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Preliminary communication

DIVERSE BEHAVIOUR OF IMIDOYL BRIDGES TOWARDS NEUTRAL NUCLEOPHILES: BRIDGE CLEAVAGE, ISONITRILE ELIMINATION, AND FORMATION OF ZWITTERIONIC PALLADIUM COMPLEXES. X-RAY STRUCTURE OF $[(\mathrm{tmen})\overset{+}{\mathrm{Pd}}\{\mu\text{-}\mathrm{C(C_6F_5)}{=}\mathrm{NMe}\}_2\overset{-}{\mathrm{P}}\mathrm{dCl_2}]$

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Summary

Dimeric pentafluoro-*N*-methylbenzimidoyl-bridged palladium(II) derivatives react with isonitriles to give monomeric, terminal imidoyl complexes, whereas $\mathrm{PPh_3}$ causes elimination of methyl isonitrile from the imidoyl group; reaction of $[\{\mathrm{Pd_2}(\mu\text{-Cl})_2\{\mu\text{-C(C_6F_5)}{=}\mathrm{NMe}\}_2\}_n]$ with N—N-chelate ligands affords zwitterionic dimeric complexes, $[(\mathrm{N{-}N})\overset{+}{\mathrm{Pd}}\{\mu\text{-}\mathrm{C(C_6F_5)}{=}\mathrm{NMe}\}_2\overset{-}{\mathrm{P}}\mathrm{dCl_2}]$ (confirmed by X-ray crystallography).

We recently reported [1] the preparation of *cis*-$[\{\mathrm{Pd_2}(\mu\text{-Cl})_2\{\mu\text{-C(C_6F_5)}{=}\mathrm{NMe}\}_2\}_n]$ (1), which reacts with monodentate ligands (Pd/L 1/1) to give dimeric complexes $[\mathrm{Pd_2}\{\mu\text{-C(C_6F_5)}{=}\mathrm{NMe}\}_2\mathrm{Cl_2L_2}]$ (2); thus only the chloro-bridge of 1 is cleaved. Dimeric imidoyl complexes of palladium(II) similar to 2 have been assigned terminal imidoyl, chloro-bridged structures $[\mathrm{Pd_2}(\mu\text{-X})_2\{\mathrm{C(R')}{=}\mathrm{NR}\}_2\mathrm{L_2}]$ (X = Hal), and some have been reported to react with L (= CNR$''$ or PR$'''_3$) to give mononuclear complexes $[\mathrm{Pd}\{\mathrm{C(R')}{=}\mathrm{NR}\}\mathrm{XL_2}]$ [2]. We observe three types of reaction of 1 and 2 with CNMe, $\mathrm{PPh_3}$ and bidentate ligands (all of which are potential cleaving agents for the imidoyl bridge).

(i) $[\mathrm{Pd_2}\{\mu\text{-C(C_6F_5)}{=}\mathrm{NMe}\}_2\mathrm{Cl_2(CNMe)_2}]$ with excess of CNMe gives colourless crystals of $[\mathrm{Pd}\{\mathrm{C(C_6F_5)}{=}\mathrm{NMe}\}\mathrm{Cl(CNMe)_2}]$ (3), characterized by microanalysis, molecular weight (isopiestic method in $\mathrm{CHCl_3}$, 446) and NMR spectroscopy. The ^{1}H NMR spectrum (100 MHz, $\mathrm{CDCl_3}$) shows two resonances, at δ 3.44 (s, 6H), and 3.74 (s, 3H) as expected for mutually *trans*-CNMe groups. The ^{19}F NMR spectrum is typical of an AA$'$MXX$'$ spin system, i.e. the two *ortho*-F are iso-

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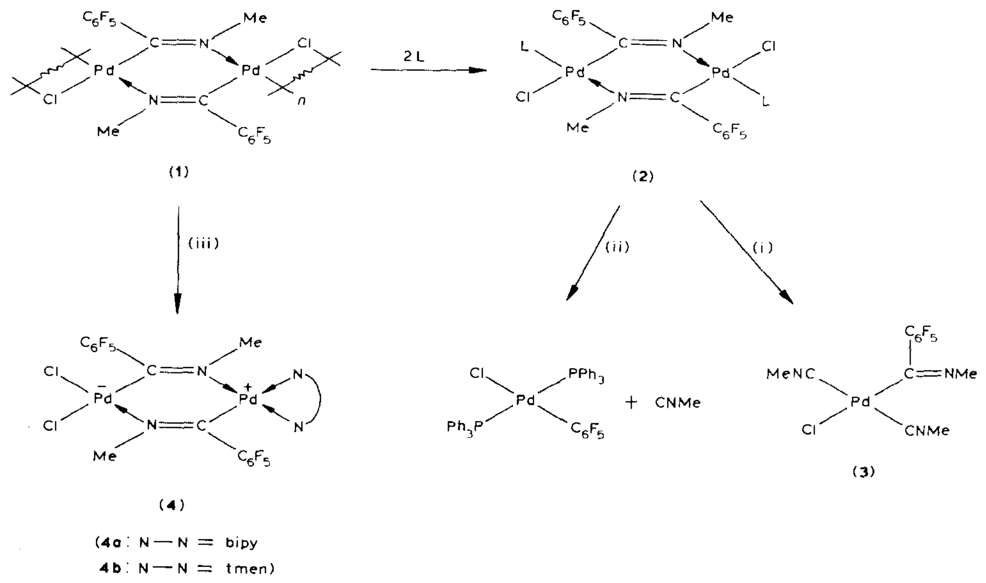

SCHEME 1. (i) L = CNMe, + CNMe; (ii) L = PPh_3, + PPh_3; (iii) +N—N = 2,2′-bipy, tmen).

chronous and so are the two *meta*-F, in contrast to the inequivalence observed in our imidoyl-bridged complexes; this indicates free rotation of the C_6F_5 group, sterically allowed only if the imidoyl group adopts an *anti* configuration.

(ii) Reaction of $[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2Cl_2(PPh_3)_2]$ with an excess of PPh_3 in benzene is very slow at room temperature although the odour of CNMe can be detected; it becomes stronger on refluxing and 52% of $[Pd(C_6F_5)Cl(PPh_3)_2]$ can be isolated after 18 h. Whereas decarbonylation reactions of acylpalladium derivatives are well established this isonitrile elimination is unprecedented in palladium chemistry.

(iii) Treatment of 1 with 2,2′-bipyridyl in acetone (Pd/bipy 1/1) produces a yellow precipitate (4a) for which microanalysis shows Pd/bipy 2/1. An analogous reaction with *N,N,N′,N′*-tetramethylethylenediamine affords a more soluble, non-conducting complex (4b). The X-ray analysis showed that 4b is formally zwitterionic (Fig. 1); thus the imidoyl bridging system has been preserved throughout the reaction.

Crystal data: 4b, $C_{22}H_{22}Cl_2N_6F_{10}Pd_2$, M_r = 844.15. Orange crystals were obtained from acetonitrile/ethanol. Orthorhombic, *Pbca*, *a* 12.849(2), *b* 32.430(8), *c* 13.479(2) Å, *U* 5617 Å^3, Z = 8, D_X 2.00 g cm^{-3}, $F(000)$ 3184, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 1.5 mm^{-1}. 3568 absorption-corrected reflections $>4\sigma(F)$; final R 0.047, R_w 0.042; non-H atoms anisotropic, isotropic H atoms included in refinement using a riding model. The structure (with selected bond lengths) is shown in Fig. 1*.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

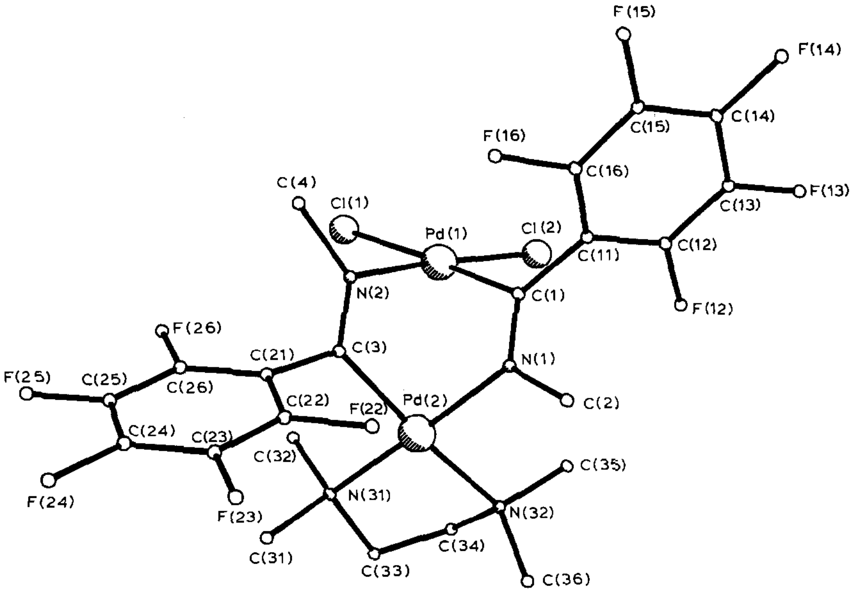

Fig. 1. The molecular structure of **4b**. Selected bond lengths: Pd(1)—Cl(1), 2.376(2); Pd(1)—Cl(2), 2.319(Pd(1)—C(1), 1.960(5); Pd(2)—C(3), 1.994(6); Pd(1)—N(2), 2.028(4); Pd(2)—N(1), 2.029(4); Pd(2)—N(31), 2.104(5); Pd(2)—N(32), 2.137(5); C(1)—N(1), 1.285(7); C(3)—N(2), 1.273(7).

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