Dipalladium complexes with a bridging arylene or diarylene ligand. Synthesis and CNR′ and CO insertion into the Pd–C bonds

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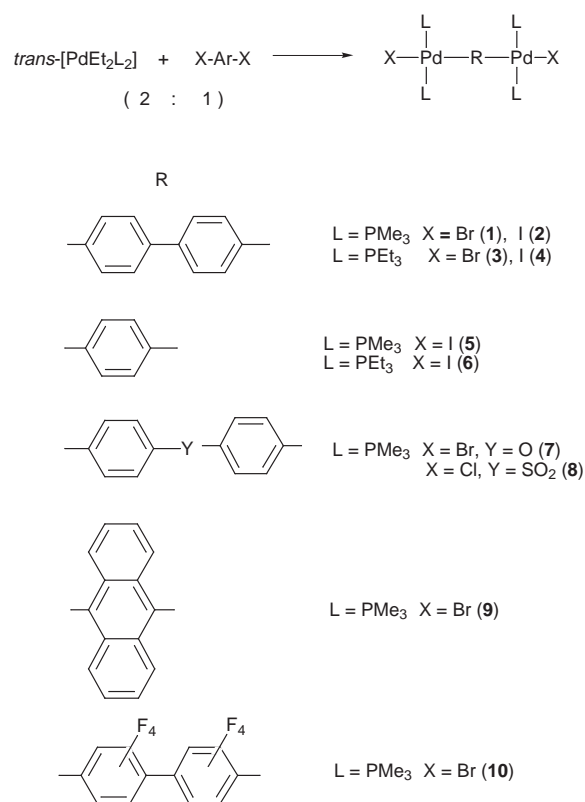
The complexes *trans*-[PdEt$_2$L$_2$] (L = PMe$_3$ or PEt$_3$) reacted with 4,4′-dibromobiphenyl, 4,4′-diiodobiphenyl, 1.4-diiodobenzene, di(4-bromophenyl) ether, di(4-chlorophenyl) sulfone, 9,10-dibromoanthracene and 4,4′-dibromooctafluorobiphenyl to give various bimetallic palladium(II) complexes with a bridging arylene or diarylene ligand, *trans,trans*-[L$_2$XPdRPdXL$_2$] (L = PMe$_3$ or PEt$_3$; R = C$_6$H$_4$C$_6$H$_4$, C$_6$H$_4$, C$_6$H$_4$OC$_6$H$_4$, C$_6$H$_4$SO$_2$C$_6$H$_4$, C$_{14}$H$_8$ or C$_6$F$_4$C$_6$F$_4$; X = Br, Cl or I). The structure of *trans,trans*-[(Et$_3$P)$_2$BrPdC$_6$H$_4$C$_6$H$_4$PdBr-(PEt$_3$)$_2$] has been determined by X-ray crystallography. The complex *trans,trans*-[(Me$_3$P)$_2$BrPdC$_6$H$_4$C$_6$H$_4$PdBr-(PMe$_3$)$_2$] reacts with *tert*-butyl, cyclohexyl and phenyl isocyanides to give the iminoacylpalladium complexes *trans,trans*-[(Me$_3$P)$_2$BrPdC(=NR′)C$_6$H$_4$C$_6$H$_4$C(=NR′)PdBr(PMe$_3$)$_2$] (R′ = Bu^t, C$_6$H$_4$ or Ph) through insertion of the isocyanide into the two aryl–palladium bonds. Reactions of *trans,trans*-[L$_2$IPdRPdIL$_2$] (R = C$_6$H$_4$C$_6$H$_4$, L = PEt$_3$; R = C$_6$H$_4$, L = PMe$_3$ or PEt$_3$) with CO (1 atm) proceeded smoothly to give *trans,trans*-[(Et$_3$P)$_2$IPdCOC$_6$H$_4$-C$_6$H$_4$PdI(PEt$_3$)$_2$] and *trans,trans*-[L$_2$IPdCOC$_6$H$_4$PdIL$_2$] (L = PMe$_3$ or PEt$_3$), respectively, through insertion of CO into one of the aryl–palladium bonds.

Dinuclear transition metal complexes with a bridging arylene or diarylene ligand, L$_n$MRML$_n$ or L$_n$MRRML$_n$, possess a unique structure containing the π-conjugated ligand between two metal centres and have a rigid rod-like arrangement of the molecule. Diplatinum complexes with diarylene ligands have been used as the precursor of transition metal-containing macrocycles which can include various guest molecules.[1] Analogous dinuclear complexes of Ni and Pd would show unique chemical properties such as insertion of small molecules into the metal–carbon bonds since they have two aryl–nickel[2] or palladium[3] bonds with higher reactivity than aryl–platinum bonds.[4] Oxidative addition of arylene dihalides to zerovalent complexes of group 10 metals is expected to provide a convenient synthetic route of the above complexes. We have previously reported the synthesis of several arylene bridged dinickel(II) complexes[5] in connection with the reaction mechanism of dehalogenative polycondensation of dibromoarenes promoted by nickel(0) complexes.[6] Stang and his co-workers[7] have applied the bis-oxidative addition to synthesis of diarylene bridged dipalladium and diplatinum complexes. These reactions are more easily performed than an alternative metathesis reaction of dichloro complexes of Group 10 metals with arylating reagents.[8] In this paper we will describe the preparation of dinuclear palladium complexes with a bridging arylene ligand *via* oxidative addition of dihalogenoarylene compounds and their reaction with isocyanides and CO resulting in insertion into the palladium–aryl bonds.

Results and Discussion

Preparation and structures of arylene bridged dipalladium complexes

Reactions of *trans*-[PdEt$_2$(PMe$_3$)$_2$] {or *trans*-[PdEt$_2$(PEt$_3$)$_2$]} with 4,4′-dibromobiphenyl, 4,4′-diiodobiphenyl, 1,4-diiodo-

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Non-SI unit employed: atm = 101 325 Pa.

Scheme 1

benzene, di(4-bromophenyl) ether, di(4-chlorophenyl) sulfone, 9,10-dibromoanthracene and 4,4′-dibromooctafluorobiphenyl in a 2 : 1 ratio at 55 °C in thf or toluene give the corresponding dinuclear complexes *trans,trans*-[L$_2$XPdRPdXL$_2$] (Scheme 1). The reactions are believed to involve oxidative addition of two C–Cl, C–Br or C–I bonds of the substrate to two molecules of [Pd(CH$_2$=CH$_2$)L$_2$] (L = PMe$_3$ or PEt$_3$) generated through

Table 1 Yields and analytical data of the complexes

Complex		Colour	Yield (%)	Analysis[a] (%)		
				C	H	N
1	[{(Me₃P)₂BrPdC₆H₄}₂]	Off-white	52	35.22 (34.77)	5.35 (5.35)	
2	[{(Me₃P)₂IPdC₆H₄}₂]	Colorless	53	31.07 (31.23)	5.01 (4.80)	
3	[{(Et₃P)₂BrPdC₆H₄}₂]	Colorless	62	43.04 (43.35)	6.76 (6.87)	
4	[{(Et₃P)₂IPdC₆H₄}₂]	Colorless	52	40.01 (39.62)	6.53 (6.28)	
5	[{I(Me₃P)₂Pd}₂C₆H₄]	Colorless	68	25.89 (25.52)	4.81 (4.76)	
6	[{I(Et₃P)₂Pd}₂C₆H₄]	Colorless	53	35.51 (35.49)	6.42 (6.35)	
7	[{(Me₃P)₂BrPdC₆H₄}₂O]	Colorless	58	34.31 (34.11)	5.49 (5.25)	
8	[{(Me₃P)₂ClPdC₆H₄}₂SO₂][b]	Colorless	34	35.64 (35.84)	5.61 (5.51)	
9	[{I(Me₃P)₂BrPd}₂C₁₄H₈]	Pale green	62	36.84 (36.60)	5.09 (5.20)	
10	[{(Me₃P)₂BrPdC₆F₄}₂]	Colorless	69	29.95 (29.62)	3.87 (3.73)	
11	[PdBr(C₆H₄C₆H₄Br)(PMe₃)₂]	Colorless	57	37.59 (37.89)	4.61 (4.59)	
12	[PdBr(C₁₄H₈Br)(PMe₃)₂]	Pale green	69	40.64 (40.40)	4.50 (4.41)	
13	[{(Me₃P)₂BrPd(CNBuᵗ)C₆H₄}₂]	Pale green	68	41.02 (41.03)	6.26 (6.28)	2.18 (2.81)
14	[{(Me₃P)₂BrPd(CNC₆H₁₁)C₆H₄}₂]	Pale yellow	85	43.47 (43.57)	6.43 (6.35)	2.63 (2.67)
15	[{(Me₃P)₂BrPd(CNPh)C₆H₄}₂]	Pale yellow	89	43.91 (44.08)	5.49 (5.26)	2.77 (2.71)
16	[{(Me₃P)₂IPd(CNBuᵗ)C₆H₄}₂]	Yellow	60	33.07 (33.19)	5.77 (5.77)	2.46 (2.76)
17	[{(Et₃P)₂IPd}₂COC₆H₄C₆H₄]	Yellow	58	39.70 (39.54)	6.33 (6.12)	
18	[{(Me₃P)₂IPd}₂COC₆H₄]	Pale yellow	98	25.91 (26.08)	4.26 (4.61)	
19	[{(Et₃P)₂IPd}₂COC₆H₄]	Yellow	84	35.83 (35.69)	6.31 (6.18)	

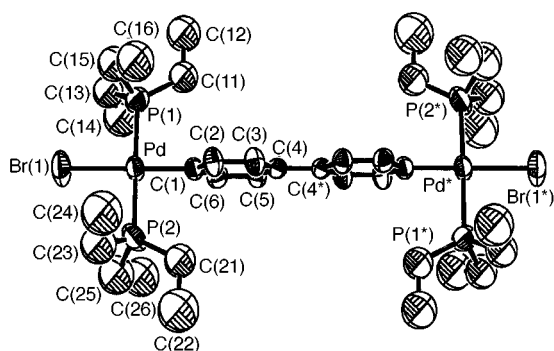[a] Required values are given in parentheses. [b] S 4.47 (3.99)%.

Fig. 1 An ORTEP[11] drawing of complex **3** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Symmetry-equivalent atoms are generated by the crystallographic inversion center located midway between C(4) and C(4*). Selected bond distances and angles: Pd–C(1) 2.008(8), Pd–P(2) 2.298(3), Pd–P(1) 2.307(3), Pd–Br(1) 2.5254(14) and C(4)–C(4*) 1.50(2) Å; C(1)–Pd–P(2) 89.2(3), P(1)–Pd–Br(1) 90.53(9), C(1)–Pd–P(1) 89.9(2), C(2)–C(1)–C(6) 116.0(8), P(2)–Pd–P(1) 177.2(1), C(2)–C(1)–Pd 121.2(7), C(1)–Pd–Br(1) 179.2(3), C(6)–C(1)–Pd 112.8(7) and P(2)–Pd–Br(1) 90.39(9)°

β-hydrogen elimination of an ethyl ligand of [PdEt₂L₂] (L = PMe₃ or PEt₃) and ensuing reductive elimination of ethane.[9] Yields and analytical and spectroscopic data of the complexes are summarized in Tables 1 and 2. Complexes **2**, **4** and **5** are obtained also from the reaction of diiodoaromatic compounds with [Pd(CH₂=CHPh)(PMe₃)₂] at room temperature. The aromatic dihalides, including sterically demanding 9,10-dibromoanthracene[5] and a dichloroarylene compound, undergo smooth oxidative addition of both carbon–halogen bonds in the molecule to give the desired dinuclear complexes in moderate yields. A *trans* configuration around the Pd is supported by the ¹H and ¹³C NMR signals of PMe₃ or PEt₃ ligands showing apparent triplets (PCH₃) or quintet (CH₃ or PEt₃) arising from virtual coupling.[10] Complexes **1–4**, **7** and **8** show the ¹³C NMR signals due to *ipso*- and *ortho*-carbons in the arylene ligand as triplets [J(CP) = 4–7 Hz], revealing that the two PR₃ ligands are magnetically equivalent.

Fig. 1 shows the molecular structure of complex **3** determined by X-ray crystallography. The molecule contains a crystallographic inversion centre at the midpoint of the C–C bond between two phenylene rings. The co-ordination sphere of each Pd can be described as a slightly distorted square plane with average atomic displacement of 0.022 Å. The two phenyl rings are essentially planar and lie nearly perpendicular to the molecular plane, defined by Pd, P(1), P(2), Br(1) and C(1), with a dihedral angle of 82.2(1)°. This structure is similar to reported analogues of Ni and Pd, *trans,trans*-[(Et₃P)₂BrNiC₆-H₄C₆H₄NiBr(PEt₃)₂][5] and *trans,trans*-[(Et₃P)₂IPtC₆H₄C₆H₄-PtI(PEt₃)₂].[7]

Reactions of 4,4′-diiodobiphenyl and of 1,4-diiodobenzene giving complexes **2**, **4** and **5** proceed smoothly even at room temperature, whereas similar reactions of 4,4′-dibromobiphenyl and 9,10-dibromoanthracene with the palladium complex in a 1:2 molar ratio *at room temperature* give the mononuclear complexes *trans*-[PdBr(RBr-*p*)(PMe₃)₂] (R = C₆H₄C₆H₄ **11** or C₁₄H₈ **12**). These results imply the easier oxidative addition of the C–I than the C–Br bond to the palladium(0) center, which is consistent with the previous observations that the relative reactivity of carbon(aryl)–halogen bonds toward oxidative addition to PdL₄ (L = tertiary phosphine) decreases in the order C–I > C–Br > C–Cl.[12] The C–Br bond of **11** and **12** remaining intact could react with palladium(0) complexes at elevated temperature since the reactions in Scheme 1 were completed at 55 °C. In order to obtain further insight on the pathway of reactions we have examined the reaction of **11** with a palladium(0) complex [Pd(CH₂=CHPh)-(PMe₃)₂], which has a similar structure to that of [Pd(CH₂=CH₂)(PMe₃)₂] at 55 °C. Complex **1** was formed in 55% yield as shown in Scheme 2, suggesting stepwise oxidative addition of the two C–Br bonds in the substrate to the palladium(0) centers in the reactions in Scheme 1.

Reaction of CNR and CO with the diarylene bridged dipalladium complexes

The diarylene bridged dipalladium complexes prepared readily react with isocyanides and CO to give several new dinuclear complexes. Reactions of **1** with *tert*-butyl, cyclohexyl and phenyl isocyanides in a 1:2 molar ratio at room temperature proceed smoothly to afford *trans*-[(Me₃P)₂BrPdC(=NR′)C₆H₄-C₆H₄C(=NR′)PdBr(PMe₃)₂] **13–15** in 68–89% yields, as shown in Scheme 3. Complexes **13–15** do not undergo further insertion of the isocyanide into the Pd–CNR bonds at room temperature. Their IR spectra show a characteristic ν(C=N) band at 1530–1590 cm⁻¹. The ¹³C-{¹H} NMR peaks due to the C=N carbons are observed at δ 176–184. The ¹H and ¹³C NMR spectra clearly

Table 2 The NMR data of the complexes (δ, J/Hz)

Complex	^{1}H^a PR″$_3$	R	^{13}C-{^{1}H}^{b}	^{31}P-{^{1}H}^{c}
1	1.23 (36 H, CH$_3$)^d	7.26 (ABq, 8 H)	14.4,^{d} 125.6, 135.7, 135.8 (t, J = 5), 152.8 (t, J = 6)	−18.1
2	1.31 (36 H, CH$_3$)^d	7.26 (ABq, 8 H)	15.8,^{d} 125.6, 135.4 (t, J = 5), 135.8, 155.9 (t, J = 6)	−19.9
3	1.10 (36 H, CH$_3$)^e 1.61 (m, 24 H, CH$_2$)^e	7.26 (ABq, 8 H)	8.2, 14.7,^{d} 125.3, 135.1, 136.5 (t, J = 4), 152.7 (t, J = 6)	12.3
4	1.08 (36 H, CH$_3$)^e 1.67 (m, 24 H, CH$_2$)	7.27 (ABq, 8 H)	8.2, 16.0,^{d} 125.3, 135.21, 136.5 (t, J = 4), 155.2	13.0
5	1.30 (36 H, CH$_3$)^d	6.90 (s, 4 H)	16.2,^{d} 136.0, 149.7	−20.5
6	1.08 (36 H, CH$_3$)^e	6.86 (s, 4 H)	8.2, 15.9,^{d} 136.4, 148.7	11.8
7	1.22 (36 H, CH$_3$)^d	6.70 (d, 4 H) 7.12 (d, 4 H)	14.4,^{d} 118.7, 135.7 (t, J = 5), 146.0 (t, J = 6)	−17.5
8	1.12 (36 H, CH$_3$)^d	7.36 (d, 4 H) 7.55 (d, 4 H)	13.3,^{d} 125.3, 136.1 (t, J = 5), 137.4, 164.5 (t, J = 7)	−14.8
9	0.98 (36 H, CH$_3$)^e 1.67 (m, 24 H, CH$_2$)	7.34 (m, 4 H) 8.68 (m, 4 H)	f	−16.2
10	1.36 (36 H, CH$_3$)^d		15.0^{d,g}	−13.8
11	1.12 (18 H, CH$_3$)^d	7.28 (m, 4 H) 7.46 (m, 4 H)	14.4,^{d} 120.6, 125.9, 128.1, 131.8, 134.4, 136.1 (t, J = 5), 140.2, 155.0 (t, J = 6)	−18.0
12	0.99 (18 H, CH$_3$)^d	7.47 (m, 2 H) 7.53 (m, 2 H) 8.46, 8.82 (d, 4 H)	14.7,^{d} 118.1, 124.1, 126.9, 128.0, 130.6, 133.5, 137.5 (t, J = 4), 164.3	−15.7
13	1.32 (36 H, CH$_3$)^d	7.60 (d, 4 H) 8.28 (d, 4 H)	15.1,^{d} 31.1, 57.3, 126.2, 130.8, 140.5, 144.1, 176.2 (C=N)	−19.5
14	1.38 (36 H, CH$_3$)^d	7.59 (d, 4 H) 8.21 (d, 4 H)	15.4,^{d} 24.6, 25.7, 34.0, 68.5, 126.4, 129.8, 140.7, 142.8, 182.2 (C=N)	−17.8
15	1.25 (36 H, CH$_3$)^d	7.71 (d, 4 H) 8.39 (d, 4 H)	15.0,^{d} 121.1, 125.4, 126.6, 128.7, 130.6, 141.3, 143.9, 151.2, 184.0 (C=N)	−18.8
16	1.39 (36 H, CH$_3$)^d	8.14 (s, 4 H)	16.4,^{d} 31.2, 58.1, 129.9, 145.2, 179.1 (C=N)	−21.7
17	1.08 (36 H, CH$_3$)^d 1.70 (18 H, CH$_2$) 1.86 (6 H, CH$_2$)	7.34 (m, 4 H) 7.69 (d, 2 H) 8.18 (d, 2 H)	8.06, 8.18, 15.9,^{d} 16.2,^{d} 125.8, 126.0, 129.9, 133.6, 137.0, 140.7, 144.9, 159.1, 234.4 (CO)	10.7 13.0
18	1.28 (18 H, CH$_3$)^d 1.36 (18 H, CH$_3$)^d	7.42 (d, 2 H) 7.57 (d, 2 H)	16.0,^{d} 16.1,^{d} 128.3, 135.6 (t, J = 5), 138.6 (t, J = 15), 169.7 (t, J = 5), 235.4 (CO)	−19.4 −21.7
19	1.07 (36 H, CH$_3$)^e 1.67 (18 H, CH$_2$) 1.86 (6 H, CH$_2$)	7.36 (d, 2 H) 7.84 (d, 2 H)	8.01, 8.14, 16.1,^{d} 16.2,^{d} 136.3 (t, J = 5), 138.6, 168.6, 233.8 (CO)	10.0 12.5

^{a} Obtained in CDCl$_3$ at 25 °C. Peak positions were referenced to internal SiMe$_4$. The ^{1}H NMR peaks not included are as follows: **13**, 1.59 (s, CH$_3$, 18 H); **14**, 1.43 (m, 4 H, CH$_2$), 1.74 (m, 10 H, CH$_2$) and 1.86 (m, 4 H, CH$_2$); **15**, 7.20 (t, 2 H, C$_6$H$_5$), 7.43 (t, 4 H, C$_6$H$_5$) and 7.78 (d, 2 H, C$_6$H$_5$); **16**, 1.61 (s, CH$_3$, 18 H). ^{b} Obtained in CDCl$_3$ at 25 °C. Peak positions were referenced to internal SiMe$_4$. ^{c} Obtained in CDCl$_3$ at 25 °C. Peak positions were referenced to external 85% H$_3$PO$_4$. ^{d} Observed as an apparent triplet due to virtual coupling. ^{e} Observed as an apparent quintet due to virtual coupling. ^{f} ^{13}C NMR spectrum not obtained due to low solubility of the complex. ^{g} Precise assignment of the peaks is not feasible due to severe splitting caused by C–F coupling.

Scheme 2
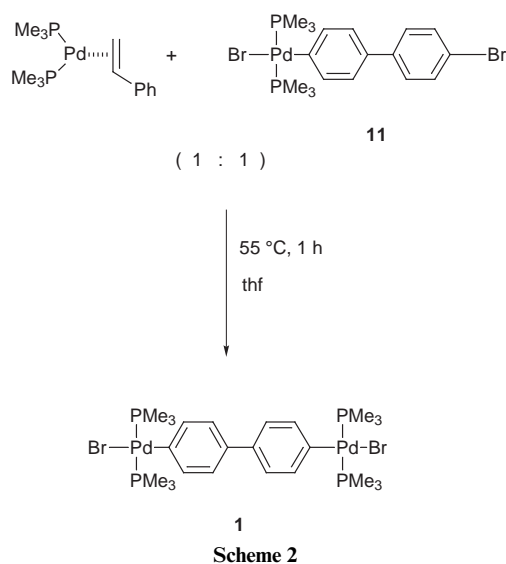
indicate the symmetrical structure of the molecules formed through insertion of the isocyanide into the two aryl–palladium bonds.

Reaction of complex **5** with 2 mol equivalents of *tert*-butyl isocyanide gives a neutral complex with symmetrical structure,
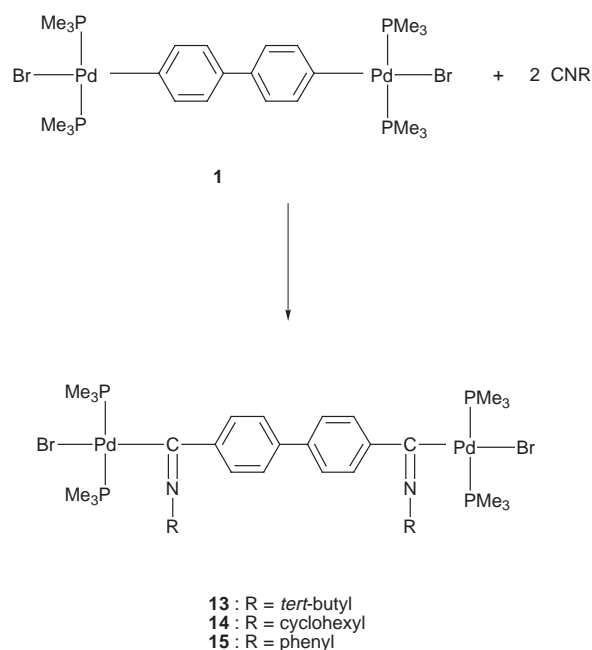
trans,trans-[(Me$_3$P)$_2$IPdC(=NBu^t)C$_6$H$_4$C(=NBu^t)PdI(PMe$_3$)$_2$] **16** after recrystallization of the product. The crude product before purification shows an IR peak at 2160 cm^{-1} assigned to ν(C≡N) of the isocyanide co-ordinated to a Pd. These results suggest that the reaction gives not only **16** but also cationic complexes such as [(Me$_3$P)$_2$(CNR′)PdC$_6$H$_4$CPd(CNR′)-(PMe$_3$)$_2$]I$_2$ or [(Me$_3$P)$_2$IPd(C=NR′)C$_6$H$_4$Pd(CNR′)I(PMe$_3$)$_2$] (R′ = Bu^t) which may be regarded as the intermediate for formation of **16**.

Isocyanides which are isoelectronic to CO have been known to undergo facile insertion into Pd–C bonds.[13] Bimetallic palladium complexes with a bridging dialkynyl ligand have been reported to undergo successive insertion of two or more molecules of aromatic isocyanide into a palladium–alkynyl bond giving the dinuclear product with unsymmetrical structure.[14] A bimetallic platinum complex with a bridging thienylene group also reacts with aryl isocyanides to give unsymmetric or symmetric iminoacylplatinum complexes at much higher temperature.[15] Reactions in Scheme 3 occur smoothly at room temperature, which implies facile insertion of the isocyanide into the palladium–aryl bond.
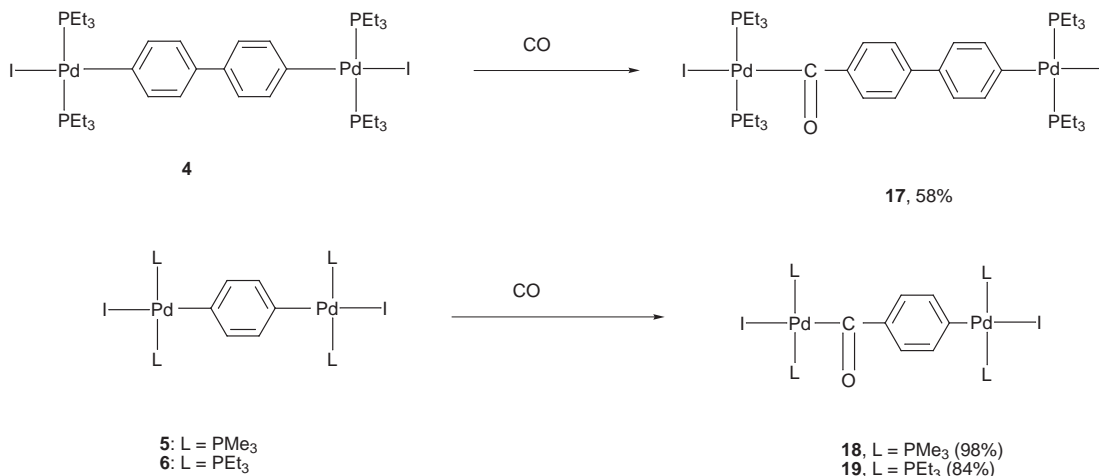
Reactions of CO (1 atm) with complexes **4**, **5** and **6** at room temperature result in insertion of a CO molecule into a Pd–C bond to give the aroylpalladium complexes **17**, **18** and **19**, respectively, as shown in Scheme 4. The products are obtained as yellow solids and are characterized by spectroscopic meas-

urement and elemental analyses. The IR spectra show a strong $v(CO)$ absorption in the range 1618–1630 cm^{-1} which is comparable with the $v(CO)$ of a benzoyl group co-ordinated to palladium.[3] The ^{13}C NMR signals at δ 234–235 support the single insertion of CO into the palladium–aryl bond. Two triplets for PMe$_3$ (**18**) and two triplets and two singlets for PEt$_3$ (**17** and **19**) in the ^{13}C NMR spectra as well as two singlets in the ^{31}P-{^{1}H} NMR spectra support the presence of unequivalent phosphine ligands due to the unsymmetrical molecule structure. The presence of the aroyl group in the complex at one Pd prevents further reaction of CO with the other Pd. This co-operation effect of the bimetallic system enabled synthesis of the unsymmetrical bimetallic palladium complexes with a bridging COR ligand.

As described above, one can easily prepare arylene-bridged dinuclear complexes from the reaction of diethylpalladium(II) complexes with various dihalogenoaromatic compounds. The sulfonyl group of ClC$_6$H$_4$SO$_2$C$_6$H$_4$Cl facilitated oxidative addition of both C–Cl bonds in the molecule, whereas oxidative addition of aryl chloride with palladium(0) complexes is not common.[16] The arylene bridged dinuclear palladium complexes undergo insertion of small molecules such as isocyanides and CO into their Pd–C bonds at room temperature; CO reacts with one of bonds, while insertion of isocyanide occurs at both sides of the arylene ligand.

13 : R = *tert*-butyl
14 : R = cyclohexyl
15 : R = phenyl

Scheme 3

Experimental

General, materials and measurements

Preparations

Complexes 1–10. To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.707 g, 2.23 mmol) at 0 °C were added 4,4′-dibromobiphenyl (0.348 g, 1.12 mmol) and thf (5 cm^3) in that order. The mixture was heated at 55 °C for 1 h to give an orange solution. Stirring at room temperature for 2 h resulted in a reddish yellow solid, which was filtered off, washed with Et$_2$O (2 cm^3) and recrystallized from CH$_2$Cl$_2$–hexane to give *trans*,*trans*-[(Me$_3$P)$_2$BrPdC$_6$H$_4$C$_6$H$_4$PdBr(PMe$_3$)$_2$] **1** as slightly gray crystals (0.481 g, 52%). Complexes **2–10** were prepared analogously.

Complexes **2**, **4** and **5** were alternatively prepared by the following method. To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.352 g, 1.11 mmol) at 0 °C were added styrene (0.462 g, 4.44 mmol) and thf (3 cm^3) in that order. The mixture was heated at 55 °C for 1 h to give a homogeneous yellow solution. This was cooled to room temperature and 4,4′-diiodobiphenyl (0.451 g, 1.11 mmol) added. Stirring for 2 h at room temperature resulted in white solids which were filtered off, washed with Et$_2$O (2 cm^3 × 2), hexane (2 cm^3) and recrystallized from CH$_2$Cl$_2$–hexane to give white solid **2** (0.543 g, 53%).

Complexes 11 and 12. To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.354 g, 1.12 mmol) at 0 °C were added styrene (0.581 g, 5.60 mmol) and thf (4 cm^3) in that order. The mixture was heated at 55 °C for 1 h to give a homogeneous yellow solution. This was cooled to room temperature and 4,4′-dibromobiphenyl (0.350 g, 1.12 mmol) added. Stirring for 2 h at room temperature resulted in white solids which were filtered off, washed with Et$_2$O (2 cm^3 × 2), hexane (2 cm^3) and recrystal-

4

17, 58%

5: L = PMe$_3$
6: L = PEt$_3$

18, L = PMe$_3$ (98%)
19, L = PEt$_3$ (84%)

Scheme 4

lized from CH_2Cl_2–hexane to give white solid **11** (0.362 g, 57%). Complex **12** was prepared analogously.

Reaction of [Pd(CH₂=CHPh)(PMe₃)₂] with complex 11. To a Schlenk flask containing *trans*-[PdEt₂(PMe₃)₂] (0.127 g, 0.40 mmol) at 0 °C were added styrene (0.168 g, 1.60 mmol) and thf (4 cm³) in that order. The mixture was heated at 55 °C for 1 h to give a yellow solution. This was cooled to room temperature and complex **11** (0.230 g, 0.40 mmol) added. The reaction mixture was stirred at 55 °C for 1 h, and the resulting reddish purple solids were filtered off, washed with hexane, Et₂O, and recrystallized to give analytically pure **1** (0.186 g, 55%).

Reactions of isocyanides with complexes 1 and 5. To a CH_2Cl_2 (3 cm³) solution of complex **1** (0.203 g, 0.245 mmol) was added *tert*-butyl isocyanide (46 mg, 0.563 mmol) at room temperature. Stirring the mixture for 2 h resulted in pale green solids which were filtered off, washed with hexane, and recrystallized from CH_2Cl_2–hexane to give pale green crystals of *trans*-[(Me₃P)₂BrPdC(=NBuᵗ)C₆H₄C₆H₄C(=NBuᵗ)PdBr(PMe₃)₂] **13** (0.165 g, 68%). IR (KBr): ν(C=N)/cm⁻¹ 1586. Reactions of cyclohexyl isocyanide and of phenyl isocyanide with **1** were carried out analogously to give *trans*-[(Me₃P)₂BrPdC(=NC₆H₁₁)-C₆H₄C₆H₄C(=NC₆H₁₁)PdBr(PMe₃)₂] **14** and *trans*-[(Me₃P)₂-BrPdC(=NPh)C₆H₄C₆H₄C(=NPh)PdBr(PMe₃)₂] **15**, respectively. IR (KBr): ν(C=N)/cm⁻¹ 1576 (**14**), 1534 (**15**).

Reactions of *tert*-butyl isocyanide with complex **5** were carried out analogously to give *trans,trans*-[(Me₃P)₂IPdC-(=NBuᵗ)C₆H₄C(=NBuᵗ)PdI(PMe₃)₂] **16** as yellow crystals (yield 60%). IR (KBr): ν(C=N)/cm⁻¹ 1590.

Reactions of CO with complexes 4, 5 and 6. Complex **5** (0.227 g, 0.268 mmol) was dissolved in CH_2Cl_2 (3 cm³) at room temperature. After evacuation of the system CO (1 atm) was introduced and the initial colorless solution immediately turned to yellow. After stirring for 3 h at room temperature the solvent was evaporated under reduced pressure to give a yellow residue, which was recrystallized from CH_2Cl_2–hexane to give yellow crystals of *trans,trans*-[(Me₃P)₂IPdC(O)C₆H₄PdI(PMe₃)₂] **18** (0.230 g, 98%). IR (KBr): ν(C=O)/cm⁻¹ 1620. Reactions of CO with **4** and **6** were carried out analogously to give *trans,trans*-[(Et₃P)₂IPdC(O)C₆H₄C₆H₄PdI(PEt₃)₂] **17** (58%) and *trans,trans*-[(Et₃P)₂IPdC(O)C₆H₄PdI(PEt₃)₂] **19**, respectively. IR (KBr): ν(C=O)/cm⁻¹ 1630 (**17**), 1618 (**19**).

Crystallography

Crystal data. C₃₆H₆₈Br₂P₄Pd₂ **3**, $M = 997.40$, monoclinic, space group $P2_1/n$ (no. 14), $a = 14.225(4)$, $b = 18.720(5)$, $c = 9.101(3)$ Å, $\beta = 107.31(2)°$, $U = 2314(1)$ Å³, $T = 298$ K, $Z = 2$, μ(Mo-Kα) = 2.7 mm⁻¹, 2968 reflections measured, 2774 unique ($R_{int} = 0.018$), from which 2766 with $I > 2\sigma(I)$ were used in refinement. Final $R1$ and $wR2$ values are 0.0587 and 0.1326.

Full-matrix least squares refinement was carried out with Pd, P, Br, and carbons of the aryl group anisotropic and with PEt₃ carbons isotropic. Many carbon atoms of the PEt₃ ligands showed severe disorder, and determination of reasonable occupancy of the possible positions of the ethyl groups was not feasible. Hydrogens were located in calculated positions.

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See http://www.rsc.org/suppdata/dt/1998/1775/ for crystallographic files in .cif format.

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