Synthesis and Reactivity of 2-Aminophenylpalladium(II) Complexes: Insertion Reactions of Oxygen and Carbon Monoxide into Carbon–Palladium Bonds—New Examples of "Transphobia"

José Vicente,*[a] José-Antonio Abad,*[a] Andrew D. Frankland[a] and M. Carmen Ramírez de Arellano[b]

Abstract: Mixtures of "$Pd(dba)_2$" (dba = dibenzylideneacetone) and neutral ligands react with an excess of 2-iodoaniline to give $[Pd(C_6H_4NH_2\text{-}2)I(bpy)]$ (**1**) or *trans*-$[Pd(C_6H_4NH_2\text{-}2)I(PR_3)_2]$ [R = Ph (**2a**), *p*-tolyl (Tol) (**2b**), cyclohexyl (Cy) (**2c**), Me (**2d**)]. Complex **2a** reacts with benzaldehyde to give *trans*-$[Pd\{C_6H_4(N{=}CHPh)\text{-}2\}I(PPh_3)_2]$ (**3**). Complexes **1**–**3** react with CO to give the insertion compounds $[Pd\{C(O)C_6H_4NH_2\text{-}2\}I(bpy)]$ (**4**), *trans*-$[Pd\{C(O)C_6H_4NH_2\text{-}2\}I(PR_3)_2]$ [R = Ph (**5a**), Tol (**5b**), Cy (**5c**), Me (**5d**)] and *trans*-$[Pd\{C(O)C_6H_4N(=CHPh)\text{-}2\}I(PPh_3)_2]$ (**6**), respectively. Complexes **3**, **4**, **5a** and **5b** react with TlOTf (OTf = CF_3SO_3) and atmospheric oxygen to give $[Ph_3PC_6H_4N{=}CHPh\text{-}2]OTf$ (**7**), $[Pd\{\kappa^2\text{-}C(O)C_6H_4NH_2\}(bpy)]OTf$ (**8**) and $[(R_3P)_2Pd(\kappa^3\text{-}\mu_2\text{-}NH_2C_6H_4CO_2\text{-}2)Pd\{\kappa^2\text{-}C(O)C_6H_4NH_2\text{-}2\}(PR_3)_2](OTf)_2$ [R = Ph (**9a**), Tol (**9b**)], respectively. When complexes **2a** and **2b** are treated with TlOTf under an atmosphere of CO, the cyclopalladated acyl complexes *cis*-$[Pd\{\kappa^2\text{-}C(O)C_6H_4NH_2\text{-}2\}(PR_3)_2]OTf$ [R = Ph (**10a**), Tol (**10b**)] are obtained. Complex **9a** reacts with an excess of PPh_3 and atmospheric oxygen to give *cis*-$[Pd\{\kappa^2\text{-}OC(O)C_6H_4NH_2\text{-}2\}(PR_3)_2]OTf$ (**11**). The crystal structures of **2a**, **3**, **5d**, **7**, **8** and **9a** have been determined by X-ray diffraction studies.

Keywords: insertions · oxygenations · palladium · structure elucidation · "transphobia"

Introduction

Palladium-catalysed carbon–carbon bond formation processes constitute a topic of great interest with important applications in organic synthesis.[1, 2] In particular, the carbonylation of organic substrates is a useful tool for the synthesis of a variety of organic compounds.[3, 4] It is assumed that such carbonylation reactions take place through acylpalladium intermediates and, for this reason, the insertion of CO into carbon–palladium bonds is being extensively studied.[3, 5, 6] These acyl derivatives are also relevant in the Pd-catalysed copolymerization of CO and unsaturated organic substrates.[7–13]

[a] Prof. J. Vicente, Dr. J.-A. Abad, Dr. A. D. Frankland
Grupo de Química Organometálica
Departamento de Química Inorgánica
Facultad de Química, Universidad de Murcia
Aptdo. 4021, E-30071 Murcia (Spain)
E-mail: jvs@fcu.um.es, jaab@fcu.um.es
WWW: http://www.scc.um.es/gi/gqo/

[b] Dr. M. Carmen Ramírez de Arellano[+]
Present address: Departamento de Química Orgánica
Facultad de Química, Universidad de Valencia
E-46071 Valencia (Spain)
E-mail: mcra@fcu.um.es

[+] Corresponding author for the X-ray diffraction studies

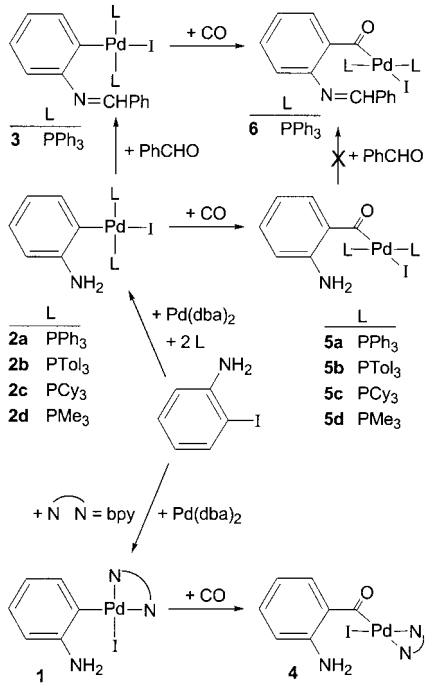
2-Aminophenylpalladium complexes appear to be intermediates in the palladium-catalysed formation of nitrogen-containing heterocycles from *o*-iodo- or *o*-bromoanilines and, for example, alkynes,[14–17] dienes,[18] or vinyl cyclopropanes and cyclobutanes,[19] as well as in intramolecular cascade cyclizations.[20–22] A palladium-catalysed synthesis of 2-aryl and 2-vinyl-4*H*-3,1-benzoxazin-4-ones from 2-iodoaniline, carbon monoxide and the appropriate organic halides or triflates has been reported.[23] Recently, a palladium-catalysed domino process to 1-benzazepines from 2-iodoaniline and homoallylic alcohols has been developed.[24] These results have prompted us to isolate 2-aminophenylpalladium complexes, which could be intermediates in such reactions, and study their reactions with carbon monoxide in order to gain more insight into the mechanisms of palladium-catalysed carbon–carbon bond formation reactions. We have previously used arylmercurials in order to prepare 2-amino-5-nitrophenylplatinum compounds,[25] and oxidative addition of 2-amino-nitrophenyl bromide to prepare similar palladium complexes.[26]

The insertion of O_2 into metal–carbon bonds is a reaction of central importance to understand the metal-catalysed oxidations of organic compounds.[27, 28] Herein we report the room-temperature oxygenation of a benzoyl to a benzoate palladium complex. Some of the results discussed have previously been communicated.[29]

0947-6539/99/0510-3066 $ 17.50+.50/0

Results

Synthesis and reactivity of 2-aminophenyl complexes of palladium(II): Mixtures of $[Pd_2(dba)_3]\cdot dba$ ("$Pd(dba)_2$"; dba = dibenzylideneacetone) and neutral ligands L (L = 2,2′-bipyridine = bpy, PR_3) react at low temperatures (0 to −5 °C) with an excess of 2-iodoaniline ($Pd:L:IC_6H_4NH_2$-2 = 1:2:2 to 1:2:3 molar ratios) to give the new complexes [Pd($C_6H_4NH_2$-2)I(bpy)] (**1**) and *trans*-[Pd($C_6H_4NH_2$-2)I(PR_3)$_2$] [R = Ph (**2a**), R = Tol (**2b**), R = Cy (**2c**)] (Scheme 1). When L = PMe_3, *trans*-[Pd($C_6H_4NH_2$-2)I(PMe_3)$_2$] (**2d**) is formed as

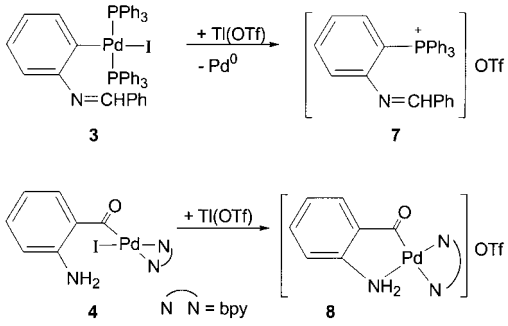


Scheme 1. Synthesis of complexes **1**–**6**.

expected. However, the presence of aromatic signals in its ^{1}H NMR spectrum, which are not assignable to **2d**, and the elemental analysis show that the solid contains some dba derivative. Our attempts to purify the compound failed although the crystal structure of one derivative could be solved (see below). Complex **2a** reacts with benzaldehyde to give the palladated imine **3**. Complexes **1** and **2** are air stable and easily accessible which makes them good candidates for reactivity studies, in particular, of insertion reactions as discussed in the following paragraphs.

CO insertion reactions: When CO is bubbled through a solution of **1** in CH_2Cl_2 at room temperature, the 2-aminobenzoyl complex [Pd{C(O)$C_6H_4NH_2$-2}I(bpy)] (**4**) precipitates. Similarly, complexes **2a–c** and **3** react with carbon monoxide to give high yields of the air-stable derivatives *trans*-[Pd{C(O)$C_6H_4NH_2$-2}I(PR_3)$_2$] [R = Ph (**5a**), *p*-tolyl (Tol) (**5b**), Cy (**5c**), Me (**5d**)] and *trans*-[Pd{C(O)C_6H_4N(=CHPh)-2}I(PPh_3)$_2$] (**6**) (Scheme 1). Carbonylation of **2c** is not complete as the ^{31}P NMR spectrum of **5c** shows resonances of **2c**. Similar to the precursor **2d**, we could not isolate complex **5d** as a pure substance but were able to obtain a single crystal from this mixture whose X-ray diffraction study confirmed the proposed structure. Complex **5a** does not react with benzaldehyde to give **6**.

When complexes **3–5** are treated with TlOTf (OTf = CF_3SO_3; 1:1 molar ratio) in order to obtain C,N-cyclometallated species, different reaction behaviours are observed. Thus, complex **3** reacts with TlOTf to give metallic palladium and the phosphonium salt ($Ph_3PC_6H_4N$=CHPh-2)OTf (**7**) resulting from a C–P coupling process (Scheme 2), instead of



Scheme 2. Synthesis of complexes **7** and **8**.

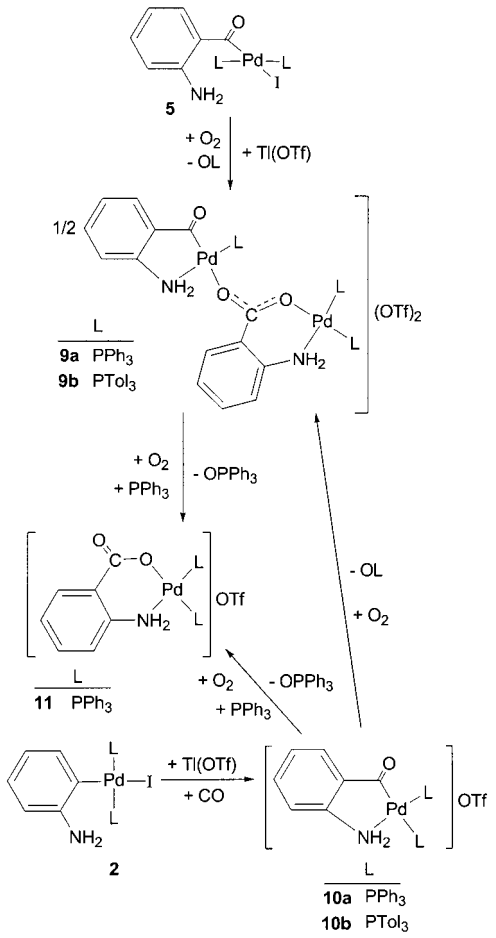
the expected *cis*-[Pd(κ^2-C_6H_4N=CHPh-2)(PPh_3)$_2$]OTf. We have reported a similar behaviour when trying to prepare the cyclopalladated complex *cis*-[Pd(κ^2-C_6H_3N=NC_6H_4R-2, R-5)(PPh_3)$_2$] (R = H, Me).[30] On the other hand, complex **4** reacts with TlOTf to give the expected [Pd{κ^2-C(O)$C_6H_4NH_2$}(bpy)]OTf (**8**) (Scheme 2). Finally, the complexes **5a–d** react with TlOTf to give the dimers [$(R_3P)_2$Pd(κ^3-μ_2-$NH_2C_6H_4CO_2$-2)Pd{κ^2-C(O)$C_6H_4NH_2$-2}(PR_3)$_2$](OTf)$_2$ [R = Ph (**9a**), Tol (**9b**)] instead of the expected *cis*-[Pd{κ^2-C(O)$C_6H_4NH_2$-2}(PR_3)$_2$]OTf [R = Ph (**10a**), R = Tol (**10b**)] (Scheme 3). Complexes **10a–b** can be isolated by reacting **2** with TlOTf under a CO atmosphere (Scheme 3). When solutions of **10** are stirred in open air, complexes **9a–b** can be isolated. The reaction of PPh_3 with **9a** or with **10a** in the presence of oxygen gives the anthranilato complex *cis*-[Pd{κ^2-OC(O)$C_6H_4NH_2$-2}(PR_3)$_2$]OTf (**11**).

Discussion

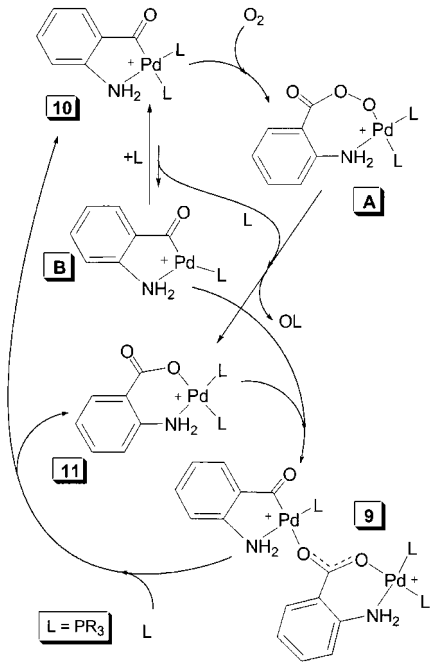
The oxidative addition reaction of 2-iodoaniline to "$Pd(dba)_2$" in the presence of bpy or tertiary phosphanes occurs at 0 to −5 °C to give complexes **1** or **2**, respectively. This process has been postulated as the first step in many palladium-catalysed processes involving the formation of nitrogen-containing heterocycles from 2-iodoaniline or related compounds.[14–24]

It is well known that imines are palladated in such a way that a five-membered ring is formed.[31–36] Therefore, *N*-benzylideneaniline would be palladated on the benzaldehyde aryl group and **3**, which was prepared by condensation of benzaldehyde with complex **2a**, would not have been obtained by cyclopalladation reaction.

The insertion of CO into an aryl–palladium bond, as observed in the synthesis of complexes **4–6** (Scheme 2), is a well-known process.[37–42] However, there are few reported



Scheme 3. Synthesis of complexes **9**–**11**.



Scheme 4. Proposed reaction pathways for the synthesis of complexes **9** and **11** from **10**.

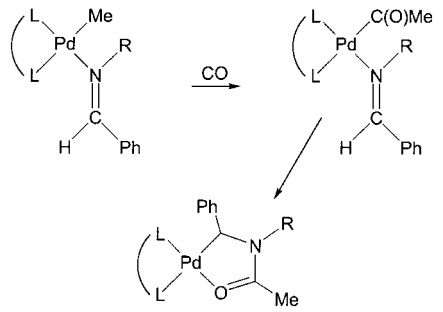
palladium complexes with a phosphane *trans* to an acyl group and they are too unstable to be isolated as pure compounds.[43–45] Therefore, as far as we are aware, complexes **10** resulting from the reaction of **2** with TlOTf, are the first complexes isolated with these ligands in the *trans* positions.

We believe that the mutual *trans* positions of carbon and phosphorus ligands in palladium(II) complexes lead to a weakening of both C–Pd and P–Pd bonds which is responsible for the instability of **10** and related complexes.[43–45] We have found that this so-called "transphobia"[46] leads to C–P bond coupling processes,[30] such as that observed in the formation of **7**. In the present case, the weakening of the C–Pd bond *trans* to the phosphane ligand probably facilitates the insertion of a dioxygen molecule into the C–Pd bond of **10** resulting in the formation of the peroxo species **A** (Scheme 4). We have also found that oxygen can oxidize the phosphorus atom coordinated *trans* to the aryl ligand in *cis*-[Pd(κ^2-C_6H_4N=NPh-2){κ^2-$(PPh_2)_2CH_2$}]SbF_6 to give the corresponding complex with $Ph_2PCH_2P(O)Ph_2$, instead of inserting into the C–Pd bond.[46] The formation of organoperoxometal complexes by insertion of O_2 into a R–[M] bond has been described.[47–51] Although we are not aware of O_2 insertion into an acyl transition metal complex, di(acyl)nickel complexes are proposed to be intermediates in reactions of benzyne Ni^0 complexes with CO in the presence of traces of air giving phthalatonickel(II) complexes.[52] Photolysis of $Me_3SiC(O)R$ ($R = H$, Me, Ph) in O_2-doped argon matrices gives mainly $Me_3SiO_2C(O)R$.[53] With a less oxophilic metal ion, such as Pd^{II}, the insertion of oxygen into the metal–carbon bond requires better oxidizing agents.[54–61] This contrasts the easy oxidation that leads to complexes **9** from **5** or **10**.

Consistent with the weak Pd–P(trans to C) bond, complexes **10** show broad resonances in the ^{31}P NMR spectra at room temperature which sharpen to a pair of doublets at $-60\,^{\circ}C$. Therefore, the peroxo derivative **A** could react with free phosphane from **10** giving OPR_3 and **11**, which could then go on to react with the intermediate **B** to give the dimers **9**, as depicted in Scheme 4. We have shown by NMR spectroscopy that complexes **10** and **11** do not react with each other to give **9**. This could be interpreted as a result of the equilibrium between **10** and **B** + L that is not sufficiently displaced to the right as to permit such reaction. However, the removal of L by the peroxo complex **A** allows formation of **B**; thus its reaction with **11** would then give complexes **9**. Additionally, i) compound **9a** is formed by stirring a solution of **10a** in the open air , ii) the formation of $OPPh_3$ has been observed by ^{31}P NMR spectroscopy and iii) peroxopalladium(II) complexes [Pd(R)(O_2R′)L_2] (R = activated alkyl; R′ = H, *t*Bu; L = phosphane) have been shown to react with free PPh_3 to give $OPPh_3$.[62] The stability of the bpy complex **8**, when compared with its PR_3 homologue **10**, emphasizes the role of the aryl/PR_3 mutual "transphobia" in the chemical reactivity of complexes **10**. Such "transphobia" can also explain the fact that, whereas stable acyl or aryl palladium complexes with a nitrogen donor ligand *trans* to the carbonyl group are well documented in the literature,[9, 63–69] the few reported palladium complexes with a phosphane ligand *trans* to an acyl group are too unstable to be isolated as pure compounds.[43–45] Very recently, a surprising insertion of an imine into a Pd–C(O)Me bond has been reported:[70] the complexes *cis*-

0947-6539/99/0510-3068 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 10

$[PdMe(NR{=}CHPh)L_2]^+$ react with CO (room temperature, 3.4 bar) to give *cis*-$[Pd\{C(O)Me\}(NR{=}CHPh)L_2]^+$. However, in contrast to complexes with $L_2 = bpy$ or $(Me_2NCH_2)_2$ those with $L_2 =$ diphosphane transform into the amido complexes $[Pd\{\kappa^2\text{-}CH(Ph)NRC(O)Me\}L_2]$ at room temperature (Scheme 5). The insertion of the imine could indicate that



Scheme 5.

the "transphobia" is in the order $C(O)Me/PR_3 > CH(Ph)N(R)C(O)Me/PR_3$. The formation of complex **11** by reacting **9a** or **10a** with PPh_3 in open air can easily be understood, in accord with the above arguments (Scheme 4).

We have attempted to further extend these studies to analogous complexes although the results are not as clear. Thus, reaction of **5c** with TlOTf did not give the corresponding cyclometallated complex **10c** but an ill-defined mixture. A similar result was achieved with **6**.

Finally, it should be emphasized that the C–P coupling observed in the synthesis of the phosphonium salt **7** is another consequence of the aryl/PR_3 "transphobia", as probably are C–C, C–N and C–O coupling processes ocurring in Stille, Suzuki, Hartwig and Buchwald catalytic systems.[71–74] This C–P coupling is also connected to similar results previously reported by us,[30] to some aryl–aryl interchange reactions between palladium and phosphane ligands in oxidative addition reactions of aryl halides to triarylphosphanyl complexes of Pd^0 [75–77] and to palladium-catalysed formation of phosphonium salts from aryl halides and triarylphosphanes.[78]

Structures of complexes: The structure of **9a** (Figure 1) has previously been reported by us.[29] The structures of complexes **2a** (Figure 2, left, Table 1), **5d** (Figure 2, right, Table 1) and **8** (Figure 3, left, Table 1) show a square-planar coordination around the palladium atom. The structure of compound **3** (Figure 3, centre, Table 1) displays a distorted square-planar geometry for the palladium centre with an angle of 12.3° between the P1-Pd-I and P2-Pd-C1 planes. Both phosphanes are in *trans* positions in **2a**, **3** and **5d** and the expected *cis* geometry is observed for complex **8**. The $C_6H_4N{=}CHPh$-2 group in **3** is more strongly bonded to palladium [Pd–C1 2.009(2) Å] and has a greater *trans* influence [Pd–I 2.7056(4) Å] than the $C_6H_4NH_2$-2 group in **2a** [Pd–C1 2.041(7), Pd–I 2.7012(6) Å]. The Pd–P bond lengths are similar [2.3297(12), 2.3301(12)(**2a**), 2.3262(6), 2.3293(6)(**3**) Å]. The Pd–C bond length in **5d** [2.012(2) Å] is similar to that in **3** and the *trans* influence of the $C(O)C_6H_4NH_2$-2 group is intermediate between that of $C_6H_4N{=}CHPh$-2 and $C_6H_4NH_2$-2 groups [Pd–I 2.7036(6) Å]. The Pd–P bond lengths in **5d** are significantly different [2.3196(6), 2.3268(6) Å]. The lower *trans* influence of the O and N donor ligands than that of P donor ligands determines in **9a** shorter Pd–P bond lengths [Pd1–P1 2.2961(9), Pd1–P2 2.2555(9), Pd2–P3 2.2764(9) Å] (Figure 1) than those in

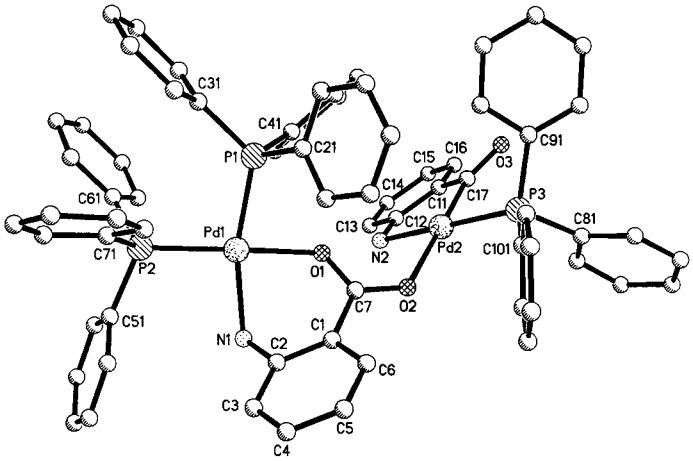


Figure 1. Structure of the cation of **9a**. H atoms omitted for clarity.

complexes **2a**, **3** and **5d**. The cationic nature of complex **8** is probably the main factor contributing to the shortening of the Pd–C bond [1.976(3) Å] when compared with that of the same group in complex **5d** [2.012(2) Å] taking into account that iodide and bpy have similar *trans* influence. Thus, the Pd–I bond lengths in some *trans*-$[PdI_2L_2]$ complexes are in the

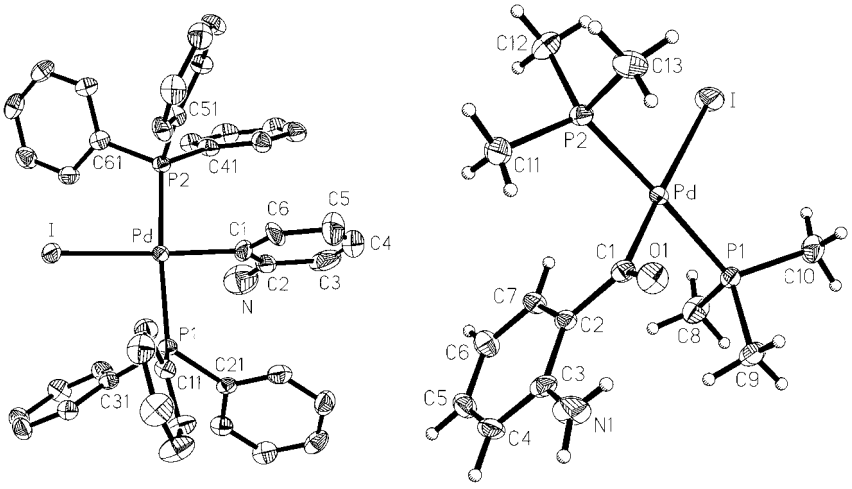


Figure 2. Ellipsoid representation of **2a** (left) and **5d** (right) with 50% probability ellipsoids and the labeling scheme. H atoms omitted for clarity (**2a**).

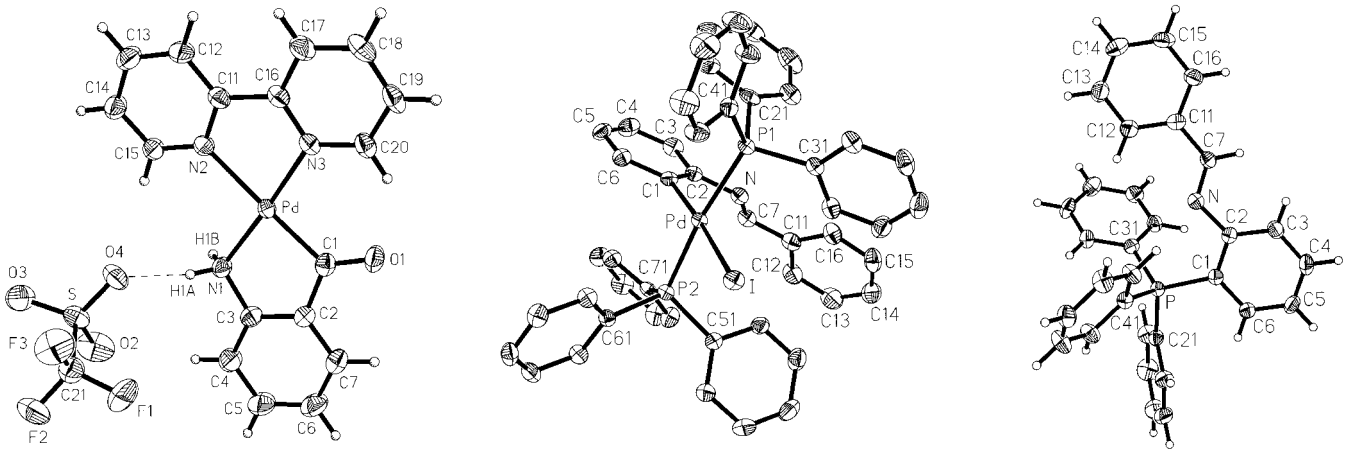


Figure 3. Ellipsoid representation of **8** (left), **3** (centre) and **7** (right) with 50% probability ellipsoids and the labeling scheme.

range 2.593–2.625 Å[79–81] and in some [PdI(R)(bpy)] complexes are in the range 2.575–2.591 Å.[82, 83] The C–O bond lengths in **5d**, **8** and **9a** are similar [1.231(3), 1.220(3), 1.209(4) Å]. In **9a**, the C–O bond lengths of the CO_2 group are significantly different [C7–O1 1.284(4), C7–O2 1.247(4) Å] (Figure 1). This is probably a result of the fact that the $Pd(PPh_3)_2^{2+}$ group demands more electron density of the anthralinato ligand than does the $Pd\{\kappa^2\text{-}C(O)C_6H_4NH_2\}(PPh_3)^+$ group. This suggests that **9a** can be viewed as **11** acting as a ligand to complete the coordination sphere of the other palladium centre. The greater *trans* influence of the carbon atom in the $C(O)C_6H_4NH_2$-2 group than PPh_3 is shown by the longer Pd2–O2 bond length [2.165(2) Å] when compared with the Pd1–O1 bond length [2.074(2) Å]. In complex **3** (Figure 3, centre) and in the phosphonium salt **7** (Figure 3, right, Table 1) the C_6H_4N and CHPh planes form an angle of 18.9° and 61.2°, respectively. The C=N bond lengths in these two compounds are very similar [1.277(3) (**3**), 1.274(3) (**7**) Å].

In complex **2a** dimers are formed through two unusual C–H···I···H–C interactions. In accord with their distances and directionalities each C–H···I can be considered a hydrogen bond [C15···IA 4.017(5), C55···IA 3.955(5), H15···IA 3.163(5) and H55···IA 3.066(5) Å; C15–H(15)···IA 150.41(9) and C55–H55···IA 156.41(9)°; symmetry operations A: $-x, -y+1, -z+1$][84] (Figure 4, left). Complex **5d** shows two types of hydrogen bonds that establish intramolecular NH···O [N1···O1 2.719(3) Å, H1···O1 2.10(3) Å and N1–H1···O1 132(3)°] and intermolecular NH···Pd contacts [N1···PdA 3.478(2) Å, H2···PdA 2.85(3) Å, N1–H2···PdA 136(3)°, symmetry operations A: $-x+1, +y+0.5, -z+0.5$] (Figure 4, right). The last ones lead to a polymeric structure. The aryl group plane and the N1–H2 vector form angles of 91.3° and 54.3° with the coordination plane, respectively. Other compounds containing N–H···M interactions have previously been reported, and in most of them the interactions are intra- rather than intermolecular.[85, 86] Intermolecular N–H···M interactions with quaternary amino cations as hydrogen-bond donors[87] or with $[PtCl_4]^{2-}$ as hydrogen-bond acceptor[88] have been reported. Compound **5d** shows an intermolecular N–H···M interaction which involves a neutral hydrogen-bond donor and acceptor. The cation and the anion in **8** interact through an NH···O hydrogen bond [N1···O4 2.888(3) Å, H1A···O4 1.977(3) Å, N1–H1A···O4, 170.13(9)°] (Figure 3).

Table 1. Selected bond lengths [Å] and angles [°] in **2**, **5d**, **8**, **3** and **7**.

Compound 2			
Pd–C1	2.041(7)	Pd–P1	2.3297(12)
Pd–P2	2.3301(12)	Pd–I	2.7012(6)
C1-Pd-P1	89.8(3)	C1-Pd-P2	85.4(3)
P1-Pd-I	91.14(3)	P2-Pd-I	94.24(3)
Compound 5d			
Pd–C1	2.012(2)	Pd–P2	2.3196(6)
Pd–P1	2.3268(6)	Pd–I	2.7036(3)
C1-Pd-P2	87.22(6)	C1-Pd-P1	87.29(6)
P2-Pd-I	92.36(2)	P1-Pd-I	92.93(2)
Compound 8			
Pd–C1	1.976(3)	Pd–N1	2.066(2)
Pd–N3	2.075(2)	Pd–N2	2.163(2)
O1–C1	1.220(3)	S–O2	1.432(2)
S–O3	1.433(2)	S–O4	1.437(2)
C1-Pd-N1	82.88(10)	C1-Pd-N3	100.44(10)
N1-Pd-N2	98.45(8)	N3-Pd-N2	78.23(8)
C3-N1-Pd	112.1(2)	O1-C1-C2	120.9(2)
O1-C1-Pd	126.2(2)	C2-C1-Pd	112.9(2)
O2-S-O3	114.1(2)	O2-S-O4	115.45(14)
O3-S-O4	114.67(13)		
Compound 3			
I–Pd	2.7056(4)	Pd–C1	2.009(2)
Pd–P1	2.3262(6)	Pd–P2	2.3293(6)
C1-Pd-P1	87.95(6)	C1-Pd-P2	89.60(6)
P1-Pd-I	93.556(14)	P2-Pd-I	90.04(2)
Compound 7			
P–C41	1.799(3)	P–C31	1.800(3)
P–C21	1.808(3)	P–C1	1.815(3)
N–C7	1.274(3)	N–C2	1.414(3)
S–O1	1.436(2)	S–O2	1.425(2)
S–O3	1.436(2)	S–C99	1.817(3)
C41-P-C31	109.14(12)	C41-P-C21	107.54(12)
C31-P-C21	108.01(12)	C41-P-C1	110.83(12)
C31-P-C1	113.24(12)	C21-P-C1	107.88(12)
C7-N-C2	118.8(2)	N-C7-C11	122.7(2)
O2-S-O1	116.0(2)	O2-S-O3	115.7(2)
O1-S-O3	114.07(13)	O2-S-C99	102.88(14)
O1-S-C99	101.90(14)	O3-S-C99	103.49(13)

0947-6539/99/0510-3070 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 10

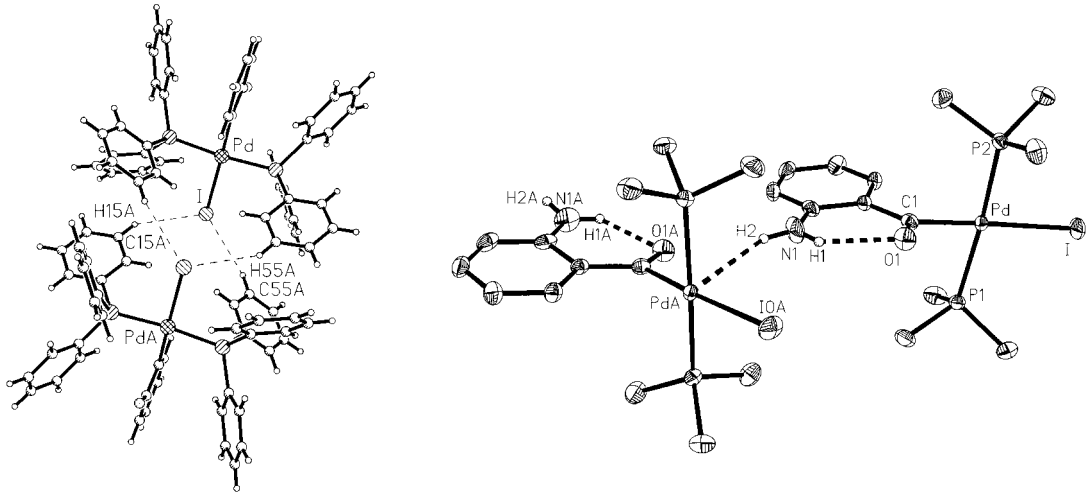


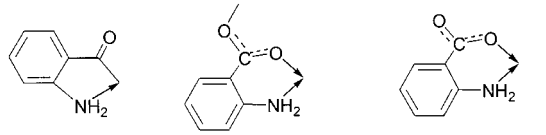
Figure 4. Left: A view of the dimers formed in **2a** through C–H···I···H–C hydrogen bonds. Right: YA view of the polymeric structure of **5d** formed through N–H···Pd and N–H···O hydrogen bonds.

Conclusion

Oxidative addition reactions of 2-iodoaniline to Pd^0 complexes lead to $[Pd(C_6H_4NH_2\text{-}2)IL_2]$ complexes from which products of benzaldehyde condensation or CO insertion have been isolated. All these processes occur at room or below room temperature and at atmospheric pressure. The product of benzaldehyde condensation *trans*-$[Pd\{C_6H_4(N{=}CHPh)\text{-}2\}I(PPh_3)_2]$, which is the first *N*-phenyl imine palladated at the *N*-phenyl group, reacts with thallium triflate to give a phosphonium salt resulting from a C–P coupling of the aryl and PPh_3 ligands. An insertion of one oxygen atom into the C–Pd bond occurs when the products of the CO insertion *trans*-$[Pd\{C(O)C_6H_4NH_2\text{-}2\}I(PR_3)_2]$ are treated with thallium triflate in the open air or when solutions of *cis*-$[Pd\{C(O)C_6H_4NH_2\text{-}2\}(PR_3)_2]^+$ are in contact with atmospheric oxygen. These reactions probably occur with insertion of dioxygen to give peroxo complexes which then oxidize PPh_3 and finally give anthranilato palladium(II) complexes. The facile C–P coupling and O_2 insertion processes can be explained by the weakening of both C–Pd and P–Pd bonds when they are mutually *trans*—the phenomenon known as "transphobia".[46] The X-ray crystal structures of some of these complexes show unusual C–H···I···H–C and intermolecular NH···Pd interactions.

Experimental Section

C, H, N and S analyses, melting point measurements, infrared and NMR spectra, and purification of solvents were carried out as described previously.[89] Some ^{13}C NMR spectroscopic assignments were carried out with DEPT techniques. The starting material "$Pd(dba)_2$" ($[Pd_2(dba)_3]\cdot$dba; dba = dibenzylideneacetone) was prepared following described procedures.[1, 90] Some ligands and their notations are depicted below.



κ^2–C(O)$C_6H_4NH_2$-2 μ_2–κ^3–$NH_2C_6H_4CO_2$-2 κ^2–OC(O)$C_6H_4NH_2$-2

$[Pd(C_6H_4NH_2\text{-}2)I(bpy)]$ (1): "$Pd(dba)_2$" (120 mg, 0.21 mmol), bpy (66 mg, 0.42 mmol) and *o*-iodoaniline (131 mg, 0.6 mmol) were mixed under nitrogen in toluene (7 mL), and allowed to react at 0 °C for 6 h. The solvent was evaporated and the residue extracted with CH_2Cl_2 ($10+3\times3$ mL), the combined extracts were filtered over anhydrous $MgSO_4$, the resultant solution concentrated to about 2 mL and Et_2O added. The resulting solid was separated by filtration, recrystallized from CH_2Cl_2/Et_2O, dried in an oven at 70 °C, and in a dessicator in vacuo in the presence of P_2O_5 for several days to give crude **1** as a yellow solid (56 mg, 55%; 30 mg, 30% recrystallized). Decomposition point: 198 °C; IR (Nujol): $\tilde{\nu}=3404$ (NH), 3318 (NH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.63$ (br d, $^3J_{H,H}=5$ Hz, 1H, bpy), 8.2–7.9 (m, 4H), 7.73 (br, 1H, $J_{H,H}=5$ Hz), 7.60–7.52 (m, 1H), 7.42–7.33 (m, 1H), 7.25–7.22 (m, 1H), 6.90–6.82 (m, 1H), 6.66–6.58 (m, 1H), 6.57–6.50 (m, 1H), 1.25 (br s, NH_2); $^{13}C\{^1H\}$ NMR: not soluble; anal. calcd for $C_{16}H_{13}IN_2OPd$: C 39.90, H 2.93, N 8.72; found: C 39.81, H 2.84, N 8.34.

***trans*-$[Pd(C_6H_4NH_2\text{-}2)I(PPh_3)_2]$ (2a)**: "$Pd(dba)_2$" (110 mg, 0.19 mmol) and PPh_3 (100 mg, 0.38 mmol) were mixed in dry, degassed toluene (15 mL) at -5 °C and stirred for 5 min under N_2. $IC_6H_4NH_2$-2 (120 mg, 0.55 mmol) was added and the temperature of the reaction mixture maintained for further 4 h. The resulting suspension was evaporated to dryness, the residue extracted with CH_2Cl_2 and filtered over anhydrous $MgSO_4$. The golden yellow solution was concentrated and Et_2O added to precipitate **2a** as a bright yellow solid (124 mg, 78%). Decomposition point: 145 °C; IR (Nujol): $\tilde{\nu}=3428$ (NH), 3339 (NH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.77-7.21$ (m, 30H, PPh_3), 6.62 (dd, $^3J_{H,H}=7.5$ Hz, $^4J_{H,H}=1.2$ Hz, 1H, H6), 6.30 (t, $^3J_{H,H}=7.5$ Hz, 1H, H4 or H5), 5.93 (t, $^3J_{H,H}=7.5$ Hz, 1H, H4 or H5), 5.63 (dd, $^3J_{H,H}=7.5$ Hz, $^4J_{H,H}=1.2$ Hz, 1H, H3), 3.35 (s, 2H, NH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=147.7$ (C1 or C2), 144.6 (C2 or C1), 135.0 (C_6H_4), 134.9 ("t", $|^2J_{P,C}+{}^4J_{P,C}|=6$ Hz, *o*-C PPh_3), 132.0 ("t" $|^1J_{P,C}+{}^3J_{P,C}|=23.3$ Hz, C_{ipso} PPh_3), 129.7 (s, *p*-C PPh_3), 127.6 ("t", $|^3J_{P,C}+{}^5J_{P,C}|=5$ Hz, *m*-C PPh_3), 123.8 (C_6H_4), 118.2 (C_6H_4), 115.9 (C_6H_4); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 22.68 (s); anal. calcd for $C_{42}H_{36}INP_2Pd$: C 59.35; H 4.27, N 1.65; found: C 59.11, H 4.31, N 1.58.

***trans*-$[Pd(C_6H_4NH_2\text{-}2)I(PTol_3)_2]$ (2b)**: This compound was prepared in a similar manner from "$Pd(dba)_2$" (200 mg, 0.35 mmol), $PTol_3$ (215 mg, 0.71 mmol; Tol = *p*-tolyl) and *o*-iodoaniline (153 mg, 0.70 mmol) to give **2b** as a yellow solid (250 mg, 77%). M.p. 96–98 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.37$ (m, 12H, $PTol_3$), 7.02 (m, 12H, $PTol_3$), 6.59 (dd, $^3J_{H,H}=7.5$ Hz, $^4J_{H,H}=1.5$ Hz, 1H, H6), 6.29 (t, $^3J_{H,H}=7.5$ Hz, 1H, H4 or H5), 5.91 (t, $^3J_{H,H}=7.5$ Hz, 1H, H4 or H5), 5.60 (dd, $^3J_{H,H}=7.5$ Hz, $^4J_{H,H}=1.2$ Hz, 1H, H3), 3.33 (s, 2H, NH_2), 2.31 (s, 18H, Me); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=147.67$ (t, $^2J_{P,C}=4$ Hz, C1 or C2), 145.24 (t, $^3J_{P,C}=4$ Hz, C2 or C1), 143.27 (C_6H_4), 139.55 (d, $J_{P,C}=1$ Hz, *p*-C $PTol_3$), 134.72 ("t", $|^2J_{P,C}+{}^4J_{P,C}|=6.5$ Hz, *o*-C $PTol_3$), 129.06 ("t", $|^1J_{P,C}+{}^3J_{P,C}|=24.5$ HzC_{ipso}, $PTol_3$), 128.31 ("t", $|^3J_{P,C}+{}^5J_{P,C}|=5$ Hz, *m*-C PPh_3), 123.34 (C_6H_4), 118.06 (C_6H_4), 115.73 (C_6H_4), 21.35 (Me); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta=20.78$ (s); anal. calcd for $C_{48}H_{48}INP_2Pd$: C 61.71, H 5.18, N 1.50; found: C 61.62, H 5.21, N 1.77.

***trans*-[Pd($C_6H_4NH_2$-2)I{PCy_3}$_2$] (2c)**: "Pd(dba)$_2$" (300 mg, 0.53 mmol) and PCy_3 (300 mg, 1.07 mmol; Cy = cyclohexyl) were added to dry, degassed toluene (15 mL) at −5 °C and stirred for 5 min under N_2. $IC_6H_4NH_2$-2 (230 mg, 1.06 mmol) was added and the temperature of the reaction mixture maintained for further 4 h. The resulting suspension was evaporated to dryness, the residue extracted with CH_2Cl_2 and filtered over anhydrous $MgSO_4$. The golden yellow solution was concentrated and Et_2O added to give **2c** as a pale yellow solid (202 mg, 43 %). Decomposition point: 195 °C; IR (Nujol): $\tilde{\nu}$ = 3466 (NH), 3366 (NH) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.09 (d, $^3J_{H,H}$ = 7 Hz, 1H, H6), 6.79 (t, $^3J_{H,H}$ = 7 Hz, 1H, H4 or H5), 6.54 (t, $^3J_{H,H}$ = 7 Hz, 1H, H4 or H5), 6.29 (d, $^3J_{H,H}$ = 7 Hz, 1H, H3), 4.10 (br, 2H, NH_2), 2.36–1.02 (m, 20H, Cy); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 148.78 (t, $^2J_{P,C}$ = 2.4 Hz, C1), 140.72 (C2), 138.34 (s, C_6H_4), 123.97 (s, C_6H_4), 118.64 (s, C_6H_4), 114.11 (s, C_6H_4), 35.21 ("t", $|^1J_{P,C} + {}^3J_{P,C}|$ = 19 Hz, CH Cy), 30.36 (d, $^3J_{P,C}$ = 14 Hz, CH_2), 27.70 (q, $|^2J_{P,C} + {}^4J_{P,C}|$ = 15 Hz, CH_2), 26.50 (s, CH_2); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 21.54 (s); anal. calcd for $C_{42}H_{72}INP_2Pd$: C 56.92, H 8.19, N 1.58; found: C 56.90, H 8.29, N 1.60.

***trans*-[Pd($C_6H_4NH_2$-2)I{PMe_3}$_2$] (2d)**: "Pd(dba)$_2$" (300 mg, 0.53 mmol) and PMe_3 (81 mg, 1.06 mmol, 1M solution in toluene) were added to dry, degassed toluene (15 mL) at −5 °C and stirred for 5 min under N_2. $IC_6H_4NH_2$-2 (230 mg, 1.06 mmol) was then added, the temperature of the reaction mixture maintained for further 4 h and then allowed to warm to room temperature overnight. The resulting suspension was evaporated to dryness, the residue extracted with CH_2Cl_2 and filtered over anhydrous $MgSO_4$. The dark green solution thus obtained was concentrated. Upon addition of Et_2O a grey solid precipitated. Preparative TLC with a CH_2Cl_2/Et_2O (1:1) solvent mixture gave crude **2d** (106 mg, 42 %) contaminated with an unidentified product probably resulting from oligomerisation of dba (by ^{1}H NMR spectroscopy). IR (Nujol): $\tilde{\nu}$ = 3426 (NH), 3326 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) excluding impurity signals: δ = 6.98 (d, 1H, H6), 6.81 (t, 1H, H4 or H5), 6.56 (t, 1H, H4 or H5), 6.46 (d, 1H, H3), 3.91 (br, 2H, NH_2), 1.32 (t, 18H, PMe_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −18.74 (s, PMe_3).

***trans*-[Pd(C_6H_4N=CHPh-2)I(PPh_3)$_2$] (3)**: One equivalent of benzaldehyde (36 μL, 0.353 mmol) was added to a solution of **2a** (300 mg, 0.353 mmol) in CH_2Cl_2 and the resulting solution stirred in the presence of $MgSO_4$ for 24 h. The $MgSO_4$ was removed by filtration, the solvent removed in vacuo, and diethyl ether added to precipitate **3** as a yellow–brown solid (230 mg, 70 %). Decomposition point: 156 °C; IR (Nujol): $\tilde{\nu}$ = 1640 (C=N) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.0 (m), 6.5–6.4, 5.9–5.8 (m); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 156.96 (s, CH=N), 155.74 (t, $^3J_{C,P}$ = 2 Hz, C2), 154.89 (t, $^2J_{C,P}$ = 3 Hz, C1), 137.12 (s, C_6H_4), 135.12, 134.92 ("t", $|^2J_{P,C} + {}^4J_{P,C}|$ = 6 Hz, *o*-C PPh_3), 132.43 ("t", $|^1J_{P,C} + {}^3J_{P,C}|$ = 23 Hz, C_{ipso} PPh_3), 130.53 (s), 129.48 (s, *p*-C PPh_3), 128.59 (s, Ph), 128.56 (s, Ph), 127.39 ("t", $|^3J_{P,C} + {}^5J_{P,C}|$ = 5 Hz, *m*-C PPh_3), 124.65 (s, C_6H_4), 123.79 (s, C_6H_4), 117.59 (s, C_6H_4); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 22.29 (s); anal. calcd for $C_{49}H_{40}INP_2Pd$: C 62.74, H 4.30, N 1.49; found: C 62.42, H 4.22, N 1.47.

[Pd{C(O)$C_6H_4NH_2$-2}I(bpy)] (4): Carbon monoxide was bubbled through a stirred solution of **1** (300 mg, 0.66 mmol) in CH_2Cl_2. An immediate precipitate was observed. The reaction mixture was stirred for 30 min and the precipitate was isolated by filtration, washed with CH_2Cl_2 and dried to give **4** as a yellow solid (260 mg, 82 %). Decomposition point: 175 °C; IR (Nujol): $\tilde{\nu}$ = 3376 (NH), 3306 (NH), 1666 (CO) cm^{-1}; NMR: not soluble; anal. calcd for $C_{17}H_{14}IN_3OPd$: C 40.07, H 2.77, N 8.25; found: C 40.00, H 2.57, N 7.60.

***trans*-[Pd{C(O)$C_6H_4NH_2$-2}I(PPh_3)$_2$] (5a)**: CO was bubbled through a solution of **2a** (200 mg, 0.235 mmol) in CH_2Cl_2 for 4 h and the solution was stirred for a further 12 h under an atmosphere of CO. The solvent was then removed in vacuo and a small amount of CH_2Cl_2 and a large amount of Et_2O were added to precipitate **5a** as a yellow–brown solid (198 mg, 96 %). Decomposition point: 125 °C; IR (Nujol): $\tilde{\nu}$ = 3484 (NH), 3368 (NH), 1610 (CO) cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, −60 °C): δ = 8.83 (d, $^3J_{H,H}$ = 8 Hz, 1H, H6), 7.9–7.1 (m, 30H, PPh_3), 6.84 (td, $^3J_{H,H}$ = 8 Hz, $^5J_{H,H}$ = 1.5 Hz, 1H, H4 or H5), 6.50 (t, $^3J_{H,H}$ = 8 Hz, 1H, H4 or H5), 5.96 (d, $^3J_{H,H}$ = 8 Hz, 1H, H3), 4.82 (br, 2H, NH_2); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −60 °C): δ = 19,45 (s); anal. calcd for $C_{43}H_{36}INOP_2Pd$: C 58.82, H 4.13, N 1.60; found: C 58.59, H 4.23, N 1.57.

***trans*-[Pd{C(O)$C_6H_4NH_2$-2}I($PTol_3$)$_2$] (5b)**: This compound was prepared in a similar manner from **2b** (350 mg, 0.38 mmol). Yield: 346 mg, 96 %. Decomposition point: 130 °C; IR (Nujol): $\tilde{\nu}$ = 3446 (NH), 3330 (NH), 1612 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (br s, 1H, H6), 7.54 (d, $^3J_{H,H}$ = 12 Hz, 12H, Tol), 7.05 (d, $^3J_{H,H}$ = 12 Hz, 12H, Tol), 6.85 ("t", $^3J_{H,H}$ = 7 Hz, 1H, H4 or H5 acyl), 6.49 ("t", $^3J_{H,H}$ = 7 Hz, 1H, H4 or H5), 6.00 (br, 1H, H3), 4.79 (br, 2H, NH_2), 2.30 (s, 18H, Me); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 16.57 (br); anal. calcd for $C_{49}H_{48}INOP_2Pd$: C 61.17; H 5.03, N 1.46; found: C 61.39, H 4.93, N 1.55.

***trans*-[Pd{C(O)$C_6H_4NH_2$-2}I(PCy_3)$_2$] (5c)**: CO was bubbled through a solution of **2c** (150 mg, 0.17 mmol) in CH_2Cl_2 for 4 h and the solution was stirred for further 12 h under an atmosphere of CO. The solvent was removed in vacuo, a small amount of CH_2Cl_2 and a large amount of Et_2O were added to precipitate **5c** as a yellow–brown solid. This compound is contaminated with the starting complex **2c** (as determined by NMR spectroscopy). Yield (crude): 137 mg, 88 %. Decomposition point: 176 °C; IR (Nujol): $\tilde{\nu}$ = 3496 (NH), 3458 (NH), 3428 (NH), 3348 (NH), 3323 (NH), 1610 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.19 (d, $^3J_{H,H}$ = 8 Hz, 1H, H6), 7.15 (m, 1H, H4 or H5), 6.73 (m, 1H, H4 or H5), 6.42 (d, $^3J_{H,H}$ = 8 Hz, 1H, H3), 5.94 (br, 2H, NH_2), 2.31–1.04 (m, 20H, Cy); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.95 (s, C_{quat}), 140.36 (s, CH), 132.60 (s, CH), 127.35 (s, C_{quat}), 115.74 (s, CH), 115.60 (s, CH), 35.42 (t, $|^1J_{P,C} + {}^3J_{P,C}|$ = 9 Hz, CH), 30.31 (s, CH_2), 30.13 (s, CH_2), 27.71 (br, CH_2), 26.48 (s, CH_2); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 17.30 (s); anal. calcd for $C_{43}H_{72}INOP_2Pd$: C 56.49, H 7.94, N 1.53; found: C 56.64, H 8.01, N 1.56.

***trans*-[Pd{C(O)$C_6H_4NH_2$-2}I(PMe_3)$_2$] (5d)**: CO was bubbled through a solution of **2d** (200 mg, 0.42 mmol) in CH_2Cl_2 for 4 h and the resulting solution stirred for further 24 h under an atmosphere of CO. The solvent was then removed in vacuo and a small amount of CH_2Cl_2 and a large amount of Et_2O were added to precipitate **5d** as an impure product (see Discussion) of yellow colour (200 mg, 94 %). IR (Nujol): $\tilde{\nu}$ = 3426 (NH), 3314 (NH), 1644 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (d, $^3J_{H,H}$ = 8 Hz, 1H, H6), 6.77 (br t, $^3J_{H,H}$ = 7.5 Hz, 1H, H4 or H5), 6.56 (d, $^3J_{H,H}$ = 8 Hz, 1H, H4 or H5), 5.86 (br, 2H, NH_2), 1.38 ("t", Me, 18H) (These data are not very reliable as a result of the impurities); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ −22.53 (s, PMe_3).

***trans*-[Pd{C(O)C_6H_4N=CHPh-2}I(PPh_3)$_2$] (6)**: CO was bubbled through a solution of **3** (250 mg, 0.27 mmol) in CH_2Cl_2 for 4 h and the resulting solution stirred for further 12 h under an atmosphere of CO. The solvent was then removed in vacuo and diethyl ether added to precipitate **6** as a pale red solid (240 mg, 92 %). Decomposition point: 150 °C; IR (Nujol): $\tilde{\nu}$ = 1610 (C=N), 1572 (CO); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.04 (m, 38H, aromatic), 6.42 (m, 1H, C_6H_4), 5.82 (dd, $^3J_{H,H}$ = 7.5 Hz, $^5J_{H,H}$ = 1.5 Hz, 1H, H4 or H5); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 214.79 (s, CO), 168.53 (C_{quat}), 156.99 (s, CH=N), 155.73 (t, $^3J_{C,P}$ = 2.5 Hz, C_2), 154.91 (t, $^2J_{C,P}$ = 3.2 Hz, C1), 147.50 (C_{quat}), 135.26 (s), 135.14 (s), 134.93 ("t", $|^2J_{P,C} + {}^4J_{P,C}|$ = 6 Hz, *o*-C PPh_3), 132.44 ("t", $|^1J_{P,C} + {}^3J_{P,C}|$ = 23 Hz, C_{ipso} PPh_3), 129.57 (CH), 128.65 (CH), 127.41 ("t", $|^3J_{P,C} + {}^5J_{P,C}|$ = 5 Hz, *m*-C PPh_3), 124.73 (CH, Ph), 123.87 (CH, Ph), 117.67 (CH, Ph); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 22.32 (s); anal. calcd for $C_{50}H_{40}INOP_2Pd$: C 62.16, H 4.17, N 1.45; found: C 61.81, H 4.10, N 1.51.

($Ph_3PC_6H_4$N=CHPh-2)OTf (7): TlOTf (OTf = CF_3SO_3; 148 mg, 0.42 mmol) was added to a solution of **3** (341 mg, 0.36 mmol) in acetone (15 mL) and the resulting suspension stirred for 4 h. It was then filtered over Celite, the solvent removed in vacuo and diethyl ether added to precipitate a solid which was recrystallized from dichloromethane/diethyl ether to give **7** as a pale brown solid (173 mg, 81 %). Decomposition point: 149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1H, CH=N), 7.99 (m, 1H), 7.55–7.11 (m, 23H, C_6H_4, Ph); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 22.99 (s, PPh_3); anal. calcd for $C_{32}H_{25}F_3NO_3PS$: C 64.97, H 4.26, N 2.37, S 5.42; found: C 64.83, H 4.28, N 2.59, S 5.37.

[Pd{κ^2-C(O)$C_6H_4NH_2$}(bpy)]OTf (8): A stoichiometric amount of TlOTf (145 mg, 0.41 mmol) was added to a suspension of **4** (200 mg, 0.41 mmol) in acetone and the resulting suspension stirred for 12 h. It was then filtered, the resulting solution concentrated and diethyl ether added to give a suspension which was filtered and the solid washed with CH_2Cl_2 to give **8** as a yellow solid (140 mg, 64 %). Decomposition point: 186 °C; IR (Nujol): $\tilde{\nu}$ = 3376 (NH), 3326 (NH), 1676 (CO) cm^{-1}; NMR: not soluble; anal. calcd for $C_{18}H_{14}F_3N_3O_4PdS$: C 40.66, H 2.65, N 7.90, S 6.03; found: C 40.44, H 2.59, N 7.85, S 5.96.

0947-6539/99/0510-3072 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 10

[(Ph$_3$P)$_2$Pd(κ^3-μ_2-NH$_2$C$_6$H$_4$CO$_2$-2)Pd{κ^2-C(O)C$_6$H$_4$NH$_2$-2}(PPh$_3$)$_2$](OTf)$_2$ (9a): A small excess of TlOTf (91 mg, 0.26 mmol) was added to a solution of **5a** (150 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture stirred for 12 h. The suspension was then filtered through $MgSO_4$ and the solvent removed in vacuo . Addition of a small amount of CH_2Cl_2 and a large excess of Et_2O resulted in precipitation of **9a** as a yellow–brown solid (108 mg, 70%). M.p. 132–134 °C; IR (Nujol): $\tilde{\nu}$ = 1670 (CO), 1550 (CO_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, $^3J_{H,H}$ = 8 Hz, 1H, C_6H_4), 7.8–7.0 (m, 50H, PPh_3), 6.79 (d, $^3J_{H,H}$ = 7 Hz, 1H, C_6H_4), 5.96 (d, $^3J_{H,H}$ = 7 Hz, C_6H_4, 1H), 5.60 (br, 2H, NH_2), 5.45 (br, 2H, NH_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −77.8 (s); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 36.11 (s), 33.97 (d, $^2J_{P,P}$ = 21 Hz), 33.24 (d, $^2J_{P,P}$ = 21 Hz); anal. calcd for $C_{70}H_{57}F_6N_2O_9P_3Pd_2S_2$: C 54.1, H 3.70, N 1.8, S 4.13; found: C 53.45, H 3.74, N 1.39, S 3.80.

[(Tol$_3$P)$_2$Pd(κ^3-μ_2-NH$_2$C$_6$H$_4$CO$_2$-2)Pd{κ^2-C(O)C$_6$H$_4$NH$_2$-2}(PTol$_3$)$_2$](OTf)$_2$ (9b): This compound was prepared in a similar manner from **5b** (350 mg, 0.38 mmol) and TlOTf (141 mg, 0.4 mmol). Yield: 192 mg, 61%. Decomposition point: 108 °C; IR (Nujol): $\tilde{\nu}$ = 3446 (NH), 3336 (NH), 1660 (CO); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, ^3J = 8 Hz, 1H, C_6H_4), 7.7–6.8 (m, 41H), 6.61 (br, 1H, C_6H_4), 6.07 (d, $^3J_{H,H}$ = 8 Hz, 1H, C_6H_4), 5.48 (br, 2H, NH_2), 5.28 (br, 2H, NH_2), 2.40 (s, 18H, Me), 2.00 (s, 9H, Me); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −77.8 (s, CF_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 35.29 (s), 33.14 (d, $^2J_{P,P}$ = 19 Hz), 32.54 (d, $^2J_{P,P}$ = 19 Hz); anal. calcd for $C_{79}H_{75}F_6N_2O_9P_3Pd_2S_2$: C 56.47, H 4.50, N 1.67, S 3.82; found: C 56.48, H 4.64, N 1.62, S 3.75.

***Cis*-[Pd{κ^2-C(O)C$_6$H$_4$NH$_2$-2}(PPh$_3$)$_2$]OTf (10a)**: CO was bubbled through a solution of **2a** (200 mg, 0.24 mmol) in CH_2Cl_2 for 4 h and then TlOTf (90 mg, 0.25 mmol) was added. This mixture was stirred under an atmosphere of CO for a further 12 h. The resulting mixture was filtered through $MgSO_4$, the solvent removed in vacuo and a small amount of CH_2Cl_2 added. Subsequent addition of a large excess of Et_2O resulted in precipitation of **10a** as a pale yellow solid (152 mg, 72%). M.p. 125–127 °C; IR (Nujol): $\tilde{\nu}$ = 3542 (NH), 3348 (NH), 1654 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.21 (m, 34H, aromatic), 5.94 (br, 2H, NH_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −77.8 (s, CF_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 25.53 (br, PPh_3), 19.38 (br, PPh_3); −60 °C: 39.61 (d, $^2J_{P,P}$ = 50 Hz), 14.64 (d, $^2J_{P,P}$ = 50 Hz); anal. calcd for $C_{44}H_{36}F_3NO_4P_2PdS$: C 58.71, H 4.03, N 1.56, S 3.56; found: C 58.69, H 4.08, N 1.74, S 3.44.

***cis*-[Pd{κ^2-C(O)C$_6$H$_4$NH$_2$-2}(PTol$_3$)$_2$]OTf (10b)**: This compound was prepared in a similar manner from **2b** (300 mg, 0.32 mmol) and TlOTf (141 mg, 0.4 mmol). Yield: 214 mg, 68%. Decomposition point: 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–6.8 (m, 28H), 5.83 (s, 2H, NH_2), 2.31 (s, 18H, Me); −60 °C: 8–6.8 (m, 24H), 5.86 (br s, 2H, NH_2), 2.32 (s, 9H, Me), 2.23 (s, 9H, Me); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 24.74 (br), 19.38 (br); −60 °C: 38.32 (d, $^2J_{P,P}$ = 51 Hz), 13.79 (d, $^2J_{P,P}$ = 51 Hz); anal. calcd for $C_{50}H_{48}F_3NO_4P_2PdS$: C 61.01, H 4.92, N 1.42, S 3.26; found: C 60.95, H 5.14, N 1.51, S 2.83.

***cis*-[Pd{κ^2-OC(O)C$_6$H$_4$NH$_2$-2}(PPh$_3$)$_2$]OTf (11)**: An excess of PPh_3 (200 mg) was added to a solution of **9a** (300 mg, 0.20 mmol) in CH_2Cl_2 and the resulting solution stirred for 24 h. The solvent was then removed in vacuo and diethyl ether added to precipitate **11** as a pale yellow solid (259 mg, 72%). M.p. 104–106 °C; IR (Nujol): $\tilde{\nu}$ = 3446 (NH), 3326 (NH), 1616 (CO_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, $^3J_{H,H}$ = 6 Hz, 1H, C_6H_4), 7.75–7.0 (m, 30H, PPh_3), 6.8–6.7 (m, 2H, aryl ligand), 5.95 (d, $^3J_{H,H}$ = 6 Hz, 1H, aryl ligand), 5.61 (br, 2H, NH_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −77.8 (s, CF_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 33.98 (d, $^2J_{P,P}$ = 21 Hz), 33.32 (d, $^2J_{P,P}$ = 21 Hz); anal. calcd for $C_{44}H_{36}F_3NO_5P_2PdS$: C 57.68, H 3.96, N 1.53, S 3.50; found: C 58.56, H 4.04, N 1.30, S 3.18.

X-ray structure determinations: Crystals of **2a**, **3**, **5d, 7** and **8** where mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Siemens P4 with LT-2 low temperature attachment) as summarised in Table 2. Cell constants were refined from about 60 reflections in the 2θ range 10–25°. The structure of **7** was solved by direct methods and the others by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement (program SHELXL-93).[91] For compound **2a** the aniline group is disordered over two sites (70 and 30% occupancy). Hydrogen atoms for the amino group could not be located, others were included with a riding model. The largest difference picks are at approximately 1 Å of the palladium or the iodine atoms. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0434, for 453 parameters and 508 restraints. Maximum Δ/σ = 0.001, maximum $\Delta\rho$ = 1.85 e$^-$ Å^{-3}. For compound **3** hydrogen atoms were included with a riding model. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0208, for 487 parameters and 470 restraints. Maximum Δ/σ = 0.001, maximum $\Delta\rho$ = 0.33 e$^-$ Å^3. For compound **5d** the hydrogen atoms bonded to nitrogen were refined freely; others were included with rigid methyl groups or a riding model. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0185, for 185 parameters and 78 restraints. Maximum Δ/σ = 0.001, maximum $\Delta\rho$ =

Table 2. Crystal data for complexes **2a**, **3**, **5d**, **7** and **8**.

	2a	**3**	**5d**	**7**	**8**
formula	$C_{42}H_{36}INP_2Pd$	$C_{49}H_{40}INP_2Pd$	$C_{13}H_{24}INOP_2Pd$	$C_{32}H_{25}F_3NO_3PS$	$C_{18}H_{14}F_3N_3O_4PdS$
crystal size [mm]	0.52 × 0.47 × 0.36	0.48 × 0.46 × 0.24	0.62 × 0.32 × 0.10	0.64 × 0.38 × 0.27	0.40 × 0.24 × 0.14
crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	Pn	$P\bar{1}$
a [Å]	11.175(1)	10.735(1)	11.7377(6)	7.636(1)	9.237(1)
b [Å]	12.102(2)	22.825(2)	11.7436(6)	10.928(1)	10.696(1)
c [Å]	14.107(2)	17.117(2)	13.8701(5)	16.946(2)	11.4840(14)
α [°]	97.039(9)				90.985(8)
β [°]	93.224(8)	92.682(8)	109.412(3)	92.249(10)	112.504(8)
γ [°]	106.665(9)				109.392(8)
V [Å^3]	1805.7(4)	4189.4(8)	1803.2(1)	1413.1(3)	975.1(2)
Z	2	4	4	2	2
ρ_{calc}	1.563	1.487	1.862	1.390	1.811
$2\theta_{max}$ [°]	50	50	50	50	50
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
scan mode	ω scans	ω scans	ω scans	ω scans	ω scans
T [°K]	173(2)	173(2)	173(2)	173(2)	173(2)
no. reflns used	6575	15016	6310	5090	3602
no indep. reflns	6222	7357	3169	4801	3417
μ [mm^{-1}]	1.488	1.291	2.912	0.226	1.118
abs. correction	–	Psi scans	Psi scans	Psi scans	Psi scans
transmissions [%]		0.957/0.735	0.974/0.540	0.777/0.754	0.901/0.765
$R1$[a]	0.0434	0.0208	0.0185	0.0344	0.0237
w$R2$[b]	0.1211	0.0525	0.0482	0.0832	0.0562

[a] $R1 = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\,]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

0.71 $e^- Å^{-3}$. For compound **7** the origin was fixed by the method of Flack and Schwarzenbach.[92] The absolute structure was determined [Flack parameter $x = -0.11(6)$].[93] Hydrogen atoms were included with a riding model. The final $R(F)$ $[I > 2\sigma(I)]$ was 0.0344, for 370 parameters and 363 restraints. Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 0.19\ e^- Å^{-3}$. For compound **8** hydrogen atoms were included with a riding model. The final $R(F)$ $[I > 2\sigma(I)]$ was 0.0237, for 271 parameters and 244 restraints. Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 0.35\ e^- Å^{-3}$. Restraints were applied to local symmetry, and U components of neighbouring light atoms. The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from International Tables for Crystallography.[94]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116230 (**2a**), 116231 (**3**), 116232 (**5d**), 116233 (**7**), 116234 (**8**). Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

We thank DGES (PB97-1047) for financial support, Ministerio de Educación y Cultura (Spain) for the award of a grant and a contract to A.D.F. and M.C.R.A., respectively, and the experimental assistance of María-José López-Sáez.

[1] R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, **1985**.
[2] J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, UK, **1995**.
[3] Y. Yamamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433.
[4] E. Negishi, C. Coperet, S. M. Ma, T. Mita, T. Sugihara, J. M. Tour, *J. Am. Chem. Soc.* **1996**, *118*, 5904.
[5] A. Yamamoto, *J. Organomet. Chem.* **1995**, *500*, 337.
[6] K. J. Cavell, *Coord. Chem. Rev.* **1996**, *155*, 209.
[7] A. Sen, T. W. Lai, *J. Am. Chem. Soc.* **1982**, *104*, 3520.
[8] R. Vanasselt, E. Gielens, R. E. Rulke, K. Vrieze, C. J. Elsevier, *J. Am. Chem. Soc.* **1994**, *116*, 977.
[9] B. A. Markies, D. Kruis, M. H. P. Rietveld, K. A. N. Verkerk, J. Boersma, H. Kooijman, M. T. Lakin, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1995**, *117*, 5263.
[10] A. Abu-Surrah, B. Rieger, *Angew. Chem.* **1996**, *108*, 2627; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2475.
[11] K. Nozaki, S. Naomasa, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, N. Koga, *J. Am. Chem. Soc.* **1997**, *119*, 12779.
[12] A. L. Safir, B. M. Novak, *J. Am. Chem. Soc.* **1998**, *120*, 643.
[13] S. Mecking, M. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888.
[14] R. C. Larock, E. K. Yum, *J. Am. Chem. Soc.* **1991**, *113*, 6689.
[15] R. C. Larock, M. J. Doty, S. J. Cacchi, *J. Org. Chem.* **1995**, *60*, 3270.
[16] M. C. Fagnola, I. Candiani, G. Visentin, W. Cabri, F. Zarini, N. Mongelli, A. Bedeschi, *Tetrahedron Lett.* **1997**, *38*, 2307.
[17] H. C. Zhang, K. K. Brumfield, B. E. Maryanoff, *Tetrahedron Lett.* **1997**, *38*, 2439.
[18] R. C. Larock, L. Q. Guo, *Synlett* **1995**, 465.
[19] R. C. Larock, E. K. Yum, *Tetrahedron* **1996**, *52*, 2743.
[20] R. Grigg, P. Fretwell, C. Meerholtz, V. Sridharan, *Tetrahedron* **1994**, *50*, 359.
[21] C. C. Yang, P. J. Sun, J. M. Fang, *J. Chem. Soc. Chem. Commun.* **1994**, 2629.
[22] S. Brown, S. Clarkson, R. Grigg, V. Sridharan, *J. Chem. Soc. Chem. Commun.* **1995**, 1135.
[23] S. Cacchi, G. Fabrizi, F. Marinelli, *Synlett* **1996**, 997.
[24] G. Dyker, H. Markwitz, *Synthesis* **1998**, 1750.
[25] J. Vicente, J. A. Abad, F. Teruel, J. García, *J. Organomet. Chem.* **1988**, *345*, 233.
[26] J. Vicente, J. A. Abad, J. A. Sánchez, *J. Organomet. Chem.* **1988**, *352*, 257.
[27] A. Hess, M. R. Hörz, L. M. Liable-Sands, D. C. Lindner, A. L. Rheingold, K. H. Theopold, *Angew. Chem.* **1999**, *111*, 126; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 166.
[28] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, London, **1981**.
[29] J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramírez de Arellano, *Chem. Commun.* **1997**, 959.
[30] J. Vicente, A. Arcas, D. Bautista, A. Tiripicchio, M. Tiripicchio-Camellini, *New J. Chem.* **1996**, *20*, 345.
[31] A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403.
[32] M. Gómez, J. Granell, M. Martínez, *J. Chem. Soc. Dalton Trans.* **1998**, 37.
[33] J. Albert, J. Granell, R. Moragas, M. Fontbardia, X. Solans, *J. Organomet. Chem.* **1996**, *522*, 59.
[34] J. Albert, J. Granell, A. Luque, M. Fontbardia, X. Solans, *J. Organomet. Chem.* **1997**, *546*, 131.
[35] M. Gomez, J. Granell, M. Martinez, *Organometallics* **1997**, *16*, 2539.
[36] V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *Russ. Chem. Rev.* **1988**, *57*, 250.
[37] G. K. Anderson, R. J. Cross, *Acc. Chem. Res.* **1984**, *17*, 67.
[38] V. V. Grushin, H. Alper, *Organometallics* **1993**, *12*, 1890.
[39] J. L. Hoare, K. J. Cavell, R. Hecker, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1996**, 2197.
[40] P. E. Garrou, R. F. Heck, *J. Am. Chem. Soc.* **1976**, *98*, 4115.
[41] Y. Kayaki, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917.
[42] Y. J. Kim, S. W. Song, S. C. Lee, S. W. Lee, K. Osakada, T. Yamamoto, *J. Chem. Soc. Dalton Trans.* **1998**, 1775.
[43] F. Ozawa, T. Hayashi, H. Koide, A. Yamamoto, *J. Chem. Soc. Chem. Commun.* **1991**, 1469.
[44] P. W. N. M. van Leeuwen, C. F. Roobeek, H. van der Heijden, *J. Am. Chem. Soc.* **1994**, *116*, 12117.
[45] C. G. Anklin, P. S. Pregosin, *J. Organomet. Chem.* **1983**, *243*, 101.
[46] J. Vicente, A. Arcas, D. Bautista, P. G. Jones, *Organometallics* **1997**, *16*, 2127.
[47] M. J. Kendrick, W. Al-Akhdar, *Inorg. Chem.* **1987**, *26*, 3971.
[48] R. D. Arasasingham, A. L. Balch, L. Latos-Grazynski, *J. Am. Chem. Soc.* **1987**, *109*, 5846.
[49] R. D. Arasasingham, A. L. Balch, C. R. Cornman, *J. Am. Chem. Soc.* **1989**, *111*, 4357.
[50] R. D. Arasasingham, A. L. Balch, R. L. Hart, L. Latos-Grazynski, *J. Am. Chem. Soc.* **1990**, *112*, 7566.
[51] G. Ferguson, P. K. Monagham, M. Parvez, R. J. Puddephatt, *Organometallics* **1985**, *4*, 1669.
[52] M. A. Bennett, D. C. R. Hockless, M. G. Humphrey, M. Schultz, E. Wenger, *Organometallics* **1996**, *15*, 928.
[53] M. Trommer, W. Sander, *Organometallics* **1996**, *15*, 189.
[54] P. L. Alsters, H. T. Teunissen, J. Boersma, A. L. Spek, G. van Koten, *Organometallics* **1993**, *12*, 4691.
[55] P. L. Alsters, J. Boersma, G. van Koten, *Organometallics* **1993**, *12*, 1629.
[56] C. Sinha, *Trans. Met. Chem.* **1994**, *19*, 41.
[57] P. K. Sinha, J. Chakravarty, S. Bhattacharya, *Polyhedron* **1996**, *15*, 2931.
[58] S. Chattopadhyay, C. Sinha, S. B. Choudhury, A. Chakravorty, *J. Organomet. Chem.* **1992**, *427*, 111.
[59] A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, *Inorg. Chem.* **1986**, *25*, 2214.
[60] J. M. Valk, R. Vanbelzen, J. Boersma, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **1994**, 2293.
[61] R. Bhawmick, H. Biswas, P. Bandyopadhyay, *J. Organomet. Chem.* **1995**, *498*, 81.
[62] G. Strukul, R. A. Michelin, R. Ros, *Inorg. Chem.* **1982**, *21*, 495.
[63] B. A. Markies, M. H. P. Rietveld, J. Boersma, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **1992**, *424*, C12.
[64] G. Dekker, A. Buijs, C. J. Elsevier, K. Vrieze, P. Vanleeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang, C. H. Stam, *Organometallics* **1992**, *11*, 1937.
[65] P. Wehman, R. E. Rulke, V. E. Kaasjager, P. C. J. Kamer, H. Kooijman, A. L. Spek, C. J. Elsevier, K. Vrieze, P. Vanleeuwen, *J. Chem. Soc. Chem. Commun.* **1995**, 331.
[66] F. C. Rix, M. Brookhart, P. S. White, *J. Am. Chem. Soc.* **1996**, *118*, 4746.
[67] R. E. Rulke, V. E. Kaasjager, D. Kliphuis, C. J. Elsevier, P. van Leeuwen, K. Vrieze, K. Goubitz, *Organometallics* **1996**, *15*, 668.

  0947-6539/99/0510-3074 $ 17.50+.50/0

[68] R. E. Rulke, J. G. P. Delis, A. M. Groot, C. J. Elsevier, P. van Leeuwen, K. Vrieze, K. Goubitz, H. Schenk, *J. Organomet. Chem.* **1996**, *508*, 109.
[69] J. H. Groen, J. G. P. Delis, P. van Leeuwen, K. Vrieze, *Organometallics* **1997**, *16*, 68.
[70] S. Kacker, J. S. Kim, A. Sen, *Angew. Chem.* **1998**, *110*, 1335; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1251.
[71] J. K. Stille, *Angew. Chem.* **1986**, *98*, 508; *Angew. Chem. Int. Ed. Engl.* **1986**, *98*, 504.
[72] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.
[73] J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2047.
[74] J. P. Sadighi, M. C. Harris, S. L. Buchwald, *Tetrahedron Lett.* **1998**, *39*, 5327.
[75] F. E. Goodson, T. I. Wallow, B. M. Novak, *J. Am. Chem. Soc.* **1997**, *119*, 12441.
[76] B. E. Segelstein, T. W. Butler, B. L. Chenard, *J. Org. Chem.* **1995**, *60*, 12.
[77] M. Sakamoto, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1995**, 1101.
[78] M. H. Kowalski, R. J. Hinkle, P. J. Stang, *J. Org. Chem.* **1989**, *54*, 2783.
[79] M. Kubota, S. Ohba, Y. Saito, *Acta Crystallogr. Sect. C* **1991**, *47*, 1727.
[80] J. H. Guo, A. Mayr, *Inorg. Chim. Acta* **1997**, *261*, 141.
[81] A. Oskarsson, B. Noren, C. Svensson, L. I. Elding, *Acta Crystallogr. Sect. B* **1990**, *46*, 748.
[82] B. A. Markies, A. J. Canty, W. Degraaf, J. Boersma, M. D. Janssen, M. P. Hogerheide, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **1994**, *482*, 191.
[83] B. A. Markies, K. A. N. Verkerk, M. H. P. Rietveld, J. Boersma, H. Kooijman, A. L. Spek, G. van Koten, *J. Chem. Soc. Chem. Commun.* **1993**, 1317.
[84] T. Steiner, G. R. Desiraju, *Chem. Commun.* **1998**, 891.
[85] L. Brammer, D. Zhao, F. T. Ladipo, J. Braddockwilking, *Acta Crystallogr. Sect. B* **1995**, *51*, 632.
[86] L. Brammer, J. M. Charnock, P. L. Goggin, R. J. Goodfellow, A. G. Orpen, T. F. Koetzle, *J. Chem. Soc. Dalton Trans.* **1991**, 1789.
[87] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G. R. Desiraju, *Organometallics* **1997**, *16*, 1846.
[88] L. Brammer, J. M. Charnock, P. L. Goggin, R. J. Goodfellow, T. F. Koetzle, A. G. Orpen, *J. Chem. Soc. Chem. Commun.* **1987**, 443.
[89] J. Vicente, J. A. Abad, J. Gil-Rubio, P. G. Jones, *Organometallics* **1995**, *14*, 2677.
[90] A. K. Yatsimirsky, G. M. Kazankov, A. D. Ryabov, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1295.
[91] G. M. Sheldrick, SHELXL 93, University of Göttingen, Göttingen, Germany, **1993**.
[92] H. D. Flack, D. Schwarzenbach, *Acta Crystallogr. Sect. A* **1988**, *44*, 499.
[93] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876.
[94] *International Tables for Crystallography* (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands **1992**, Vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199).

Received: March 22, 1999 [F1687]