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Palladium-assisted Rearrangement of $HC(O)C_6H_2(OMe)_3$-3,4,5 to $HC(O)C_6H_2(OMe)_3$-2,3,4. X-Ray Structures of $[PdR(PPh_3)(bipy)](CF_3SO_3)$ [R = $C_6H(CHO)$-6,$(OMe)_3$-2,3,4 and $C_6H(CHO)$-2,$(OMe)_3$-3,4,5; bipy = 2,2′-bipyridyl]

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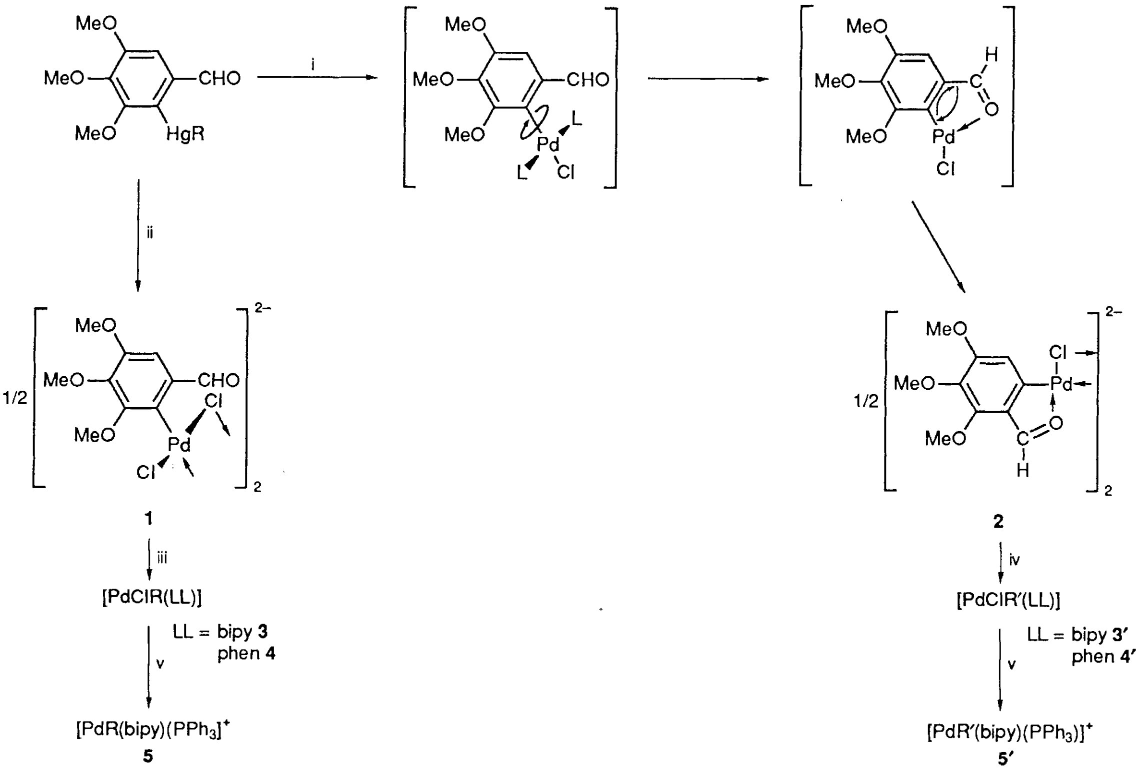
The anionic complex $[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]^{2-}$ {**1**, R = $C_6H(CHO)$-6,$(OMe)_3$-2,3,4} and the neutral $[Pd_2R'_2(\mu\text{-}Cl)_2]$ {**2**, R′ = $C_6H(CHO)$-2,$(OMe)_3$-3,4,5} are both obtained by reaction of HgR_2 with appropriate palladium precursors; the isomerization of R to R′ was confirmed by X-ray studies of the derivatives $[PdR(PPh_3)(bipy)](CF_3SO_3)$ **5** and $[PdR'(PPh_3)(bipy)](CF_3SO_3)$ **5′**.

We are currently investigating the use of organomercury compounds as transmetallating agents for the synthesis of functionalized aryl complexes. We have used this method for the synthesis of 2-nitro-,[1] 2-phenylazo-,[2] 2-dimethylamino-methyl-[3] and 2-amino-phenyl[4] complexes of Rh^{III},[1] Pd^{II},[5] Pt^{II},[4] Au^{I}[6] and Au^{III},[3] Tl^{III},[2] and Sn^{IV}.[7] These functionalized aryl complexes are of interest because they represent new types of complexes of these elements. Thus, for example, we have reported on the bonding and IR spectral properties of the 2-nitrophenyl group,[1] the C–H activation of acetone by 2-phenyl(azophenyl)gold(III) complexes,[8] and the synthesis of biphenyls by C–C coupling from diarylgold(III) complexes.[9]



Scheme 1 *Reagents and conditions*: i, + *trans*-$[PdCl_2L_2]$ (L = PhCN), −2L, − [HgClR], Cl_2CH_2, 6 h, 0 °C, 44% yield; ii, + $[Pd_2Cl_6]^{2-}$, − [HgClR], Me_2CO, 8 h, room temp., 80% yield; iii, + LL, − Cl^-, Cl_2CH_2, 30 min, room temp.; iv, + LL, Cl_2CH_2, 30 min, room temp.; v + PPh_3, + $K(CF_3SO_3)$, − KCl, Cl_2CH_2, 1 h, room temp.; R = $C_6H(CHO)$ − 6,$(OMe)_3$-2,3,4

We have now begun a study of transmetallation reactions involving a 2-formyl substituted aryl group. Because we wished to co-ordinate the C=O group, we decided to incorporate electron-releasing groups on the aryl ligand and chose $HC(O)C_6H_2(OMe)_3$-3,4,5. The mercuriated arene[10] was used as a transmetallating agent to prepare palladium complexes. Because $Pd(O_2CMe)_2$ does not react with this arene (20 min refluxing in toluene), our synthetic approach to these complexes is a new example of the importance of the 'organomercury route.'

$[Hg\{C_6H(CHO)\text{-}6,(OMe)_3\text{-}2,3,4\}_2]$ reacts with $Q_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ {Q = $(PhCH_2)Ph_3P$} to give $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ **1** (see Scheme 1). When the transmetallation reaction is carried out with $[PdCl_2(NCPh)_2]$ a complex of formula $[Pd(aryl)(\mu\text{-}Cl)]_2$ **2**† is obtained. Complexes **1** and **2** react with 2,2′-bipyridyl (bipy) to give complexes of stoichiometry [PdRCl(bipy)] **3** and **3′**, respectively and with 1,10-phenanthroline (phen) to give complexes of stoichiometry [PdRCl(phen)] **4** and **4′**, respectively. The primed and unprimed isomers have different spectroscopic and physical properties, which are maintained when complexes **3** and **3′** react with PPh_3 in the presence of $K(CF_3SO_3)$ to give complexes of stoichiometry $[PdR(PPh_3)(bipy)](CF_3SO_3)$, **5** and **5′** respectively (see Scheme 1).‡

The isomers **5** and **5′** could be distinguished unambiguously by single crystal X-ray diffraction studies,§ revealing that complex **5**, obtained from **1**, contains the original aryl ligand R whereas **5′**, prepared from **2**, contains the aryl group R′ = $C_6H(CHO)$-2,$(OMe)_3$-3,4,5 as the result of an unusual rearrangement of the arene substituents (Fig. 1*a*,*b*). It is important to determine at which stage the isomerization takes place; does complex **2** contain R or R′? Attempts to grow crystals of **2** were unsuccessful, but its reaction wth HCl allows the isolation of R′H, indicating that the rearrangement occurs on formation of **2** and, correspondingly, that complexes **3′** and **4′** also contain the R′ group.

We propose that the rearrangement occurs as follows. (*i*) Starting from $[PdCl_2(NCPh)_2]$, the product of the transmetallation reaction $[Pd(R)Cl(NCPh)_2]$ tends to induce chelation by the aryl group, replacing the labile PhCN ligand, whereas in complex **1** the Pd–Cl bonds are not so labile. (*ii*) The formation of the chelate ring would force the observed rearrangement in order to avoid the repulsion between the 2-MeO group and the ligand *trans* to the coordinated oxygen atom, whereas the R group in **1** can easily be accommodated perpendicular to the molecular plane (Scheme 1). Related rearrangements are known in arene chemistry; polyalkylbenzenes isomerize on heating in the presence of AlX_3 or BX_3 and HX;[11] polyalkyl- and polyhalo-benzenes rearrange under sulphonation conditions (Jacobsen rearrangement);[12] aromatic dicarboxylates can also rearrange when heated in the presence of a catalytic amount of cadmium (Henkel reaction).[13] Two noteworthy features of our reaction are firstly, the substituent migration occurring under very mild conditions (complex **2** is prepared at 0 °C) and, secondly, the unusual nature of the substituents (CHO and the palladium moiety) involved in the rearrangement.

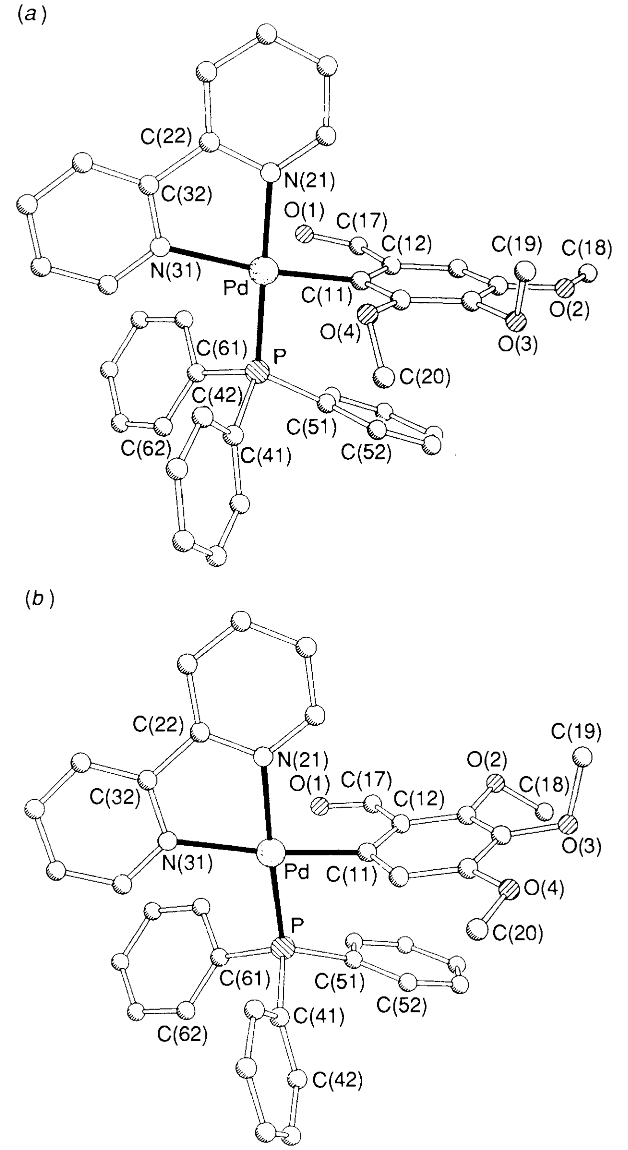


Fig. 1 (*a*) The cation of complex **5** in the crystal. Radii are arbitrary; H atoms omitted for clarity. *Crystal data* (at −95 °C): $C_{39}H_{34}F_3N_2O_7PPdS{\cdot}CH_2Cl_2$, M_r = 954.0, monoclinic, $P2_1/n$, a = 14.372(5), b = 13.800(5), c = 20.432(6) Å, β = 92.77(3)°, U = 4048 Å^3, Z = 4, Mo-$K\alpha$ radiation, $2\theta_{max}$ = 50°, R = 0.042 for 4424 unique observed reflections, 523 parameters. (*b*). The cation of complex **5′** in the crystal. Radii are arbitrary; H atoms omitted for clarity. *Crystal data* (at −95 °C): $C_{39}H_{34}F_3N_2O_7PPdS$, M_r = 869.1, triclinic, $P\bar{1}$, a = 10.709(3), b = 12.803(3), c = 14.633(5) Å, α = 77.60(3), β = 73.35(3), γ = 75.81(23)°, U = 1841 Å^3, Z = 2, Mo-$K\alpha$ radiation, $2\theta_{max}$ = 50°, R = 0.035 for 4922 unique observed reflections, 496 parameters. Full details of the structure determinations (experimental details, atomic coordinates, complete bond lengths and angles, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54958. Atomic coordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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† The dimeric nature of complex **2** was established by a pycnometric determination in chloroform solution. The tetracoordination is achieved by bonding of the C=O group as shown by IR spectroscopy (see footnote ‡).

‡ Selected spectroscopic data for new compounds: IR (Nujol) ν(C=O) in cm^{-1}, NMR ($CDCl_3$) chemical shifts in ppm relative to internal tetramethylsilane (^1H) or external H_3PO_4 ($^{31}P\{^1H\}$), coupling constants in Hz. **1**: ν(C=O): 1670. Its limited solubility in organic solvents has prevented us from recording its NMR spectra. **2**: ν(C=O): 1505; ^1H: δ 9.02 (s, CHO, 1H), 6.41 (s, R′-H, 1H), 4.07, 3.92, and 3.76 (s, MeO, 3H). **3**: ν(C=O): 1665; ^1H: δ 11.11 (s, CHO, 1H), 4.13, 4.00, and 3.90 (s, MeO, 3H). **3′**: ν(C=O): 1655; ^1H: δ 10.79 (s, CHO, 1H), 7.14 (s, R′-H, 1H), 3.99 (s, MeO, 3H), 3.92, and 3.88 (s, MeO, 3H). **4**: ν(C=O): 1665; ^1H: δ 11.18 (s, CHO, 1H), 7.36 (s, R-H, 1H), 4.16, 4.03, and 3.93 (s, MeO, 3H). **4′**: ν(C=O): 1660; ^1H: δ 10.80 (s, CHO, 1H), 7.19 (s, R′-H, 1H), 3.99, 3.91, and 3.88 (s, MeO, 3H). **5**: ν(C=O): 1670; ^1H: δ 10.12 (s, CHO, 1H), 6.95 (s, R-H, 1H), 3.82, 3.73, and 3.62 (s, MeO, 3H); $^{31}P\{^1H\}$: 32.2 (s). **5′**: ν(C=O): 1670; ^1H: δ 9.78 (s, CHO, 1H), 6.90 (d, R′-H, 1H, $^4J_{(PH)}$ 3), 3.78, 3.76, and 3.67 (s, MeO, 3H); $^{31}P\{^1H\}$: 31.7 (s).

§ The –CHO and –OMe substituents were clearly distinguishable on the basis of (*i*) bond lengths, (*ii*) thermal parameters and (*iii*) identification of H atoms in difference syntheses.

The crystal structures of complexes **5** and **5′** (Fig. 1*a*,*b*) show the expected planar geometry at palladium. There are some moderate but significant differences in bond lengths at Pd: Pd–C(11) 2.010(5), 1.986(3), Pd–N(31) 2.143(4), 2.137(3), Pd–N(21) 2.099(4), 2.114(3), Pd–P 2.263(2), 2.252(1), Pd · · · O(1) 2.921(5), 2.926(3) Å (values for **5** and **5′** respectively).

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