Reactions of μ-Ethynediyl Complexes of Transition Metals: Selective Double Insertion of Isocyanides and Molecular Structure of $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$‡

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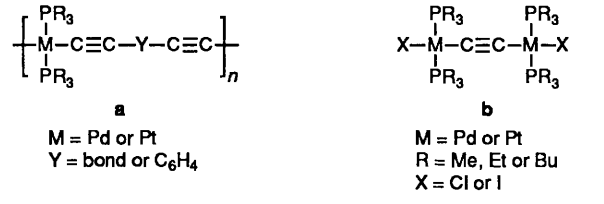
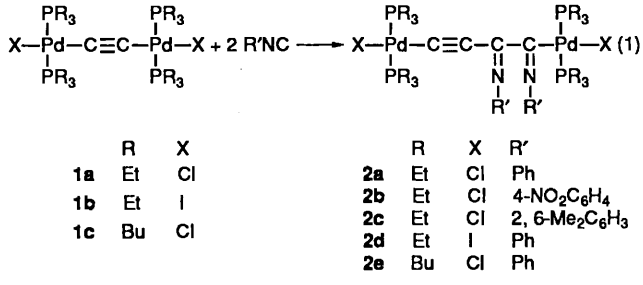
The μ-ethynediyl-dipalladium complexes $[X(R_3P)_2PdC{\equiv}CPd(PR_3)_2X]$ **1** (X = Cl or I, R = Et or Bu) react with aryl isocyanides R'NC(R' = Ph, 4-$NO_2C_6H_4$, or 2,6-$Me_2C_6H_3$) to give double-insertion products $[X(R_3P)_2PdC{\equiv}CC(=NR')C(=NR')Pd(PR_3)_2X]$ **2**, selectively. Complexes **2** have been characterized by IR, mass, ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} NMR spectra. Selective double insertion is peculiar to the μ-ethynediyl dinuclear complexes, and other dipalladium complexes $[Cl(R_3P)_2PdC{\equiv}CYC{\equiv}CPd(PR_3)_2Cl]$ (Y = bond or C_6H_4) and mononuclear acetylide complexes $[Pd(PEt_3)_2Cl(C{\equiv}CR)]$ (R = Ph or 4-$MeOC_6H_4$) give normal single-insertion products, respectively. The dicationic complex $[(PhNC)(Et_3P)_2PdC{\equiv}CPd(PEt_3)_2(CNPh)][PF_6]_2$ has been isolated as an intermediate, which reacts with NR_4X (R = Et or C_5H_{11}; X = Cl, Br or I) to give double-insertion products **2**. The structure of $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$ has been determined by X-ray analysis: space group $P2_1/c$, a = 11.488(3), b = 24.997(5), c = 18.659(4) Å, β = 112.91(2)°, and Z = 4.

Many transition-metal complexes containing σ-bonded acetylene ligands have been prepared and structurally characterized.[1] Some of them, especially Group 11 metal compounds, are useful reagents in organic synthesis.[2] Some reactions of transition-metal acetylide complexes have been described,[3] but there are few reports on insertion reactions into the metal–carbon bonds of such complexes[4] though insertion is a common reaction for transition metal alkyls.

We have been studying the transition metal–poly(yne) polymers **a** in which metals are linked by conjugated acetylenes such as butadiyne and *p*-diethynylbenzene.[5] We have previously reported the synthesis of μ-ethynediyl-dipalladium and -diplatinum complexes **b** as the first examples of the σ,σ co-ordination mode of acetylene for Group 10 metals (Scheme 1).[6] The μ-ethynediyl complexes, in which two metal atoms are linked together by just one acetylene unit, may be expected to have novel properties owing to the mutual interaction between the two metals through the carbon–carbon triple bond. Hence we have examined the reactivity of μ-ethynediyl-dipalladium complexes and found the selective double-insertion of isocyanides into just one of the two metal–carbon bonds.[7] In this paper we describe the novel double insertion in detail and an X-ray crystallographic study of the resulting complex.



Scheme 1



Scheme 2

Results and Discussion

Reaction of μ-Ethynediyl Complexes with Isocyanides.—The μ-ethynediyl dipalladium complex **1a** was treated with phenyl isocyanide in a molar ratio 1:2 in dichloromethane at room temperature to give a yellow product **2a** in good yield (Scheme 2). The product **2a** is stable to air and soluble in common organic solvents except aliphatic hydrocarbons, and has been identified by spectral analyses (Table 1). The IR spectrum showed absorptions at 2080 cm^{-1} due to ν(C≡C) and at 1670 cm^{-1} due to ν(C=N). In the field desorption mass spectrum the molecular ion (*m/z* 986) was detected, indicating that the product must be derived from one molecule of **1a** and two molecules of phenyl isocyanide. The ^{31}P-{^1H} NMR spectrum of **2a** exhibited two singlets at δ 18.6 and 24.9, suggesting that phenyl isocyanide has inserted into a metal–carbon bond of **1a** to afford an iminoacyl complex having an unsymmetrical structure. Furthermore two sets of signals due to phenyl and imino groups were observed in the ^1H and ^{13}C-{^1H} NMR

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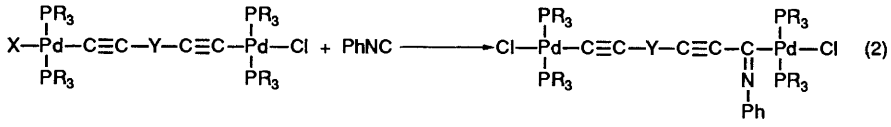
‡ μ-[3,4-Bis(phenylimino)butynylene-κC^1:κC^4]-bis[chloro(triethylphosphine)palladium].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue, 1, pp. xviii–xxii.

Table 1 Physical data for complexes **2**

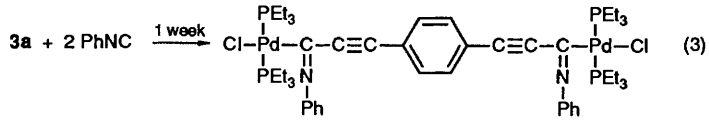
Complex	Colour	M.p.(°C)	IR/cm^{-1} ν(C≡C)	IR/cm^{-1} ν(C=N)	^{31}P-{^{1}H}NMR(δ)
2a	Yellow	83–85	2080	1570	18.6, 24.9
2b	Yellow	150–152	2080	1565, 1515	20.1, 25.5
2c	Red-orange	157–158	2090	1585, 1545	25.8, 31.0*
2d	Orange	163–165	2090	1575	15.6, 21.4
2e	Yellow	—	2075	1570	11.8, 16.2
2f	Yellow	143–145	2080	1570	17.5, 23.6

* Broad.



	R	Y
3a	Et	C_6H_4
3b	Bu	C_6H_4
3c	Bu	bond

	R	Y
4a	Et	C_6H_4
4b	Bu	C_6H_4
4c	Bu	bond



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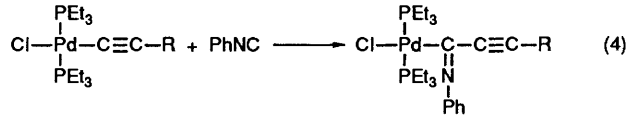
Scheme 3

Table 2 Physical data for complexes **4**, **5**, and **7**

Complex	M.p.(°C)	IR(cm^{-1}) ν(C≡C)	IR(cm^{-1}) ν(C=N)	^{31}P-{^{1}H}NMR(δ)
4a	135–138*	2170, 2110	1530	19.0, 24.4
4b	—	2170, 2110	1540	12.1, 16.2
4c	—	2040	1530	11.8, 16.6
5	165–166*		1530	19.2
7a	150–151	2170	1530	19.1
7b	129–131	2165	1535	19.0

* Decomposes.



	R
6a	Ph
6b	4-MeOC$_6$H$_4$

	R
7a	Ph
7b	4-MeOC$_6$H$_4$

Scheme 4

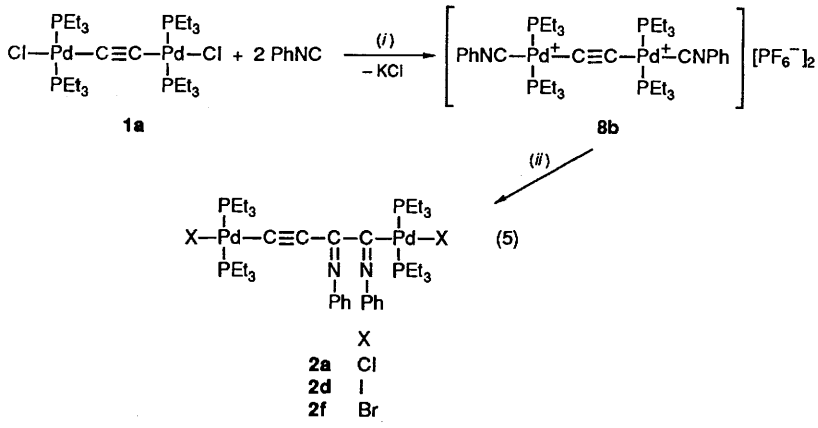
spectra. These data are consistent with the proposed structure **2a** which is produced by double insertion of phenyl isocyanide into just one of the two M–C bonds, and has been confirmed by an X-ray analysis (see below).

Similarly the treatment of complex **1a** with 4-nitrophenyl and 2,6-dimethylphenyl isocyanides gave double-insertion products **2b** and **2c**. The rate of insertion was enhanced when R′ of R′NC was an electron-withdrawing group and reduced when it was a bulky group. The rate also depends on the halide ligands on the metal and decreases in the order Cl > Br > I. Alkyl isocyanides having an electron-releasing group such as cyclohexyl and *tert*-butyl isocyanide did not lead to an insertion. Other μ-ethynediyl-dipalladium complexes **1b** and **1c** also reacted with phenyl isocyanide to give double-insertion products **2d** and **2e**, respectively.

On the other hand, for binuclear complexes **3**, in which two palladium atoms are linked by butadiyne or *p*-diethynylbenzene, normal single insertion of phenyl isocyanide was observed (Scheme 3 and Table 2). When the reaction time was prolonged to about 1 week the complex **3a** gave the product **5** by insertion of one molecule of isocyanide into each of the two M–C bonds. The reaction of the mononuclear acetylide complex **6a** or **6b** gave only a single-insertion product **7a** or **7b** (Scheme 4). The $Pd(PR_3)_2Cl$ group is known to behave as a good electron donor, comparable with that of a methoxy group.[8] Complex **6b** having a *p*-methoxyphenyl group, however, did not afford a double-insertion product, but a single-insertion one, **7b**. These results clearly show that double insertion of isocyanides is characteristic to the μ-ethynediyl complexes.

It should be noted that the reaction of complex **1a** with an equimolar amount of phenyl isocyanide did not give a single-insertion product, but yielded the double-insertion product **2a** with recovery of about half of the starting material. Treatment of the μ-ethynediyl-dipalladium complex **1a** with an excess of phenyl isocyanide gave only **2a**, and no further insertion of the isocyanide was detected. These facts reveal that complex **1a** essentially undergoes selective double insertion of isocyanides.

In general the insertion reaction of isocyanides into metal–alkyl bonds is supposed to proceed *via* an intermediate in which both isocyanide and alkyl groups are bonded to the metal.[9] In order to obtain information about the mechanism of the double-insertion reaction we carried out the reaction at low temperature. On treatment of μ-ethynediyl complex **1a** with 2 equivalents of phenyl isocyanide at −78 °C white solids were obtained. The IR spectrum of the product showed an absorption at 2170 cm^{-1} due to ν(C≡N), which is higher than that of free phenyl isocyanide, suggesting the formation of a cationic isocyanide complex $[(PhNC)(Et_3P)_2PdC{\equiv}CPd(PEt_3)_2(CNPh)]Cl_2$ **8a**. However, complex **8a** was thermally unstable and was not isolated in a pure form because it was



Scheme 5 (*i*) KPF_6; (*ii*) NR_4X

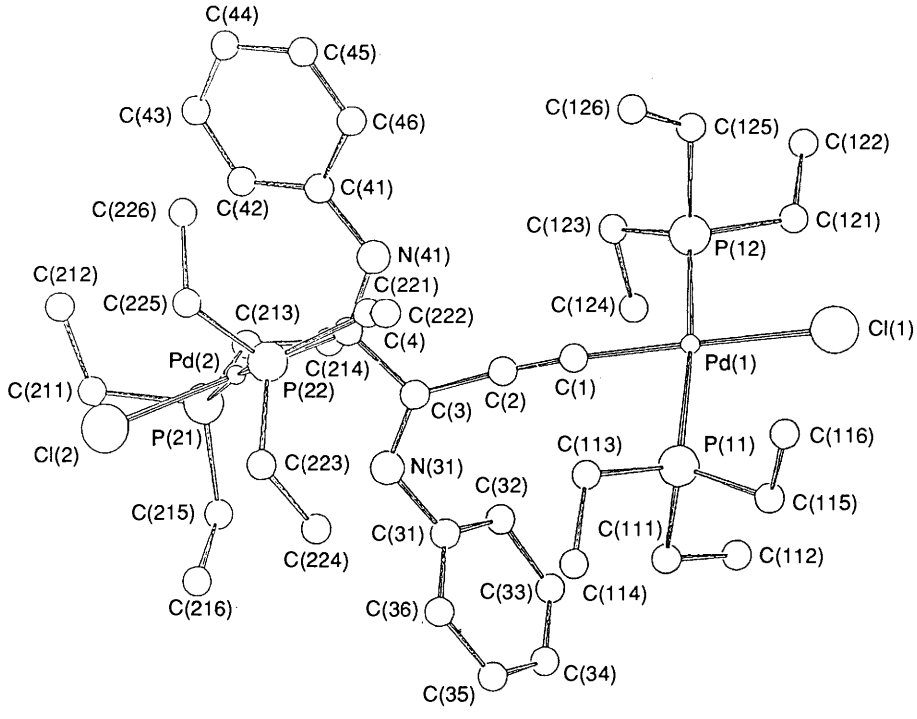


Fig. 1 A perspective view of $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$ **2a** showing the atom numbering scheme

instantaneously transformed into **2a** even in the solid state at room temperature. Hence we have traced the reaction sequence of **1a** with phenyl isocyanide in CH_2Cl_2 by means of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. A signal at δ 28.9 was observed at an initial stage of the reaction, and as the reaction proceeded this signal disappeared and signals due to the double-insertion product dominated. The signal at δ 28.9 was tentatively assigned to the cationic complex **8a** because signals due to cationic isocyanide complexes are known to appear at lower fields than those of neutral complexes.

When complex **1a** was treated with 2 equivalents of phenyl isocyanide in the presence of an excess of KPF_6 a stable cationic complex was isolated as a white solid. Its IR spectrum showed an absorption at 2180 cm^{-1} and the $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibited a signal at δ 28.8. On the basis of these data and elemental analysis the product was identified as a cationic complex $[(PhNC)(Et_3P)_2PdC{\equiv}CPd(PEt_3)_2(CNPh)][PF_6]_2$ **8b** (Scheme 5). When **8b** was treated with NR_4X (R = Et or C_5H_{11}; X = Cl, Br or I) the double insertion of phenyl isocyanides took place smoothly to give complex **2**. The rates of double insertion depend on the nature of the halide and decrease in the order Cl > Br > I. The same trend has been observed in reaction (1), suggesting that complex **8a** should be an intermediate in the double-insertion reaction.

The Structure of $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$ **2a**.—The molecular structure of complex **2a** is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 3. The molecule consists of a bis(iminoacyl) structure formed from two isocyanide molecules inserted into one of the two ethynylpalladium bonds. The five atoms (ClPdC≡CC) containing two sp carbons are collinear. Each of the vicinal N-phenyl groups bends away to minimize repulsive interactions. The dihedral angle between the two $PdClP_2C$ planes is 54.4(1)°, in contrast with the dihedral angle of 89.8(3)° between the two $PtIP_2$ planes of $[I(Me_3P)_2PtC{\equiv}CPt(PMe_3)_2I]$ **9**.[6] This difference is likely due to crystal-packing forces. The dihedral angles between Pd(2)Cl(2)P(21)P(22)C(4) and phenyl ring C(31)–C(36) or C(41)–C(46) are 92.3(3) and 107.0(3)°, respectively, larger by 10° than those between PdP_2Cl and phenyl rings in *trans*-$[PdCl\{C(=NC_6H_4OMe\text{-}4)C(Me)=NC_6H_4OMe\text{-}4\}(PPh_3)_2]$ **10**.[10] The torsion angles C(2)C(3)C(4)Pd(2) and N(31)C(3)C(4)N(41) are −155.4(7) and −159.6(8)°, respectively. The Pd(2)–Cl(2) bond length of 2.401(3) Å is comparable

Table 3 Selected interatomic distances (Å) and angles (°) for $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$ **2a**

Pd(1)–Cl(1)	2.339(3)	Pd(2)–C(4)	1.992(8)
Pd(1)–P(11)	2.319(3)	C(1)–C(2)	1.200(12)
Pd(1)–P(12)	2.313(4)	C(2)–C(3)	1.450(12)
Pd(1)–C(1)	1.939(8)	C(3)–C(4)	1.509(12)
Pd(2)–Cl(2)	2.401(3)	C(3)–N(31)	1.279(13)
Pd(2)–P(21)	2.349(2)	C(4)–N(41)	1.267(13)
Pd(2)–P(22)	2.318(3)		
Cl(1)–Pd(1)–P(11)	93.7(1)	P(21)–Pd(2)–C(4)	92.9(2)
Cl(1)–Pd(1)–P(12)	92.0(1)	P(22)–Pd(2)–C(4)	89.6(2)
Cl(1)–Pd(1)–C(1)	179.1(3)	Pd(1)–C(1)–C(2)	176.8(9)
P(11)–Pd(1)–P(12)	171.9(1)	C(1)–C(2)–C(3)	173.8(11)
P(11)–Pd(1)–C(1)	85.7(3)	C(2)–C(3)–C(4)	118.0(8)
P(12)–Pd(1)–C(1)	88.5(3)	C(2)–C(3)–N(31)	125.4(8)
Cl(2)–Pd(2)–P(21)	90.5(1)	C(4)–C(3)–N(31)	116.5(7)
Cl(2)–Pd(2)–P(22)	87.0(1)	Pd(2)–C(4)–N(41)	129.5(6)
Cl(2)–Pd(2)–C(4)	176.5(2)	Pd(2)–C(4)–C(3)	115.6(7)
P(21)–Pd(2)–P(22)	174.0(1)	C(3)–C(4)–N(41)	114.9(7)

with that [2.41(1) Å] in **10**, but is longer than Pd(1)–Cl(1) 2.339(3) Å, mainly due to the influence of the *trans* ligand. The Pd(2)–C(4) bond length of 1.992(8) Å is longer than Pd(1)–C(1) 1.939(8) Å, owing to the sp and sp^2 carbons, respectively. The bond lengths of C(2)–C(3) and C(3)–C(4) are 1.450(12) and 1.509(12) Å, respectively, again due to the difference in hybridization at carbon. The C(1)–C(2) triple bond length of 1.20(1) Å is slightly longer than that (1.18 Å) of complex **9**. The bond angles Cl(1)–Pd(1)–P(11) and Cl(1)–Pd(1)–P(12) are 93.7(1) and 92.0(1)°, respectively. This minimizes the repulsive interaction between the Cl atom and phosphine ligands, but similar bond angles at the other palladium site are 90.5(3)° for Cl(2)–Pd(2)–P(21) and 87.0(1)° for Cl(2)–Pd(2)–P(22). This geometry is adopted to minimize the intramolecular interaction between the phosphine ligands and the N-phenyl groups. The close intramolecular contacts are 3.59(1) Å for C(46) · · · C(34), 3.62 Å for C(46) · · · C(223), and 3.66(2) Å for C(44) · · · C(215). The closest intermolecular contact associated with carbon atoms is 3.62(2) Å of C(46) · · · C(223) ($x + 1, 0.5 - y, 0.5 + z$) and that associated with chlorine atoms is 3.64(2) Å of Cl(1) · · · C(112) (x, $0.5 - y$, $0.5 + z$). No unusual interaction was observed.

Experimental

All the reactions were carried out under a nitrogen atmosphere. Proton (in $CDCl_3$) and ^{13}C-{^1H} (in CD_2Cl_2) NMR spectra were recorded on a Bruker AM-360 spectrometer, using $SiMe_4$ as an internal standard, ^{31}P-{^1H} NMR spectra on a JEOL FX-100 spectrometer in CH_2Cl_2 against external PPh_3 (in C_6D_6), infrared spectra on a Hitachi 295 spectrophotometer, and field-desorption mass spectra on a JMS-01SG-2 spectrometer. Elemental analyses were performed by the Material Analysis Center at Osaka University.

μ-Ethynediyl-dipalladium complexes were prepared from the reaction of *trans*-$[Pd(PR_3)_2(C{\equiv}CH)_2]$ and 3 equivalents of *trans*-$[Pd(PR_3)_2Cl_2]$ in the presence of CuCl as catalyst in diethylamine as previously reported.[6] Other dipalladium and mononuclear palladium complexes were similarly prepared.[5] Isocyanides were prepared by the literature method.[11]

Reactions.—$[Cl(Et_3P)_2PdC{\equiv}CPd(PEt_3)_2Cl]$ **1a** *with phenyl isocyanide.* To a stirred solution of complex **1a** (390 mg, 0.5 mmol) in dichloromethane (30 cm^3) was added phenyl isocyanide (103 mg, 1 mmol) at room temperature. After 11 h the solvent was removed *in vacuo*, and the residue was purified by chromatography on alumina with benzene–dichloromethane (1:1 v/v) as eluent. Recrystallization from dichloromethane–hexane gave yellow crystals of $[Cl(Et_3P)_2PdC{\equiv}CC(=NPh)C(=NPh)Pd(PEt_3)_2Cl]$ **2a** (400 mg, 81%) (Found: C, 48.50; H, 6.90; Cl, 7.30; N, 3.05; P, 12.90%; M^+ 986. $C_{40}H_{70}Cl_2N_2P_4Pd_2$ requires C, 48.70; H, 7.15; Cl, 7.20; N, 2.85; P, 12.55%; M 986).

Complex **1a** *with 4-nitrophenyl and 2,6-dimethylphenyl isocyanides.* These reactions were carried out by a method similar to that with phenyl isocyanide. 4-Nitrophenyl isocyanide completely reacted with complex **1a** in 5 h, but 2,6-dimethylphenyl isocyanide needed a longer reaction time (40 h). Recrystallization from toluene–hexane gave yellow crystals of **2b** in 98% yield and red-orange crystals of **2c** in 65% yield (Found: C, 44.80; H, 6.15; Cl, 6.55; N, 5.40; P, 11.80%; M^+ 1075. $C_{40}H_{68}Cl_2N_4O_4P_4Pd_2$ **2b** requires C, 44.65; H, 6.35; Cl, 6.60; N, 5.20; P, 11.50%; M 1075). An analytically pure sample of complex **2c** has not yet been obtained owing to partial dissociation of the triethylphosphine ligand, confirmed by ^{31}P-{^1H} NMR spectroscopy.

Complex **1b** *with phenyl isocyanide.* Complex **1b** (289 mg, 0.3 mmol) was treated with phenyl isocyanide (62 mg, 0.6 mmol) in dichloromethane (30 cm^3) for 40 h. After a similar work-up, recrystallization from dichloromethane–hexane gave orange crystals of complex **2d** (317 mg, 90%) (Found: C, 41.35; H, 6.05; I, 21.60; N, 2.40; P, 10.45. $C_{40}H_{70}I_2N_2P_4Pd_2$ requires C, 41.10; H, 6.05; I, 21.70; N, 2.40; P, 10.60%).

Complex **1c** *with phenyl isocyanide.* Phenyl isocyanide (83 mg, 0.8 mmol) was added to a dichloromethane solution of complex **1c** (447 mg, 0.4 mmol). The mixture was stirred for 17 h at room temperature and then the solvent was removed under reduced pressure. Purification by column chromatography on alumina with benzene as an eluent gave a yellow oil in 76% yield (Found: C, 58.05; H, 8.75; Cl, 5.20; N, 2.00; P, 9.55. $C_{64}H_{118}Cl_2N_2P_4Pd_2$ requires C, 58.10; H, 8.90; Cl, 5.35; N, 2.10; P, 9.35%).

Complex **3a** *with phenyl isocyanide.* Complex **3a** (235 mg, 0.27 mmol) was treated with phenyl isocyanide (28 mg, 0.27 mmol) in dichloromethane (30 cm^3) at room temperature. After 20 h the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on alumina, using dichloromethane as eluent. Recrystallization from toluene–hexane gave yellow crystals (206 mg, 78%) (Found: C, 50.20; H, 6.85; Cl, 7.45; N, 1.35; P, 12.55. $C_{41}H_{69}Cl_2NP_4Pd_2$ requires C, 50.05; H, 7.05; Cl, 7.20; N, 1.40; P, 12.60%).

Complexes **3b** *and* **3c** *with phenyl isocyanide.* Treatment of these complexes with phenyl isocyanide by a method similar to that for **3a** gave yellow oils **4b** (74% yield) and **4c** (62% yield), respectively. Benzene was used as the eluent for purification by chromatography (Found: C, 59.25; H, 8.65; Cl, 5.65; N, 1.05; P, 9.35. $C_{65}H_{117}Cl_2NP_4Pd_2$ **4b** requires C, 59.15; H, 8.95; Cl, 5.35; N, 1.05; P, 9.40%. Found: C, 57.15; H, 9.20; Cl, 5.75; N, 1.25; P, 9.85. $C_{59}H_{113}Cl_2NP_4Pd_2$ **4c** requires C, 56.95; H, 9.15; Cl, 5.70; N, 1.15; P, 9.95%).

Complex **3a** *with 2 equivalents of phenyl isocyanide.* The reaction between complex **3a** and 2 equivalents of phenyl isocyanide at room temperature for 1 week gave complex **5** in 29% yield (Found: C, 53.01; H, 6.75; Cl, 6.25; N, 2.35; P, 11.30. $C_{48}H_{74}Cl_2N_2P_4Pd_2$ requires C, 53.05; H, 6.85; Cl, 6.50; N, 2.60; P, 11.40%).

Complex **6a** *with phenyl isocyanide.* A mixture of complex **6a** (194 mg, 0.3 mmol) and phenyl isocyanide was stirred in dichloromethane for 20 h. The solvent was removed and the residue chromatographed on alumina using dichloromethane as eluent. Recrystallization from dichloromethane–hexane gave yellow crystals of complex **7a** (145 mg, 65% yield) (Found: C, 55.60; H, 6.65; Cl, 5.90; N, 2.65; P, 10.70. $C_{27}H_{40}ClNP_2Pd$ requires C, 55.70; H, 6.90; Cl, 6.10; N, 2.40; P, 10.65%).

Complex **6b** *with phenyl isocyanide.* The reaction was carried out by a method similar to that for complex **6a**. Yellow crystals of complex **7b** were obtained in 72% yield (Found: C, 55.00; H, 6.80; Cl, 5.70; N, 2.50; P, 10.30. $C_{28}H_{42}ClNOP_2Pd$ requires C, 54.90; H, 6.90; Cl, 5.80; N, 2.30; P, 10.10%).

Preparation of $[(PhNC)(Et_3P)_2PdC{\equiv}CPd(PEt_3)_2(CNPh)][PF_6]_2$ **8b**.—Complex **1a** (234 mg, 0.3 mmol) reacted with phenyl isocyanide (62 mg, 0.6 mmol) in the presence of KPF_6

Table 4 Positional parameters ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Pd(1)	2454(1)	354(0)	1667(0)	C(46)	−784(8)	2477(4)	1829(6)
Pd(2)	1765(1)	3212(0)	765(0)	C(111)	4346(8)	464(4)	647(6)
Cl(1)	2316(4)	−575(1)	1765(2)	C(112)	5269(10)	115(4)	1349(7)
Cl(2)	1496(3)	3985(1)	−50(2)	C(113)	1789(10)	809(4)	−259(6)
P(11)	2690(2)	311(1)	489(2)	C(114)	2134(12)	823(5)	−982(7)
P(12)	2449(3)	484(1)	2894(2)	C(115)	2445(9)	−341(4)	−15(6)
P(21)	3579(2)	3595(1)	1713(2)	C(116)	1031(10)	−518(5)	−308(7)
P(22)	92(3)	2833(1)	−256(2)	C(121)	3064(18)	−96(6)	3532(9)
N(31)	3784(7)	2337(3)	1192(5)	C(122)	3050(17)	−69(7)	4363(9)
N(41)	1284(6)	2403(3)	1778(4)	C(123)	3132(18)	1072(8)	3427(11)
C(1)	2589(7)	1123(3)	1582(5)	C(124)	4546(20)	1001(9)	3541(13)
C(2)	2726(7)	1595(3)	1523(5)	C(125)	856(23)	430(14)	2971(14)
C(3)	2894(7)	2152(3)	1370(5)	C(126)	−25(21)	739(9)	2543(14)
C(4)	1914(7)	2549(3)	1385(5)	C(211)	3466(12)	4340(5)	1744(9)
C(31)	4826(8)	2005(4)	1220(6)	C(212)	2327(11)	4531(5)	1891(9)
C(32)	5577(9)	1748(4)	1911(7)	C(213)	4094(15)	3444(6)	2754(9)
C(33)	6673(10)	1458(4)	1937(7)	C(214)	4474(16)	2944(7)	3065(11)
C(34)	6898(10)	1430(4)	1280(8)	C(215)	5027(10)	3521(5)	1528(8)
C(35)	6150(10)	1673(5)	574(8)	C(216)	4871(11)	3571(5)	686(7)
C(36)	5100(10)	1981(5)	560(8)	C(221)	−480(10)	2174(4)	−90(7)
C(41)	342(7)	2731(3)	1871(5)	C(222)	−1554(13)	1941(6)	−846(8)
C(42)	513(8)	3271(4)	2052(6)	C(223)	507(13)	2792(6)	−1103(7)
C(43)	−438(9)	3562(4)	2159(7)	C(224)	1723(15)	2490(7)	−928(9)
C(44)	−1580(9)	3317(4)	2080(6)	C(225)	−1362(11)	3285(5)	−631(7)
C(45)	−1748(9)	2770(4)	1907(7)	C(226)	−1946(14)	3357(7)	−37(9)

(184 mg, 1.0 mmol) in acetone. After 30 min the solvent was evaporated *in vacuo*, and the residue was extracted with dichloromethane. The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Reprecipitation from dichloromethane into diethyl ether gave a white solid (281 mg, 78%), m.p. 110–113 °C (decomp.) (Found: C, 40.10; H, 5.60; F, 18.65; N, 2.40; P, 15.25. $C_{40}H_{70}F_{12}N_2P_6Pd_2$ requires C, 39.85; H, 5.85; F, 18.90; N, 2.30; P, 15.40%); ν(C≡N) 2180 cm^{-1}; δ_P 28.8.

Reactions of Complex **8b**.—*With tetraethylammonium chloride.* To a solution of complex **8b** (240 mg, 0.2 mmol) in acetone was added an acetone solution of NEt_4Cl (103 mg, 0.8 mmol). The mixture was stirred for 8 h at room temperature. The solvent was then evaporated to dryness *in vacuo*, and the residue purified by alumina column chromatography using benzene–dichloromethane (1:1 v/v) as eluent. Recrystallization from dichloromethane–hexane gave yellow crystals (104 mg, 53%) of complex **2a**.

With tetrapentylammonium bromide and tetraethylammonium iodide. These reactions were carried out by a method similar to that above, but required longer reaction times (24 h). Reaction with $N(C_5H_{11})_4Br$ gave complex **2f** in 60% yield and that with NEt_4I gave **2e** in 47% yield (Found: C, 44.90; H, 6.50; Br, 14.85; N, 2.75; P, 11.30. $C_{40}H_{70}Br_2N_2P_4Pd_2$ **2f** requires C, 44.65; H, 6.55; Br, 14.85; N, 2.60; P, 11.50%).

X-Ray Structure Determination for Complex **2a**.—The preliminary data collection showed the crystal to be monoclinic, with systematic extinctions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) consistent with the space group $P2_1/c$.

Crystal data. $C_{40}H_{70}Cl_2N_2P_4Pd_2$, M 986.6; a = 11.488(3), b = 24.997(5), c = 18.659(4) Å, β = 112.91(2)°, U = 4935.8(19) $Å^3$, Z = 4, D_c = 1.327 g cm^{-3}, and $F(000)$ = 2040.

Data collection was carried out on Rigaku AFC-5FOS diffractometer using graphite-monchromated Mo-Kα (λ = 0.7107 Å) radiation with $1.5 < 2\theta < 55°$ and the ω–2θ ($<20°$) and ω ($>20°$) scan techniques with a scan rate of 8° min^{-1}. Of 17 982 reflections measured, 6067 [$F_o > 3\sigma(F_o)$] were used in the calculations. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient was μ = 9.83 cm^{-1}, and no absorption correction was made. The positions of the Pd atoms were determined by a heavy-atom method using the UNICS III system.[12] The other non-hydrogen atom positions were subsequently found from a series of Fourier difference maps. Of the 50 non-hydrogen atoms, 46 were refined anisotropically, using block-diagonal least-squares methods, minimizing $\Sigma w(F_o - |F_c|)$. The final R ($=\Sigma||F_o| - |F_c||/\Sigma|F_o|$) and R' $\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$ values were 0.0622 and 0.0825 ($w = 1/\sigma^2$, number of variables refined = 242), respectively. The GOF value was 1.89. A final Fourier difference map showed no residual peaks more than 1.3 e $Å^{-3}$ around the heavy atoms and no residual peaks greater than 0.7 e $Å^{-3}$ associated with other ligand atoms. Somewhat large thermal parameters for the ethyl carbons of triethylphosphine are due to the fact that some residuals in the final difference map are peaks with weak intensities near the ethyl carbons. No attempt was made to locate the hydrogen atoms. Anomalous dispersion effects were included in the calculation of F_c by using $\Delta f'$ and $\Delta f''$. The atomic scattering factors for Pd, Cl, P and C were from ref. 13. The final atomic coordinates are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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