolar mixture of palladium(II) halides and a palladium(0) complex induces facile Pd–Pd bond formation to give anionic, neutral and cationic Pd^{I}–Pd^{I} dinuclear complexes containing bridging 1,3-diene ligands.

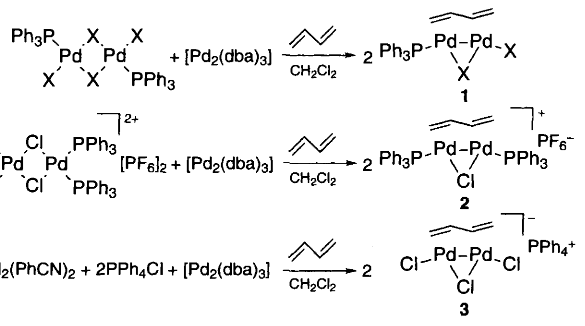
Increasing attention has been paid to organopalladium complexes containing a Pd–Pd bond bridged by 4e-donating hydrocarbon ligands, such as alkyne,[1] allyl,[2] allenyl/prop-2-ynyl,[3] cyclopentadienyl,[2] or arene.[4] Another ubiquitous 4e donor, 1,3-diene, has been used only rarely as a bridging ligand at Pd–Pd, an example being [(isoprene)Pd_2(μ-PBu^t_2)($PHBu^t_2$)$_2$]$^+$, recently prepared by exchange of a bridging $PHBu^t_2$ ligand on Pd–Pd with the diene;[5] by contrast the 1,3-diene chemistry of mononuclear palladium-(II) and -(0) complexes has been extensively developed.[6] We report here a convenient method for the synthesis of 1,3-diene complexes containing Pd–Pd moieties, including two new fragments, [Pd_2X_2(μ-X)]$^-$ and [Pd_2X(μ-X)(PPh_3)], which involves a directed Pd–Pd bond formation as a key step. This method is novel when compared to those for the known 1,3-diene complexes of di- or poly-nuclear metal systems[7] employing a simple ligand substitution on the pre-formed metal–metal bond,† as above.[5]

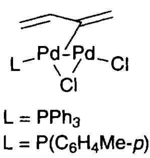
A mixture of [$Pd_2X_4(PPh_3)_2$] (X = Cl, Br, I) and [$Pd_2(dba)_3$] (dba = dibenzylideneacetone) was stirred in CH_2Cl_2, through which buta-1,3-diene was bubbled for 0.5 h at room temperature, to give a deep-red solution. From this solution deep-red crystals of **1** were obtained (X = Cl **1a**, Br **1b**, I **1c**) in 70–82% yield after crystallization.‡ The synthetic route to **1** could be used in the preparation of the corresponding cationic orange complex **2** (70% yield) or anionic deep-red complex **3** (49% yield). The new complexes were all stable to air and water at room temperature in the solid state, while in solution **1c** was much less stable than **1a** or **1b** presumably because of the terminal iodide.

A series of isoprene analogues **4**–**10** was prepared similarly in 53–71% yield.‡ A pair of regioisomers was generated for the neutral complexes **4**, **5** (85 : 15) or **6**, **7** (85 : 15).

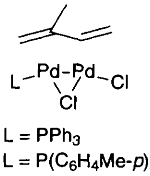
^1H–^1H NMR homodecoupling experiments on **1b** revealed an *s*-vicinal coupling of 11.2 Hz, which implies that the coordination geometry of butadiene is *s-trans* in solution. The structure of **1b** was confirmed by X-ray diffraction (Fig. 1).§ The central buta-1,3-diene carbons C(2) and C(3) were disordered with an unequal occupancy [C(2), C(3) : C(2′), C(3′) = 70 : 30] so as to give a pair of diastereoisomers due to the chiral geometry of PPh_3 in the crystal. This disorder makes a detailed discussion about the structural parameters of the buta-1,3-diene difficult. However, the geometry is deduced to be $\eta^2:\eta^2$-*s-trans* by the distance between the non-disordered terminal C(1) and C(4) atoms [3.87(2) Å]; for an *s-cis* diene this would be *ca.* 2.8 Å. The Pd–Pd distance of 2.662(1) Å is in the range of normal Pd–Pd single bonds (2.50–2.84 Å).[8] The two Pd atoms, P, Br(1) and Br(2) are virtually on the same plane.

The structure of **10** was also determined by X-ray diffraction (Fig. 2).§ Both inner carbons and the methyl group of the

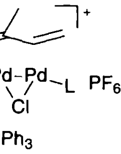




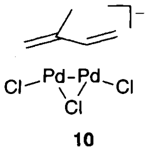
4 L = PPh_3
6 L = P(C_6H_4Me-*p*)$_3$



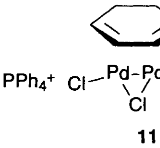
5 L = PPh_3
7 L = P(C_6H_4Me-*p*)$_3$



8 L = PPh_3
9 L = P(C_6H_4Me-*p*)$_3$



10



11

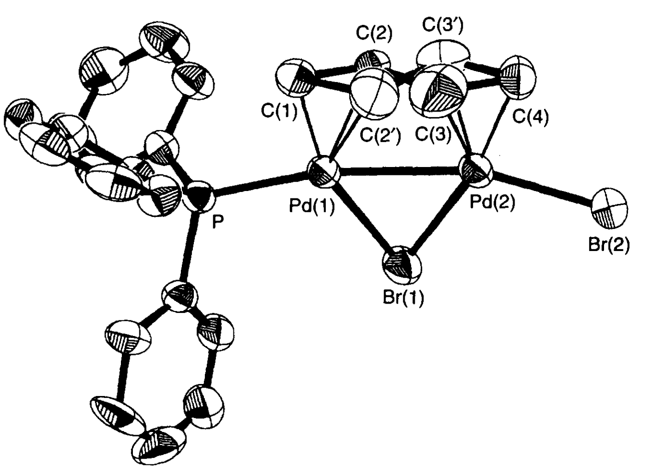


Fig. 1 ORTEP drawing of **1b** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Pd(1)–Pd(2) 2.662(1), Pd(1)–P 2.278(3), Pd(1)–Br(1) 2.448(2), Pd(2)–Br(1) 2.487(2), Pd(2)–Br(2) 2.450(2), Pd(1)–C(1) 2.12(1), Pd(1)–C(2) 2.25(2), Pd(2)–C(3) 2.15(3), Pd(2)–C(4) 2.14(1), Pd(1)–C(2′) 2.29(10), Pd(2)–C(3′) 2.17(7), C(1)–C(2) 1.40(3), C(2)–C(3) 1.44(7), C(3)–C(4) 1.42(6), C(1)–C(2′) 1.5(1), C(2′)–C(3′) 1.6(2), C(3′)–C(4) 1.42(9), P–Pd(1)–Pd(2) 167.59(8), Br(2)–Pd(2)–Pd(1) 158.85(5), P–Pd(1)–Br(1) 109.59(8), Br(2)–Pd(2)–Br(1) 102.20(5), Pd(1)–Br(1)–Pd(2) 65.28(4), C(1)–C(2)–C(3) 127(4), C(2)–C(3)–C(4) 127(6), C(1)–C(2′)–C(3′) 121(16), C(2′)–C(3′)–C(4) 115(13), Pd(1)–Pd(2)–C(4) 111.8(3), Pd(2)–Pd(1)–C(1) 101.1(3).

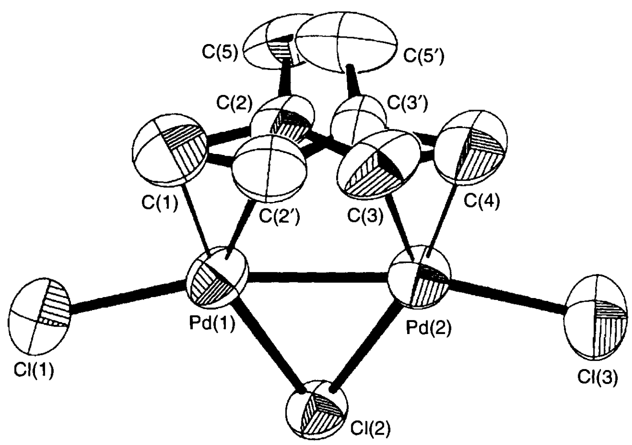


Fig. 2 ORTEP drawing of **10** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Pd(1)–Pd(2) 2.5776(2), Pd(1)–Cl(1) 2.332(2), Pd(1)–Cl(2) 2.378(1), Pd(2)–Cl(2) 2.389(1), Pd(2)–Cl(3) 2.344(2), Cl(1)–Pd(1)–Pd(2) 162.73(4), Cl(1)–Pd(1)–Cl(2) 105.61(6), Pd(1)–Cl(2)–Pd(2) 65.47(4).

isoprene are disordered giving a pair of enantiomers. The occupancy was set as 50 : 50 by refinement.¶ The geometry of the isoprene is also $\eta^2 : \eta^2$-*s-trans* [C(1)–C(4) 3.82(1) Å] and the Pd–Pd bond distance is 2.578(1) Å, shorter than in **1b**. The two Pd atoms and three Cl atoms are almost coplanar.

At first sight, our synthetic methodology appears to be a simple redox condensation reaction between Pd^{II} and Pd^0 moieties leading to Pd–Pd bond formation. However, the presence of a conjugated diene is required for this process. Thus, when a mixture of [Pd$_2$Cl$_4${P(C$_6$H$_4$Me-*p*)$_3$}$_2$] or [Pd$_2$Cl$_2${P(C$_6$H$_4$Me-*p*)$_3$}$_4$][PF$_6$]$_2$ and [Pd$_2$(dba)$_3$] was monitored by ^{31}P NMR in CDCl$_3$ or CD$_2$Cl$_2$ solution at room temperature, no reaction was observed to occur until isoprene was added, and the corresponding palladium dinuclear complexes **6**, **7** or **9** (J_{PP} = 83 Hz) began to form gradually. Use of non-conjugated dienes such as penta-1,4-diene or norborna-2,5-diene did not give the corresponding palladium dinuclear complexes. Coordination of *trans,trans*-diphenylbuta-1,3-diene to Pd–Pd was observed (^{1}H NMR monitoring experiment) only with the anionic fragment, [Pd$_2$Cl$_2$(μ-Cl)]$^-$ (δ 4.85, 3.39 for PhC*H*=C*H*–). Interestingly, cyclohexa-1,3-diene also had the ability to construct the anionic dinuclear complex **11**, but no such ability to form neutral and cationic dinuclear complexes; **11** was easily decomposed in solution to generate benzene and a palladium mirror.

A 1,3-diene ligand on Pd–Pd undergoes facile exchange with free 1,3-dienes. Equilibrium constants for competitive coordination of buta-1,3-diene and isoprene on [Pd$_2$Cl(μ-Cl)(PPh$_3$)], [Pd$_2$(μ-Cl)(PPh$_3$)$_2$]$^+$ or [Pd$_2$Cl$_2$(μ-Cl)]$^-$ showed preferential coordination of buta-1,3-diene (K_{eq} = 1.6, 4.8 or 2.9 at 25 °C in CDCl$_3$). Reactions of the new complexes with other unsaturated hydrocarbons are under investigation.

Footnotes

† Exceptions to this synthetic pathway involve metal–metal bond formation from mononuclear fragments through irradiation^{7d} or multistep processes,^{7b,c} which however result in low-yield product formation.

‡ All new complexes (except **11**) gave satisfactory elemental analyses. *Selected NMR spectroscopic data* (in CDCl$_3$). **1b**: ^{1}H, δ 7.7–7.4 (m, Ph), 4.76 (d, 1 H, *J* 6.96 Hz), 3.49 (d, 1 H, *J* 12.8 Hz), 3.35 (dddd, 1 H, *J* 6.96, 12.8, 3.30, 11.2 Hz), 3.13 (ddd, 1 H, *J* 7.52, 1.06, 3.11 Hz), 2.87 (ddd, 1 H, *J* 7.24, 12.0, 11.2 Hz), 2.52 (dd, 1 H, *J* 12.0, 1.06 Hz); ^{31}P, [ext. P(OMe)$_3$] δ −114.13(s). **8**: ^{1}H, δ 7.7–7.4 (m, Ph), 3.65 (br s, 1 H), 3.39 (br d, 1 H), 3.37 (br d, 1 H), 3.23 (br ddd, 1 H), 2.72 (dd, 1 H), 0.99 (dd, 3 H); ^{31}P, δ −109.07 (d, *J* 85 Hz), −112.26 (d); ^{13}C, δ 133.89–29.26 (Ph), 89.34 (s), 70.46 (s), 49.89 (s), 19.10 (s). **11**: ^{1}H, δ 8.0–7.6 (m, Ph), 5.21 (m, 2 H), 5.15 (m, 2 H), 1.36 (br s, 4 H).

§ *Crystal data* for **1b**·H$_2$O: C$_{24}$H$_{21}$Br$_2$OPPd$_2$, M = 707.00, triclinic, space group $P\bar{1}$ (no. 2), a = 11.463(3), b = 12.407(2), c = 8.871(1) Å, α = 100.29(1), β = 91.62(2), γ = 92.80(2)°, U = 1239.0(4) Å^3, Z = 2, F(000) = 680, D_c = 1.895 g cm^{-3}, μ(Mo-Kα) = 47.62 cm^{-1}, 276 variables refined with 4166 reflections with $I > 3\sigma(I)$ to R = 0.056, R_w = 0.070. For **10**·CH$_2$Cl$_2$: C$_{30}$H$_{30}$Cl$_5$PPd$_2$, M = 811.61, triclinic, space group $P\bar{1}$ (no. 2), a = 10.099(2), b = 18.186(4), c = 9.026(2) Å, α = 90.83(2), β = 94.11(1), γ = 104.79(1)°, U = 1597.7(5) Å^3, Z = 2, F(000) = 804, D_c = 1.687 g cm^{-3}, μ(Mo-Kα) = 16.13 cm^{-1}, 371 variables refined with 5647 reflections with $I > 3\sigma(I)$ to R = 0.049, R_w = 0.044. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/5.

¶ The geometry of PPh$_4^+$ in the crystal was chiral. However, the steric effect of this cation on the μ-isoprene geometry is thought to be negligible, so as to lead to occupancies of 50 : 50.

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