Complexes of Binucleating Ligands. XVI. Some Diazotate-bridged Palladium(II) Complexes

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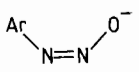
The acetate-bridged complex, $LPd_2(CH_3CO_2)$, in which L^{3-} is a binucleating ligand containing a bridging thiophenoxide unit, reacts with the syn-phenyldiazotate ion to yield the syn-diazotate-bridged complex $LPd_2(syn\text{-}C_6H_5NNO)$ and with the anti-phenyldiazotate ion to yield LPd_2 $(anti\text{-}C_6H_5NNO)$. The anti-complex isomerises to syn in boiling benzene, in contrast to the isomerisation of the free diazotate ions which proceeds spontaneously in the opposite direction. A para-nitro substituent has a pronounced labilising effect upon the isomerisation and $LPd_2(CH_3CO_2)$ reacts with sodium anti-p-nitrophenyldiazotate at room temperature to yield the syn complex, $LPd_2(syn\text{-}p\text{-}NO_2\cdot C_6H_4\cdot NNO)$. Nitrosourethane, $C_2H_5OOC\cdot NH\cdot NO$, reacts with $LPd_2(CH_3CO_2)$ to generate $LPd_2(C_2H_5OOC\cdot NNO)$.

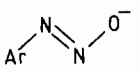
Introduction

An argument based on analogy with the chelate effect was recently presented [1], suggesting that it may be possible to generate or trap unusual or otherwise unstable entitites at a briding site between two metal centres secured in close proximity by an appropriate binucleating ligand [2], in a way which would be unlikely or impossible in the absence of the special organisation provided by the binucleating ligand. The present report is concerned with the unusual binding of diazotate ions at such a bridging site between two palladium(II) centres.

The existence of geometrically isomeric forms, *I* and *II*, of certain aromatic diazotate ions has been known since last century [3].



I

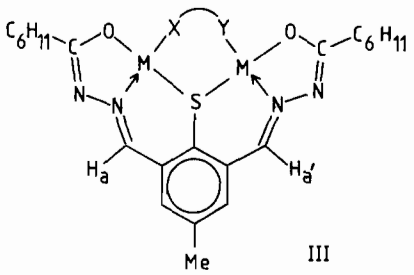


II

The first X-ray crystallographic study of an aromatic diazotate ion, reported recently [4], established that an isomer previously designated *syn* did indeed have the cis configuration, *I*. In some cases (*e.g.* where Ar in *I* and *II* = C_6H_5) both forms can be isolated. In all cases it appears that the *anti*-form, *II*, is thermodynamically the more stable but the rate of isomerisation of *syn* to *anti* varies widely, depending on the nature of the aromatic substituents. In some cases isomerisation is so facile that only the *anti* form can be isolated.

Results and Discussion

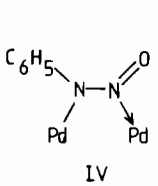
The binucleating ligand used in this work was that depicted in the generalised complex, *III*. This previously reported ligand [1, 5] is formally a trianion



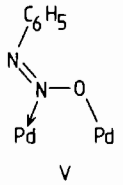
III

and is represented below as L^{3-} *e.g. III* would be represented as $LM_2(XY)$.

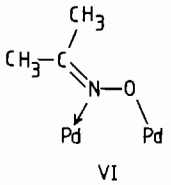
The previously reported acetate-bridged complex [5], $LPd_2(CH_3CO_2)$, reacted with potassium *syn*-phenyldiazotate in tetrahydrofuran to yield LPd_2 $(syn\text{-}C_6H_5NNO)$ in which (see below) we have no reason to believe any inversion of the *syn* configuration has occurred. Of the two bridging modes possible in this case, *IV* and *V*, the first seems the more likely on the basis of the preference of palladium(II) for nitrogen over oxygen donors. Nmr studies [1, 5] of an extensive series of $LPd_2(XY)$ derivatives,



IV



V



VI

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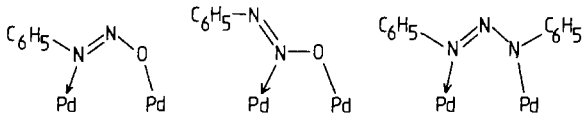
in which the two palladium centres are rendered inequivalent by the asymmetric XY bridging group, reveal that this inequivalence extends to the two ligand side chains and, in particular, what we shall call the *imine* protons, H_a and $H_{a'}$ in *III*, give rise to separate signals. In the ^1H nmr spectrum of LPd_2-(*syn*-C_6H_5NNO) the two imine resonances are superimposed at 8.04 p.p.m., which is consistent with (but by no means proves) bridging mode *IV* in which the two donor atoms, whilst not identical, are similar in nature. For comparison, the oxime complex [5], $LPd_2[(CH_3)_2CNO]$ involving the 2 atom N,O bridging mode *VI*, closely related to possibility *V*, showed comparatively widely separated imine resonances at 8.03 and 7.81 p.p.m. However, the N,O bridged nitrite derivative [5], $LPd_2(NO_2)$, which also has donor centres similar to those in possibility *V* shows less well separated imine resonances at 8.00 and 7.96 p.p.m.

Reaction between $LPd_2(CH_3CO_2)$ and potassium *anti*-phenyldiazotate in ethanol gave LPd_2(*anti*-C_6H_5-NNO) which showed ir and nmr spectra distinctly different from those of the *syn* complex, *e.g.* quite different patterns of strong bands in the 1200–1400 cm^{-1} region of the ir spectra, where vibrations associated with the NNO system might be expected [6], were observed, the strongest band for the *syn*-isomer appearing at 1400 cm^{-1} and that for the *anti* isomer at 1340 cm^{-1}. The ^1H nmr spectrum of LPd_2(*anti*-C_6H_5NNO) showed two separate imine resonances at 8.14 and 7.88 p.p.m. and also indicated the presence of a small proportion of the *syn* complex. The three atom briding mode, *VII*, seems the more likely of the two modes possible for the *anti* complex, *VII* and *VIII*, though the available evidence is inconclusive. Molecular models indicate that in bridging



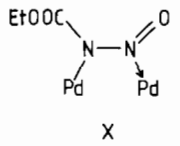
VII VIII IX

mode *VIII* the phenyl group comes into very close contact with the adjacent oxygen donor atom of the binucleating ligand, possibly prohibitively so. In bridging mode *VII* this particular steric interaction appears to be not so marked and must be very similar to the analogous interaction in the diphenyltriazine derivative, $LPd_2(C_6H_5NNNC_6H_5)$ which is quite stable and involves briding mode *IX* [5]. All attempts to obtain single crystals suitable for X-ray crystallography of either the *syn* or *anti* complexes have unfortunately failed [7].

Both isomeric forms of $LPd_2(C_6H_5NNO)$ in the solid phase are stable at 80 °C and the *syn* complex is stable in solution in boiling benzene. However, the *anti* form isomerises to *syn* in boiling benzene; in other words, the relative stabilities of the isomeric anions are inverted when they are bound at the briding site. The preference of palladium(II) for nitrogen over oxygen donors may provide the driving force for this isomerisation, although the contribution of differences in strain at the bridging group is impossible to assess.

Electron withdrawing substituents at the para position of the aromatic group are known to have a pronounced labilising effect upon the isomerisation of the free anion, $I \rightarrow II$, and isolation of *syn* diazotates from weakly basic amines such as nitroanilines is difficult or, more usually, impossible because the isomerisation is so rapid. Littler [8] has discussed the possible nature of these substituent effects. Reaction of sodium *anti*-p-nitrophenyldiazotate with LPd_2-(CH_3CO_2) in ethanol–tetrahydrofuran gave LPd_2-$(NO_2 \cdot C_6H_4 \cdot NNO)$ as a stable crystalline complex in which, we believe, the diazotate has undergone the *anti* → *syn* isomerisation, for the ^1H nmr spectrum shows the two imine resonances superimposed at 8.08 p.p.m. and the material can be recovered unchanged after heating in refluxing toluene for one hour. It appears that, whatever the mechanism of the *anti* → *syn* isomerisation at the binuclear site, the para nitro substituent has the same labilising effect as it exerts in the isomerisation (in the opposite direction) of the free anion.

The marked stability of the LPd_2(*syn*-ArNNO) complexes leads one to speculate on the possible existence of the unsubstituted $LPd_2(HNNO)$ in which the conjugate base of the highly unstable diazotic acid, HN=NOH, which formally corresponds to dinitrogen with water added across the multiple bond, is stabilised by coordination to a geometrically compatible LPd_2 unit. The existence of such an unsubstituted diazotate complex would be of considerable significance with regard to the possibility of conducting reaction upon dinitrogen (in particular, hydration) at an appropriate binuclear site. With these thoughts in mind we have sought to introduce substituted diazotate groups at the Pd_2 site which offer the possibility of subsequent transformation to $HNNO^-$. Nitrosourethane, $C_2H_5OOC \cdot NH \cdot NO$, which decomposes moderately rapidly at room temperature, reacts smoothly with $LPd_2(CH_3CO_2)$ in dichloromethane solution in the presence of aqueous sodium carbonate to generate $LPd_2(C_2H_5OOC \cdot NNO)$. This complex is stable in boiling benzene which, by comparison with the aryl diazotate complexes, suggests the 2 atom N,N bridging mode, *X*. The marked stabilisation of the diazotate group towards thermal decomposition, resulting from incorporation at the binuclear site is particularly noteworthy. The ir spectrum of the complex shows strong sharp ester-derived bands at 1200 and 1765 cm^{-1} ($\nu_{C=O}$). In contrast to the other presumed 2 atom N,N bridged complexes described above, $LPd_2(C_2H_5OOC \cdot NNO)$



X

shows two resolved but close imine resonances in its ^{1}H nmr spectrum at 7.90 and 7.85 p.p.m.

Nitramide [9], NO_2NH_2, can be conveniently generated from nitrourethane, $NO_2 \cdot NH \cdot COOC_2H_5$, by base hydrolysis of the ester followed by decarboxylation. Likewise, potassium methyldiazotate, $CH_3 \cdot N{=}N \cdot O^-K^+$, can be prepared by the action of cold concentrated potassium hydroxide upon nitrosomethylurethane, EtOOC–N(Me)–NO, again via ester hydrolysis followed by decarboxylation [10]. However all attempts, so far, at similar hydrolysis and decarboxylation of $LPd_2(C_2H_5OOC \cdot NNO)$ to yield the unsubstituted $HNNO^-$-bridged complex have led to general decomposition of the complex.

Experimental

LPd_2(syn-C_6H_5NNO)

A stock suspension of potassium *syn*-phenyldiazotate in concentrated aqueous potassium hydroxide was prepared by the method below and aliquots of this slurry were filtered on a sinter immediately prior to reactions with $LPd_2(CH_3CO_2)$. A solution at 0 °C of aniline (2.00 g) in concentrated hydrochloric acid (5.5 ml) diluted with an equal volume of water was diazotised with a solution of sodium nitrite (1.60 g) in water (7.5 ml) at 0 °C. The resulting solution was added with stirring to an aqueous slurry of potassium hydroxide at 0 °C obtained by cooling in ice-salt 80 ml of a solution saturated at room temperature. The thick suspension so obtained was allowed to warm to room temperature, whereupon the excess suspended potassium hydroxide redissolved leaving the diazotate salt in suspension.

A large excess (*ca.* 0.5 g) of the freshly collected potassium *syn*-phenyldiazotate, still damp with concentrated aqueous potassium hydroxide, was added with vigorous stirring to a partial suspension of $LPd_2(CH_3CO_2)$ (0.30 g) in tetrahydrofuran (3 ml) at room temperature. Within 2 min a thick bright yellow suspension formed. After 5 min ether (5 ml) was added with vigorous stirring. The suspended solid was collected on a sinter and washed very thoroughly with first ether and then methanol. Incomplete washing at this stage gave a solid which subsequently darkened on standing. The solid, after being dried in a stream of air, was dissolved in hot benzene (20 ml) and approximately half the benzene was removed by boiling at atmospheric pressure in order to azeotrope off any water present. The resulting mixture containing a small amount of suspended solid was filtered whilst hot and an equal volume of boiling 60–80 °C petrol was added to the boiling filtrate. Upon being cooled to room temperature the solution deposited bright yellow LPd_2(*syn*-C_6H_5NNO), which was collected, washed with benzene–petrol and dried in vacuum at 80 °C. Yield, 0.22 g. *Anal.* Found: C, 45.6; H, 4.6; N, 10.9; S, 4.6; Pd, 28.1. Calcd. for $C_{29}H_{34}N_6O_3SPd_2$: C, 45.8; H, 4.5; N, 11.1; S, 4.2; Pd, 28.1.

LPd_2(anti-C_6H_5NNO)

A suspension of $LPd_2(CH_3CO_2)$ (0.25 g) and potassium *anti*-phenyldiazotate [3] (0.25 g) in ethanol (2 ml) was stirred at 0 °C. After 10 min almost all the solid had dissolved. After 20 min ice-water (30 ml) was added to the stirred reaction mixture and the precipitated yellow solid was collected and washed with ice-water. The solid after being dried in vacuum at room temperature was dissolved in dichloromethane (1.5 ml) at 0 °C and the filtered solution was added to 60–80 °C petrol (40 ml) at 0 °C. The precipitated yellow solid was collected and dried at 80 °C in vacuum. (Attempts to recrystallise the product from solution above room temperature caused some isomerisation to the *syn* complex but in the solid form the *anti* complex appeared to be stable under the above drying conditions). Yield, 0.17 g. *Anal.* Found: C, 45.2; H, 4.6; N, 10.9; S, 4.6; Pd, 28.4. Calcd. for $C_{29}H_{34}N_6O_3SPd_2$: C, 45.8; H, 4.5; N, 11.1; S, 4.2; Pd, 28.1. The general features of the ^{1}H nmr spectrum (*e.g.* relative integrations) were entirely consistent with the formulation $LPd_2(C_6H_5NNO)$.

Isomerisation of LPd_2(anti-C_6H_5NNO) to LPd_2(syn-C_6H_5NNO)

LPd_2(*anti*-C_6H_5NNO) (0.053 g) dissolved readily in benzene (1 ml) at room temperature. The solution darkened markedly upon being heated under reflux and for this reason heating was terminated after only 20 min. The solution, after being cooled to room temperature, deposited yellow crystals of LPd_2(*syn*-C_6H_5NNO) which were collected, dried in vacuum and identified by the characteristic ir spectrum. Recovery, 0.037 g. The difference in solubility in benzene between the two isomers is marked.

LPd_2(syn-$pNO_2 \cdot C_6H_4NNO$)

$LPd_2(CH_3CO_2)$ (0.22 g) and sodium *anti*-p-nitrophenyldiazotate (0.23 g) were stirred in a mixture of ethanol (12 ml) and tetrahydrofuran (1.5 ml) at room temperature. After 4 hr the suspended solid product was collected, washed with ethanol and dried in air, the ir spectrum being indistinguishable from that of the analytically pure recrystallised material. The solid was recrystallised from chloroform–petrol (60–80 °C) as fine orange needles. Yield, 0.15 g. *Anal.* Found: C, 42.8; H, 4.2; N, 12.1; S, 3.9; Pd,

26.0. Calcd. for $C_{29}H_{33}N_7O_5SPd_2$: C, 43.3; H, 4.1; N, 12.2; S, 4.0; Pd, 26.5. The general features of the ^1H nmr spectrum were entirely consistent with the formulation $LPd_2(NO_2 \cdot C_6H_4NNO)$ *e.g.* the integrated intensity of the AB quartet arising from the p-nitro phenyl group was twice that of the 'singlet' arising from $H_a + H_{a'}$ of L.

$LPd_2(C_2H_5OOC \cdot NNO)$

Nitrosourethane [12] (0.14 g) in dichloromethane (1 ml) was added to $LPd_2(CH_3CO_2)$ (0.20 g) in dichloromethane (3 ml) at room temperature. Saturated aqueous sodium carbonate (2 ml) was added and the two phase mixture was stirred vigorously at room temperature for 4.5 hr. The liquid phases were separated, the aqueous phase washed with further dichloromethane (4 ml) and the combined dichloromethane extracts dried with stirring over sodium sulphate plus sodium carbonate. The drying agent was removed by filtration. Addition of 40–60 °C petrol to the filtrate precipitated pale yellow $LPd_2(C_2H_5OOC \cdot NNO)$ which was collected, washed with 40–60 °C petrol and dried in air. Yield, 0.152 g. The ir spectrum was identical to that of a recrystallised sample. Recrystallisation was effected from benzene–hexane. *Anal.* Found: C, 41.9; H, 4.6; N, 10.6. Calcd. for $C_{26}H_{34}N_6O_5SPd_2$: C, 41.4; H, 4.5; N, 11.1. The ^1H nmr spectrum was entirely consistent with the formulation $LPd_2(C_2H_5OOC \cdot NNO)$ *e.g.* the integrated intensity of the two singlets arising from $H_a + H_{a'}$ of L was equal to that of the quartet arising from the methylene group of the bridging unit.

Physical Measurements

Ir spectra were recorded on a Perkin-Elmer 457 spectrophotometer either as KBr discs or as nujol mulls. Nmr spectra were recorded on a Jeol FX100 spectrometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

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