Room-temperature oxidation of 2-aminobenzoyl- to 2-aminobenzoato-palladium(ii) complexes and of coordinated PPh_3 by atmospheric oxygen; X-ray crystal structure of $[(PPh_3)_2\overline{Pd(NH_2C_6H_4CO}_2\text{-}2)\overline{Pd\{C(O)C_6H_4N}H_2\text{-}2\}(PPh_3)]O_3SCF_3$

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***trans*-$[Pd(C_6H_4NH_2\text{-}2)I(PPh_3)_2]$ reacts with CO to give the insertion product *trans*-$[Pd\{C(O)(C_6H_4NH_2\text{-}2)\}(PPh_3)_2]$-$O_3SCF_3$ or, in the presence of atmospheric oxygen, $[(PPh_3)_2$-$Pd(NH_2C_6H_4CO_2\text{-}2)Pd\{C(O)C_6H_4NH_2\text{-}2\}(PPh_3)]O_3SCF_3$, whose crystal structure is solved.**

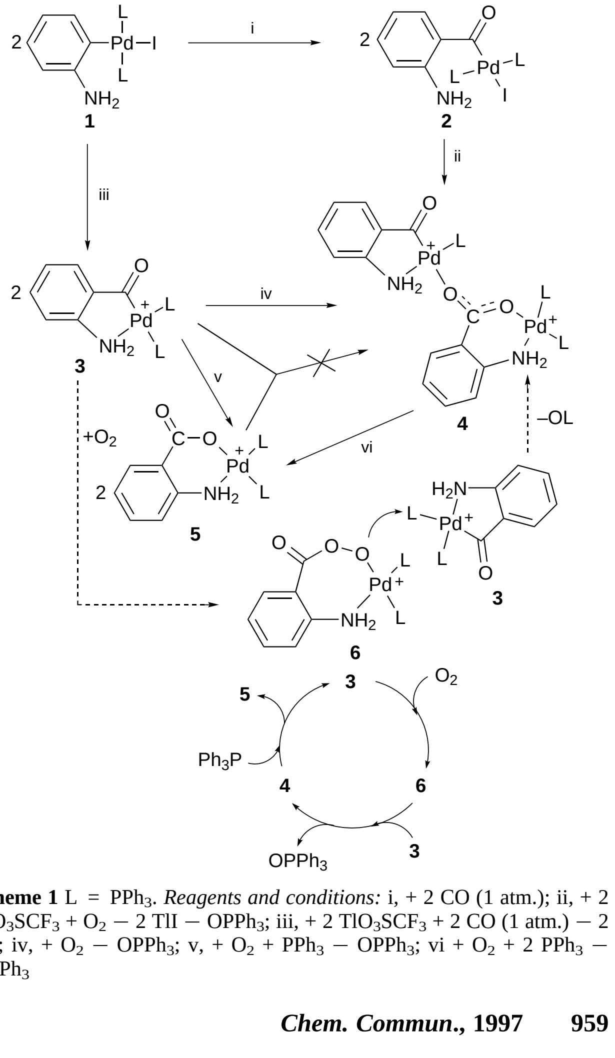
2-Aminophenylpalladium complexes appear to be intermediates in the palladium-catalysed formation of nitrogen-containing heterocycles from *o*-iodo- or *o*-bromo-anilines and, for example, alkynes,[1] dienes,[2] or vinyl cyclopropanes and cyclobutanes,[3] as well as in intramolecular cascade cyclisations.[4] Recently, a one-pot palladium catalysed synthesis of 2-aryl and 2-vinyl-4*H*-3,1-benzoxazin-4-ones from 2-iodoaniline, carbon monoxide and unsaturated halides or triflates has been reported.[5] These results have prompted us to try to isolate intermediates in such carbonylation reactions and to study their reactivity in order to gain more insight into the mechanism of the palladium-catalysed carbon–carbon bond formation.[6] Palladium-catalysed carbonylation of aryl halides and allylic compounds has been shown to occur through (acyl)palladium complexes.[7]

o-Iodoaniline reacts with $Pd(dba)_2$ in the presence of 2 equiv. of PPh_3 to give *trans*-$[Pd(C_6H_4NH_2\text{-}2)I(PPh_3)_2]$ **1**. When carbon monoxide is bubbled through dichloromethane solutions of **1**, the insertion product *trans*-$[Pd\{C(O)(C_6H_4NH_2\text{-}2)\}I(PPh_3)_2]$ **2** is formed and isolated as a moisture-stable solid (Scheme 1, step i). When complex **2** was reacted with TlO_3SCF_3, the dimer $[(PPh_3)_2\overline{Pd(NH_2C_6H_4CO}_2\text{-}2)\overline{Pd\{C(O)C_6H_4N}H_2\text{-}2\}(PPh_3)]O_3SCF_3$ **4** was isolated instead of the expected $[\overline{Pd\{C(O)C_6H_4N}H_2\text{-}2\}(PPh_3)_2]O_3SCF_3$ **3** (Scheme 1, step ii). This product can be viewed as resulting from the replacement of the PPh_3 ligand *trans* to the carbonyl group in **3**, for the complex $[\overline{Pd\{OC(O)C_6H_4N}H_2\text{-}2\}(PPh_3)_2]O_3SCF_3$ **5**. The displaced PPh_3 appears in solution as $OPPh_3$ (^{31}P NMR).

Both **3** and **5** can be independently isolated. Thus, if **1** is reacted with TlO_3SCF_3 under an atmosphere of CO the expected complex **3** is isolated (Scheme 1, step iii). It is reasonable to assume that **3** is an intermediate in the formation of **4**. In fact, when a solution of **3** is stirred in the open air it transforms into **4** (Scheme 1, step iv).

Contrary to the above mentioned relationship between complexes **3**, **4** and **5**, complexes **3** and **5** do not react with each other. This observation, and the formation of $OPPh_3$, can be interpreted assuming that the oxidation occurs not only on the benzoyl group but also on PPh_3 while it is still coordinated. We assume that this process occurs by formation of a peroxobenzoyl complex **6** which interacts with the phosphine *trans* to the carbonyl group in **3**, as depicted in Scheme 1. By reacting **3** or **4** with PPh_3 in the presence of oxygen, complex **5** can be isolated. These results can be explained by the cyclic process shown in Scheme 1.

The formation of organoperoxometal, ROO[M], complexes by insertion of O_2 into a R–[M] bond has been described.[8] However, we are not aware of such a process with an acyl transition–metal complex such as **3**. Di(acyl)nickel(ii) 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.[9] Photolysis of $Me_3SiC(O)R$ (R = H, Me, Ph) in O_2-doped argon matrices gives mainly $Me_3SiOOC(O)R$.[10] Both these results are in accordance with our proposal for the intermediate **6** in Scheme 1. With a less oxophilic metal ion like Pd^{II}, the insertion of oxygen into the metal–carbon bond requires stronger oxidizing agents.[11] In addition, peroxo-palladium(ii) and platinum(ii) complexes $[M(R)(OOR')L_2]$ (M = Pd, Pt; R = activated alkyl; R′ = H, Bu^t; L = phosphine),[12] or $[Pt\{OOC(O)Ph\}Cl(PPh_3)_2]$,[13] have



Scheme 1 L = PPh_3. *Reagents and conditions:* i, + 2 CO (1 atm.); ii, + 2 TlO_3SCF_3 + O_2 − 2 TlI − $OPPh_3$; iii, + 2 TlO_3SCF_3 + 2 CO (1 atm.) − 2 TlI; iv, + O_2 − $OPPh_3$; v, + O_2 + PPh_3 − $OPPh_3$; vi + O_2 + 2 PPh_3 − $OPPh_3$

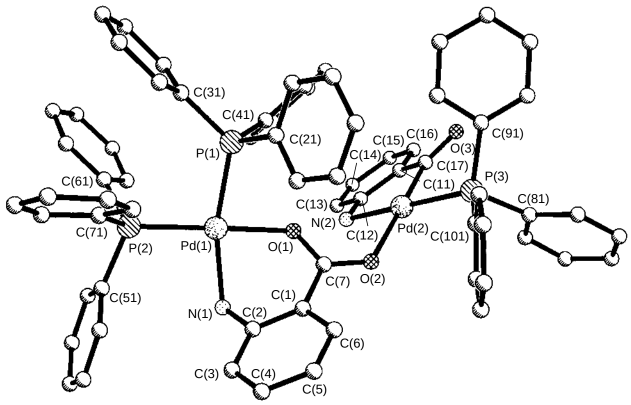


Fig. 1 Structure of complex **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–O(1) 2.074(2), Pd(1)–N(1) 2.116(3), Pd(2)–C(17) 1.959(3), Pd(2)–N(2) 2.129(3), Pd(2)–O(2) 2.165(2), O(1)–C(7) 1.284(4), O(2)–C(7) 1.247(4), O(3)–C(17) 1.209(4); O(1)–Pd(1)–N(1) 81.35(10), N(1)–Pd(1)–P(2) 96.96(8), O(1)–Pd(1)–P(1) 84.59(7), P(2)–Pd(1)–P(1) 97.45(3), C(17)–Pd(2)–N(2) 83.22(13), N(2)–Pd(2)–O(2) 93.14(10), C(17)–Pd(2)–P(3) 90.83(11), O(2)–Pd(2)–P(3) 92.71(7), O(2)–C(7)–O(1) 122.0(3).

been shown to react with free PPh_3 to give $OPPh_3$ but not with coordinated phosphines, as occurs in our case.

Acylpalladium(II) complexes are obtained by reacting CO with alkyl-,[7,14–16] π-allyl,[14] or arylpalladium(II)[17] complexes. There are few reported palladium complexes with a phosphine *trans* to an acyl group, however, they are too unstable to be isolated as pure compounds.[16,18] Therefore, as far as we are aware, complex **3** is the first isolated complex containing such ligands in *trans* positions. We believe that the mutual destabilizing effect of carbon and phosphorus ligands in *trans* positions is responsible for the instability of these complexes, the facile oxygen insertion in complex **3**, and the oxidation of the phosphine *trans* to the carbonyl group. We have found that such *trans*phobia[19] leads to C–P bond coupling processes,[20] and believe it is also responsible for other important C–C and C–N coupling reactions.

The isolated complexes **1**–**5** have been fully characterized by C, H, N analyses, IR spectroscopy and ^{1}H, ^{31}P and ^{13}C NMR (Supplementary material). The X-ray crystal structure of complex **3** (the cation of which is shown in Fig. 1 and Scheme 1),¶ shows it to be dimeric with the *o*-aminobenzoato ligand bridging, *via* the O atoms of the carboxylate group, the two metal centres. The square-planar geometry of the palladium atoms is fulfilled, in the case of Pd(1), by two phosphine ligands and the N and O atoms of the *o*-aminobenzoato group, and for Pd(2) the other O atom of this ligand, one phosphine and the *o*-aminobenzoyl ligand. All bonding distances and angles are unremarkable.

We thank Dirección General de Investigación Científica y Técnica (PB92-0982-C) for financial support. A. D. F. and M. C. R. A. are grateful to Ministerio de Educación y Ciencia for a Grant and a Contract, respectively.

Footnotes

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¶ *Crystal data*: **3**·$4CH_2Cl_2$, $C_{74}H_{65}Cl_8F_6N_2O_9P_3Pd_2S_2$, M = 1893.71, yellow prism of dimensions 0.62 × 0.60 × 0.28 mm, triclinic, space group $P\bar{1}$, a = 15.245(2), b = 16.005(2), c = 17.158(2) Å, α = 87.882(8), β = 71.080(10), γ = 86.266(8)°, U = 3951.3(9) Å^3, Z = 2, D_c = 1.592 Mg m^{-3}, $2\theta_{max}$ = 50°, Siemens P4 diffractometer, Mo-Kα (λ = 0.710 73 Å), ω-scan, T = 173 K, 18 038 reflections collected of which 13 857 were independent, ψ-scans absorption correction (max., min. transmission = 0.267, 0.208), direct primary solution and refinement on F^2 using Siemens-SHELXTL program,[21] 1009 refined parameters, riding hydrogens, $R1 = 0.0354$ [$I > 2\sigma(I)$], $wR2$ (all data) = 0.0955 [$R1 = \sigma\|F_o| - |F_c\|/\sigma|F_o|$, $wR2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{0.5}$, $w = 1/[\sigma^2(F^2) + (aP)^2 = bP]$, $P = (2F_c^2 + F_o^2)/3$]; residual electron density 1.660 (−0.901) e Å^{-3}, three of the dichloromethane molecules are disordered over two sites.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/430.

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Received in Cambridge, UK, 5th March 1997; Com. 7/01552F