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Complexes of Binucleating Ligands. XV. Formation of Some 2-Atom N,C Bridged Palladium(II) Complexes by Reactions Analogous to Cyclometallation Including an Example of an Iminazole Bridging via N3 and C4

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A previously described acetate bridged complex, $LPd_2(CH_3CO_2)$, in which L^{3-} is a binucleating ligand bearing a bridging thiophenoxide and solubility-enhancing cyclohexyl side chain substituents, reacts with certain nitrogen heterocycles by replacement of the bridging acetate with carbanionic species derived from the heterocycle by deprotonation. Indole and 3-methylindole give complexes $LPd_2(C_8H_6N)$ and $LPd_2(C_9H_8N)$ respectively in which the formally monoanionic heterocyclic moiety is incorporated as a two atom bridge via *N1 and C2 both of which have been deprotonated, one of these protons reappearing attached to C3. 3-Hydroxypyridine and 3-aminopyridine are both incorporated into the LPd_2^+ unit as monoanionic two atom bridges* via *N1 and deprotonated C2. Deuteration studies show that 1-n-propyliminazole is incorporated as a monoanionic two atom bridge* via *N3 and deprotonated C4.*

Introduction

Despite some criticism of the concept of the chelate effect, it undoubtedly is not imaginary and in some cases may be very pronounced [1]. The commonly accepted rationalisation for the larger positive entropies of formation of chelate complexes as compared with otherwise analogous non-chelated complexes is that in proceeding from starting materials to products there is a bigger increase in the number of independent particles in the chelating case than in the comparable non-chelating case. An alternative but equivalent view is that order is already built into the starting materials in the chelating case, in so far as wherever one donor centre goes, the other(s) must follow. However, the order or organisation within the chelating agent must be appropriate to the geometrical requirements of the metal ion for maximum enhancement of complex stability. Thus, 1,10-phenanthroline, which is better organised or more ordered than 2,2'-bipyridine with regard to the requirements of the metal centre, forms the more stable complexes and the difference arises mainly in the entropy term [2].

The chelate effect is manifested not only in the area of thermodynamic stabilities but also in reactivities. For example, a number of metal ion-catalysed or metal ion-promoted reactions can be seen to depend upon the formation of chelated reactive intermediates in which functional groups are coordinated and thereby activated in a way which would be unlikely or impossible in the absence of the chelate effect.

It might reasonably be expected, by analogy, that the association of a species containing two appropriately linked acceptor centres, M in I (rather than the two linked donor centres of a bidentate chelating agent, X in II) with a species Z, capable of providing dative bonds to both M s, would be unusually favourable provided the organisation built into the $M\widehat{M}$

I

II

component matched the geometrical requirements of the bridging species. Thus we might anticipate that unusual species might be generated or trapped at the bridging site between the two metal centres of a complex of an appropriate binucleating ligand in a way which would be unlikely or impossible in the absence of the special organisation already provided within the binuclear component. Extension of the analogy suggests that unusual reactivity under the influence of the organised binuclear system might also be anticipated. Work with complexes of binucleating ligands is proceeding in this laboratory in both these areas, *i.e.* unusual structures and unusual reactivity. The present report is concerned with some reactions generating unusual organometallic complexes in which adjacent nitrogen and carbon

TABLE I. Analytical Data.

ZH[a]		%C	%H	%N	%S	%Pd
Indole	Found	49.6	4.7	9.0	4.1	28.5
	Calcd. for $C_{31}H_{35}N_5O_2SPd_2$	49.3	4.7	9.3	4.2	28.3
3-Methylindole	Found	50.0	4.9	9.0	4.0	27.6
	Calcd. for $C_{32}H_{37}N_5O_2SPd_2$	50.0	4.9	9.1	4.2	27.7
3-Hydroxypyridine	Found (isomer A)	46.0	4.5	9.4	4.2	28.9
	Found (isomer B)	46.5	4.5	9.7		
	Calcd. for $C_{28}H_{33}N_5O_3SPd_2$	45.9	4.5	9.6	4.4	29.0
3-Aminopyridine	Found	46.0	5.0	11.3	4.1	28.9
	Calcd. for $C_{28}H_{34}N_6O_2SPd_2$	46.0	4.7	11.5	4.4	29.1
1-n-Propyliminazole	Found	46.4	5.1	11.4	4.1	28.2
	Calcd. for $C_{29}H_{38}N_6O_2SPd_2$	46.6	5.1	11.2	4.3	28.5

[a]ZN = neutral heterocycle providing the Z^- bridge in $LPd_2(Z)$.

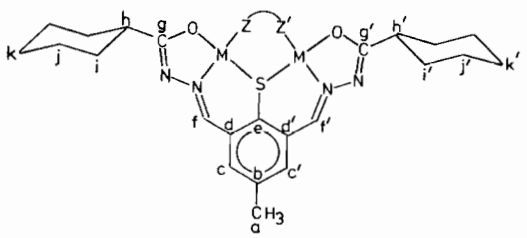


Fig. 1. A binuclear complex of L^{3-} including labelling of carbon centres.

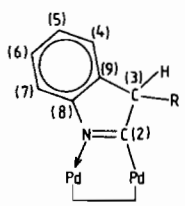
centres of the bridging species serve as donors to palladium(II).

Results and Discussion

The trianionic binucleating ligand used in this work, which is represented below as L^{3-} and a binuclear complex of which is represented in Fig. 1, was one reported earlier [3] with cyclohexyl substituents introduced into the side arms in order to enhance solubilities of derived complexes in organic solvents. The acetate-bridged derivative, $LPd_2(CH_3CO_2)$, provided a convenient starting material for the preparation of the complexes described below and also those described earlier [3], the outgoing acetate often serving as a base to deprotonate the incoming bridge.

Nitrogen heterocycles offer the possibility of as yet unobserved types of association with the LPd_2^+ unit *via* donation from the nitrogen atom to one palladium together with some sort of possibly unusual interaction between the second palladium and the carbon system adjacent to the nitrogen. A study of the interaction of $LPd_2(CH_3CO_2)$ with various nitrogen heterocycles was therefore undertaken.

Reaction of $LPd_2(CH_3CO_2)$ with pyrrole in either boiling benzene or chloroform gave dirty intractable mixtures from which we were unable to isolate any pure products. However, similar reactions with indole and 3-methylindole cleanly afforded complexes of composition $LPd_2(C_8H_6N)$ and $LPd_2(C_9H_8N)$ respectively (see Table I). The evidence presented below shows these complexes to have the bridging structure III in which a proton has been removed from both N1 and C2, one of these protons reappearing on C3.



III a) R = H
b) R = CH_3

The indole-derived product showed a two proton singlet in the benzylic region of the ^1H nmr spectrum

TABLE II. NMR Data[a] Relating to L^{3-} Component of $LPd_2(Z)$ (see Fig. 1 for labelling of atoms).

ZH[b]	$H_{f,f'}$	$C_{g,g'}$	$C_{f,f'}$	$C_{c,c'}$	C_b	$C_{d,d'}$	C_e	$C_{h,h'}$	$C_{i,i'}$	$C_{j,k}$	C_a
3-methylindole	8.14 8.24	186.0 184.3	150.8 149.0	139.6 138.5	136.8	133.4	123.0	41.6 40.4	31.3 31.1	26.2	20.7
Indole	8.13 8.20	– –	150.8 149.0	139.6 138.4	136.6	133.5	– –	41.9 40.4	31.2	26.2	20.7
3-Hydroxypyridine	7.85 8.15	183.3 182.4	151.1 150.1	139.5 138.9	136.7	133.3 132.7	123.6	41.0 40.3	30.9	26.0	20.5
3-Aminopyridine	8.09 8.37	– –	150.6	138.9 138.4	136.9	133.9 133.3	– –	41.5 40.6	31.2	26.2	20.7
1-n-propyliminazole	8.13 8.30	186.1 184.4	149.8 147.6	139.3 138.5	136.0	133.5	123.7	41.8 40.7	31.1	26.1	20.6

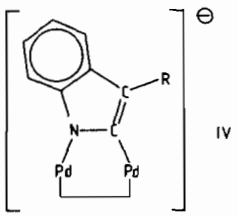
[a]Chemical shifts (p.p.m) downfield of T.M.S. All in $CDCl_3$. [b]ZH = neutral species from which bridging Z^- in complex is derived.

at 4.00 p.p.m. in contrast to free indole, in the spectrum of which all the CH protons appear in the aromatic region. The ^1H nmr spectrum of the 3-methylindole-derived complex showed a doublet at 1.61 p.p.m., (superimposed on a broad cyclohexyl signal) ascribed to the methyl group in IIIb, coupled to the adjacent proton, which in turn appeared as a quartet in the benzylic region at 3.87 p.p.m. Irradiation at the frequency corresponding to the doublet caused the quartet to collapse to a singlet.

The noise decoupled ^{13}C nmr spectrum of the 3-methylindole complex and also those of other LPd_2^+ derivatives described below were assigned by comparison with off-resonance spectra and with spectra of a wide range of related complexes described previously, one of which was completely and unambiguously assigned [3]. These comparisons leave no doubt as to which resonances (with rare exceptions) originate in the L^{3-} component (see Table II) and which arise from the bridging species. Thus a line at 57.6 p.p.m. in the ^{13}C nmr spectrum of the 3-methylindole-derived complex, which splits into a doublet in the off-resonance spectrum, can be assigned with confidence to C3, a saturated carbon centre carrying one proton and directly attached to an aromatic ring. The indole-derived complex was significantly less soluble in $CDCl_3$ than the 3-methylindole complex and not all the carbon resonances could be discerned in the less well defined ^{13}C nmr spectrum; nevertheless, all the L^{3-} derived carbon atoms except the quaternaries C_g, $C_{g'}$ and C_e (Fig. 1) could be located. C3 of the indole fragment appeared at 52.5 p.p.m. and the proton bearing carbons of the carbocycle appeared at 127.4, 124.8, 123.2 and 117.7 p.p.m., which agree closely with those of the 3-methylindole complex, identified by off-resonance at 127.3, 125.0, 122.2 and 117.6 p.p.m.

Only two of the three quaternary carbon atoms of IIIb could be located in the ^{13}C nmr spectrum, namely at 154.1 and 141.3 p.p.m., both significantly downfield from any of the carbon atoms of free 3-methylindole, the lowest field resonance of which, at 137.0 p.p.m., has been assigned to the quaternary bridgehead carbon 8 [4]. We tentatively assign the 141.3 p.p.m. peak of the complex to C8, shifted downfield by coordination of N1 and C2 and the 154.1 p.p.m. peak to the coordinated C2 which is now imine-like rather than aromatic.

Structures of the type III would be expected to aromatise very readily by proton loss from C3 to give IV, in which the bridging species is formally a dianion and the overall complex is a monoanion. Treatment of the indole-derived complex with metha-



IV

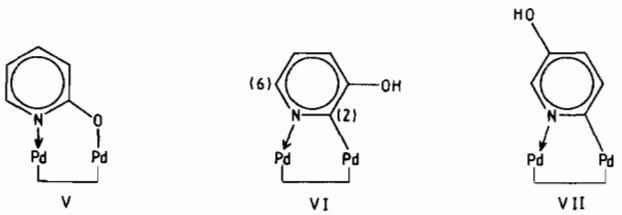
nolic potassium hydroxide gave intractable dirty brown suspensions. Addition of an excess of the fairly basic but very weakly nucleophilic 1,8-bis-dimethylaminonaphthalene (proton sponge) to a solution of IIIb in $CDCl_3$ brought about no change, even after one day, in those features of the ^1H nmr spectrum arising from the complex. However, shaking a solution of IIIb in $CDCl_3$ with a solution of NaOD in D_2O produced a slow change in the ^1H nmr spec-

trum and after 2 hours shaking the quartet arising from the proton on C3 had disappeared and the doublet due to the methyl group had collapsed to a singlet unchanged in position [5]. This indicates that the predominant complex species in solution is the C3-deuterated form of IIIb rather than the aromatised anionic complex IV, which presumably is involved merely as a relatively inaccessible intermediate in the deuterium exchange process.

Molecular models suggest that the hydrogen on C7 of the indole fragment must come into close proximity with the terminal oxygen donor of the L^{3-} side arm on the same side of the molecule. Perhaps the saturated tetrahedral C3 allows some twisting around the N–Pd bond so that this repulsive interaction is minimised and perhaps loss of the proton from C3 generating the planar dianionic bridging unit increases this interaction. This may account for the appearance of products with non-aromatic heterocyclic rings and also for the relative inaccessibility of the deprotonated aromatised form.

We have reported elsewhere [3] that pyridine, in common with a number of good monodentate donors for palladium(II), upon reaction with $LPd_2(CH_3CO_2)$ abstracts one out of four palladiums generating L_2Pd_3, the probable structure of which was discussed in that report. We now find that introduction of electron donating substituents at the 3-position of the pyridine ring allows the heterocyclic unit to be incorporated at the bridging site of the LPd_2^+ unit.

Reaction of $LPd_2(CH_3CO_2)$ with 3-hydroxypyridine in boiling benzene gave, in approximately 25% yield, a highly insoluble precipitate of composition consistent with the formulation $LPd_2(C_5H_4NO)$, which we shall call isomer B, the possible nature of which is discussed below. Addition of methanol to the filtrate obtained after removal of isomer B gave a second isomer, referred to below as isomer A, which was crystalline and soluble in chloroform. A third material of composition $LPd_2(C_5H_4NO)$ has previously been reported from the reaction of $LPd_2(CH_3CO_2)$ with 2-hydroxypyridine, in which the $C_5H_4NO^-$ anion bridges *via* nitrogen and oxygen as in V [3]. By contrast, the evidence below



V VI VII

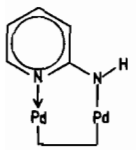
for isomer A points to a structure involving coordination of a carbon centre as in VI or VII. The ir spectrum of isomer A (either KBr disc or nujol mull) showed an OH stretching band at 3160 cm^{-1}, which was quite sharp in comparison with many OH stretching bands. The ^1H nmr spectrum of A showed a one proton signal at 9.94 p.p.m., ascribed to OH, which disappeared in the presence of D_2O. Integration of the ^1H nmr spectrum also was consistent with deprotonation at one of the carbon centres in so far as only three bridge derived CH's could be accounted for. Proton 6 of free 3-hydroxypyridine appeared in the ^1H nmr spectrum at 8.08 p.p.m. as an approximate doublet of doublets with coupling constants, from a first order analysis, of *ca.* 3.7 and 2.4 Hz, corresponding to coupling with proton 5 and proton 4 respectively. Proton 2 of free 3-hydroxypyridine appeared at 8.29 p.p.m. as a multiplet much less widely spaced and less well resolved than that for proton 6, as is consistent with its weaker coupling to other protons. The ^1H nmr spectrum of isomer A showed a bridge derived one proton signal at 8.03 p.p.m., consisting of an approximate doublet of doublets, the expanded envelope of which closely resembled that of the proton 6 in the spectrum of free 3-hydroxypyridine; first order analysis gave coupling constants of *ca.* 4.2 and 2.8 Hz. This indicates that isomer A has the bridging arrangement VI, in which the possibility exists of relatively strong coupling of a proton adjacent to nitrogen with an ortho proton, rather than structure VII where such ortho coupling is impossible.

The noise decoupled ^{13}C nmr spectrum of isomer A was assigned by off-resonance and comparison with spectra of related complexes. Lines originating in the binucleating ligand are recorded in Table II and bridge derived lines are as follows: 120.4, 120.9 and 142.9 p.p.m. arising from three pyridine carbon atoms each carrying one hydrogen, and 162.0 and 176.2 p.p.m., both arising from quaternary carbon atoms. The appearance of two quaternaries confirms the deprotonation of carbon. The ^{13}C nmr spectrum of free 3-hydroxypyridine has been assigned as follows [6]: 122.7, C5; 124.1, C4; 138.1, C2; 139.9, C6; 154.3, C3. The following tentative assignment for the complex can be made by comparison: 120.9, 120.4, C4/5; 142.9, C6; 162.0, C3; 176.2, C2. Considerable downfield shifts compared with free 3-hydroxypyridine are apparent for the coordinated carbon and also the carbons adjacent to the two coordinated atoms.

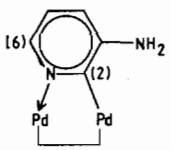
Isomer B was too insoluble to allow the observation of nmr spectra. It possibly has the isomeric structure VII but, in contrast to isomer A, it showed no detectable OH stretching band in the ir spectrum, and a polymeric structure with the phenoxide ion $C_5H_4N.O^-$ bridging *via* N and O between separate LPd_2^+ units seems more likely.

Reaction of $LPd_2(CH_3CO_2)$ with 3-aminopyridine in boiling benzene gave, after removal of a small quantity of gummy precipitate followed by addition of methanol, a crystalline product of composition

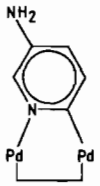
consistent with the formulation $LPd_2(C_5H_5N_2)$. An isomeric complex from 2-aminopyridine has previously been shown to have the three atom N,N′ bridged structure VIII [3]. Evidence that the hetero-



VIII



IX



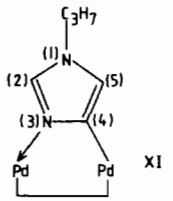
X

cyclic moiety in the 3-aminopyridine derived complex is bound as in IX rather than X closely parallels that for the 3-hydroxypyridine complex above. N–H stretching bands were observed in the i.r. spectrum (KBr disc) at 3210, 3310 and 3440 cm^{-1}. The complex was much less soluble in chloroform than the 3-hydroxypyridine complex and nmr spectra were recorded in $CDCl_3$ solution at 50 °C to maximise concentrations. The ^1H nmr spectrum showed a broad 2 proton NH signal at 5.40 p.p.m., suggesting that the deprotonation site of the bridging species was at carbon and integration of the aromatic region confirmed this, only three bridge-derived CH's being accounted for. Free 3-aminopyridine in its ^1H nmr spectrum shows both H2 and H6 as approximate doublets of doublets at 8.08 and 7.99 p.p.m. respectively, the latter being the more widely spaced as is consistent with the possibility of ortho coupling; first order analysis gives J_{H6-H5} = *ca.* 4.3 Hz and J_{H6-H4} = *ca.* 1.8 Hz. The ^1H nmr spectrum of the 3-aminopyridine complex showed H6 again as an approximate doublet of doublets but the low field component was partially obscured, appearing as a shoulder on an L^{3-} imine resonance at 8.09 p.p.m. First order analysis indicated J_{H6-H5} = *ca.* 5.4 Hz and J_{H6-H4} = *ca.* 1.5 Hz.

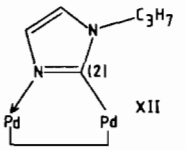
Because of the very low concentration of the almost saturated $CDCl_3$ solution of the 3-aminopyridine complex, even at 50 °C, the noise decoupled ^{13}C nmr spectrum was poorly defined and the off-resonance spectrum was not recorded. Nevertheless all the carbon resonances of L^{3-} except for C_g, $C_{g'}$ and C_e (Fig. 1) could be located (Table II) and four of the carbon resonances of the bridging pyridine unit were observed. ^{13}C resonances of free 3-aminopyridine have been assigned as follows [7]: 121.3, C4; 123.9, C5; 138.9, C6; 143.7, C3; 137.2 p.p.m., C2. By comparison the four observed pyridine resonances of the complex may be tentatively assigned as follows, it being assumed that it was the coordinated quaternary C2 that was unfortunately lost in the noise: 121.0, 118.5, C4/5; 140.8, C6; 154.4 p.p.m., C3.

An alternative to introducing electron donor substituents at the 3-position, as a means of activating carbon centres adjacent to nitrogen donors of the pyridine type is to incorporate the electron donor into the heterocyclic ring itself as in, for example, iminazoles. 1-n-propyliminazole reacted with $LPd_2(CH_3CO_2)$ in boiling benzene to produce some L_2Pd_3 in addition to a material of composition consistent with the formulation $LPd_2(C_3H_7 \cdot C_3H_2N_2)$. The reaction was apparently cleaner and more rapid in boiling benzene containing some methanol from which pure, crystalline $LPd_2(C_3H_7 \cdot C_3H_2N_2)$ (Table I) could be readily isolated.

The ^1H n.m.r. spectrum of the complex showed iminazole-derived one proton doublets at 6.82 and 7.61 p.p.m.; first order analysis indicated a coupling constant of *ca.* 1.3 Hz. On passing from 6-membered to 5-membered heterocyclic rings there is a marked decrease in *ortho* coupling constants [8], which in the case of iminazoles may be as low as 1.2 Hz [9]. The observed coupling constant for the two iminazole protons of the complex then provides no means of deciding between the alternative bridging arrangements XI and XII. Free 1-n-propyliminazole in its

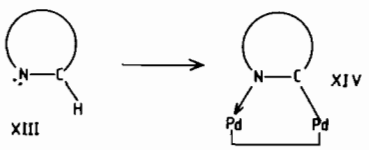


XI



XII

^1H n.m.r. spectrum shows the three aromatic protons as distinct one proton multiplets at 7.46, 7.06 and 6.90 p.p.m. assigned to H2, H5 and H4 respectively by comparison with assignments previously made for 1-methyliminazole [10]. The chemical shift of the lower field iminazole proton (7.61 p.p.m.) in the spectrum of the complex suggests that the 2-proton is still present as in isomeric form XI, but we do not have sufficient data to indicate what sorts of change in chemical shift of such protons might arise in the process XIII → XIV. The scant data we do have sug-



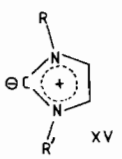
XIII XIV

gest that such changes in chemical shift for protons adjacent to the nitrogen donor are not large, *i.e.* 0.05 p.p.m. upfield in the 3-hydroxypyridine case and 0.06 p.p.m. downfield in the 3-aminopyridine case. If the complex had structure XII the 7.61 p.p.m. signal, which would then have to be assigned to H4, would correspond to a downfield change of 0.71 p.p.m., which seems very large, whereas if the structure were XI the implied changes in chemical

shift are less extreme, *i.e.* 0.15 p.p.m. downfield for H2 and 0.24 p.p.m. upfield for H5. This evidence then is inconclusive but is suggestive of structure XI.

^{13}C n.m.r. data unfortunately shed little further light on this ambiguity. Resonances originating in the binucleating ligand are recorded in Table II and the iminazole-derived aromatic resonances were observed at 123.1, 137.1 and 155.9 p.p.m., of which the latter was shown by off-resonance to correspond to a quaternary carbon, *i.e.* the coordinated carbon. The following assignment of the aromatic resonances of free 1-n-propyliminazole was made on the basis of comparison with the peviously assigned spectrum of 1-methyliminazole [11]: 118.1, C5; 128.3, C4; 136.2 p.p.m., C2. It is clear that a considerable downfield shift in the chemical shift of the carbon atom which becomes coordinated accompanies XIII → XIV but the above data do not indicate whether that carbon atom is C2 or C4.

Iminazoles can be deuterated at the 2-position with some specificity, simply by heating with D_2O [12]. When 1-n-propyliminazole was heated at 70–75 °C with D_2O for 1.5 hours, the product showed a ^1H n.m.r. spectrum almost identical to that of the starting material except that the multiplet at 7.46 p.p.m. had disappeared. Reaction of this 1-n-propyl-2-deuteroiminazole with $LPd_2(CH_3CO_2)$ in boiling benzene-methanol gave a crystalline product whose ^1H n.m.r. was identical to that of the undeuterated complex except that the doublet at 7.61 p.p.m. was absent and the doublet at 6.82 p.p.m. had been replaced by a sharp singlet in the same position. This evidence proves that the iminazole ring is incorporated *via* N3 and C4 as in X and that the resonances at 7.61 and 6.82 p.p.m. for the undeuterated complex correspond to H2 and H5 respectively. The ready H/D exchange of H2 in various uncoordinated iminazoles in D_2O which, it has been proposed [12], proceeds *via* the neutral iminazolium ylide intermediate XV (in which one or both of R and R′ may be H) suggested the possibility that 1-n-propylimina-



XV

zole bridging as in X might suffer similar exchange. It is fortunate that such exchange of the 2D with the CH_3OH of the reaction medium appears not to occur to any significant extent during the formation of the 2-deuterated complex, otherwise an unambiguous structural assignment may have been impossible. The ^{13}C resonance at 155.9 p.p.m. corresponding to the coordinated carbon atom can now be assigned unambiguously to C4 which has suffered a 27.6 p.p.m. downfield shift during the process XIII → XIV.

Complexes containing monodentate carbon-bonded iminazoles have previously been reported [13] in which the ligand is formally a neutral ylide of the type XV with C2 as the donor and Taube has referred to the possible biological importance of such bonding. There is presently a great deal of interest in N,N′-bridging iminazoles [14] arising from the presence of such bridges in enzymes such as superoxide dismutase. To the best of our knowledge the example described above is the first involving bridging *via* N3 and C4.

In conclusion we draw attention to the analogy between the reactions described herein and the cyclometallation reaction [15], without wishing to imply that the mechanisms of metal–carbon bond formation are the same in the two cases. In the cyclometallation reaction certain species coordinated *via* a 'good' donor (*e.g.* N or P) undergo intramolecular metal–carbon bond formation to produce chelate rings. Examples are known where normally very inert saturated carbon centres participate in the ring formation [16]. It seems reasonable to assume that the chelate effect plays an important part in the 'activation' of such otherwise unreactive carbon centres; or, in terms of the concepts presented in the Introduction, the unusual metal–carbon bond formation reaction reflects the compatibility between the organisation of the potential N, C (or P, C) donor chelating agent and the geometrical requirements of the single metal centre. We suggest that the metal–carbon bond formation reactions described above likewise reflect the compatibility between the organisation built into the LPd_2^+ unit and the geometrical requirements of the potential N, C bridging unit.

Experimental

Reaction with Indole

A solution of $LPd_2(CH_3CO_2)$ (0.313 g) and indole (0.241 g) in benzene (7.0 ml) was heated under reflux for 2 hours during which time pale yellow crystals separated. After the mixture had been allowed to cool and stand the crystalline solid was collected, washed with benzene and dried in vacuum at 80 °C. Yield: 0.246 g. The solid could be recrystallised from chlorobenzene but recrystallisation was not necessary.

Reaction with 3-Methylindole

A solution of $LPd_2(CH_3CO_2)$ (0.370 g) and 3-methylindole (0.207 g) in benzene (2.0 ml) was heated under reflux for 2.5 hours. Petroleum ether (b.p. 80–100 °C, 10 ml) was added and the mixture

was evaporated at atmospheric pressure to half the original volume. Further petroleum ether (b.p. 80–100 °C, 10 ml) was added and the mixture again was evaporated to half the original volume. After the mixture had been allowed to cool and stand the microcrystalline solid which separated was collected, washed with petroleum ether (60–80 °C) and dried in vacuum at 80 °C. Yield: 0.356 g. The solid was recrystallised from chloroform–petrol.

Reaction with 3-Hydroxypyridine

A solution of $LPd_2(CH_3CO_2)$ (0.198 g) and 3-hydroxypyridine (0.030 g) in benzene (12 ml) was heated under reflux for 4 hours during which time some pale yellow solid (isomer B) separated from the hot mixture. Isomer B was collected, washed with benzene and dried in vacuum at 80 °C. (Yield of isomer B, 0.049 g). An equal volume of hot methanol was added to the hot filtrate and on cooling the solution deposited yellow crystals of isomer A which were collected, washed with benzene–methanol and dried under vacuum at 80 °C. Yield of isomer A, 0.099 g. The solid could be recrystallised from benzene–methanol but this was unnecessary.

Reaction with 3-Aminopyridine

A solution of $LPd_2(CH_3CO)_2$ (0.105 g) and 3-aminopyridine (0.031 g) in benzene (4 ml) was heated under reflux for 2.5 hours during which time some gummy material separated. The mixture was filtered whilst hot and an equal volume of hot methanol was added to the hot filtrate. On standing at 5 °C the solution deposited orange crystals which were collected, washed with benzene-methanol and dried in vacuum at 80 °C. Yield: 0.048 g. The solid so obtained contained some benzene of crystallisation which was difficult to remove completely after heating in vacuum. Solvent-free material for elemental analysis was obtained by recrystallisation from chloroform–petrol.

Reaction with 1-n-propyliminazole

A solution of $LPd_2(CH_3CO)_2$ (0.103 g) and 1-n-propyliminazole (0.017 g) in benzene (1.0 ml) and methanol (0.2 ml) was heated under reflux for 6 hours. Hot methanol (4 ml) was added and the resulting clear yellow solution upon cooling deposited yellow crystals which were collected, washed with benzene-methanol and dried in vacuum at 78 °C. The material could be recrystallised from benzene–methanol but this was not necessary.

Physical Measurements

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

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References

1 D. Munro, *Chem. In Britain, 13,* 100 (1977).
2 G. Anderegg, *Helv. Chim. Acta, 46,* 2813 (1963).
3 M. Louey, P. D. Nichols and R. Robson, *Inorg. Chim. Acta, 47,* 87 (1981).
4 R. G. Parker and J. D. Roberts, *J. Org. Chem., 35,* 996 (1970).
5 S. Hodgson, undergraduate research project, University of Melbourne.
6 Sadtler Standard Spectra, No. 2216C, published by Sadtler Research Laboratories, Philadelphia.
7 Ref. 6, No. 1486C.
8 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry', 2nd Ed., 1969, Pergamon Press, p. 310.
9 G. S. Reddy, L. Mandell and J. H. Goldstein, *J. Chem. Soc.,* 1414 (1963).
10 G. S. Reddy, R. T. Hobgood and J. H. Goldstein, *J. Am. Chem. Soc., 84,* 336 (1962).
11 R. J. Pugmire, D, M. Grant, L. B. Townsend and R. K. Robins, *J. Am. Chem. Soc., 95,* 2791 (1973).
12 T. M. Harris and J. C. Randall, *Chem. and Ind.,* 1728 (1965).
13 R. J. Sundberg, R. F. Bryan, I. F. Taylor and H. Taube, *J. Am. Chem. Soc., 96,* 381 (1974) and references therein.
14 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem., 17,* 2622 (1978).
15 J. Dehand and M. Pfeffer, *Coord. Chem. Rev., 18,* 327 (1976).
16 S. Hietkamp, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem., 139,* 189 (1977).