Inorganica Chimica Acta, *85* (1984) 199–207

Complexes of Binucleating Ligands. XVII. Some 3-Atom N,C Bridged Palladium(II) Complexes

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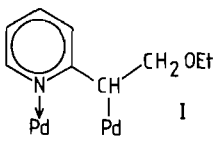
Received September 13, 1983

The acetate-bridged complex, $LPd_2(CH_3CO_2)$, in which L^{3-} is a binucleating ligand, reacts with 2-vinylpyridine in the presence of methanol or ethanol to generate the 3 atom N,C bridged complexes $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OR)$ (R = Me or Et) whose ^1H and ^{13}C nmr spectra indicate the presence in solution of two slowly interconverting forms at room temperature. The ^1H and ^{13}C nmr spectra of two closely related pairs of 3 atom N,C bridged complexes of the form $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot X)$ and LPd_2 $(HN = C(CH_3)\cdot CH\cdot X)$ (where X = $COCH_3$ or $COOCH_3$) show that the complexes with pyridine-containing bridges exist in solution at room temperature in two distinguishable forms whilst the corresponding imine-bridged complexes behave as single species. The existence of two forms of the complexes with pyridine-containing 3 atom N,C bridges, the natures of which are discussed in this paper, appears to be a consequence of steric interaction between the pyridine α hydrogen atom and the closely adjacent oxygen donor of L.

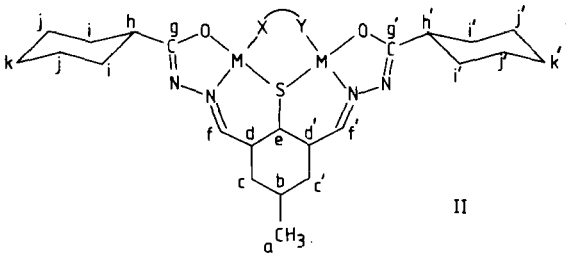
Introduction

One of the aspects of the bridging site chemistry offered by complexes of binucleating [1] ligands which we have chosen to investigate, is the generation of bridging species bound by metal–carbon bonds. The first example of such a system was a binuclear palladium(II) complex incorporating what was intended to be the 3 atom N,C bridging species I, generated at the Pd_2 site by attack of ethanol upon 2-vinylpyridine [2]. However, this complex (and most others derived from the particular binucleating ligand used in that work [2]) was insoluble in all



I

common solvents and the only structural technique that was applicable was i.r. spectroscopy which, in this case, provided very little direct information regarding the nature and coordination mode of the bridging group. The binucleating ligand (hereafter L^{3-}) depicted in the generalised complex II was developed [3] in the hope of circumventing these



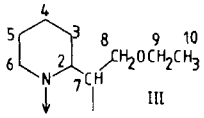
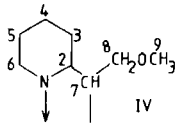
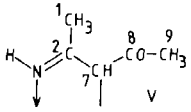
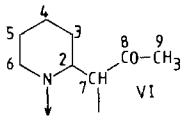
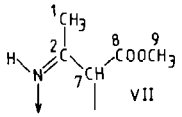
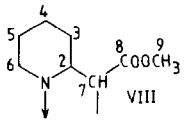
II

solubility problems and does indeed provide a wide range of palladium(II) complexes sufficiently soluble in chloroform to afford ^1H and ^{13}C nmr spectra, which have proved most useful in identifying the bridging mode of a variety of entities introduced at the Pd_2 site, including a number of unusual 2 atom N,C bridging species [4].

The work reported here was concerned initially with the generation of the bridging species I within the Pd_2 complex of L^{3-} which, it was hoped, would be sufficiently soluble to provide useful nmr data. A number of complexes incorporating related 3 atom

0020-1693/84/$3.00

TABLE I. Nmr Data[a] Relating to the Bridging Species Z in LPd_2Z.

Z	^{1}H Nmr		^{13}C Nmr									
			C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
 III	H10, 1.16(tr), (~4/5× 3H) + 1.00(tr), (~1/5× 3H); H9, ~3.5(m), (2H); H8, ~4.0(m), (2H); H7, ~4.4(m), (1H); H5, 6.85(m), (1H); H3 + H4, ~7.6(m), (2H); H6, ~8.6(m), (~4/5 H) + ~8.8(m) (~1/5 H)	Maj.		169.1	123.2	137.3	116.5	150.2	38.8	69.7	65.6	15.3
		Min.		168.5	127.4	137.6	118.0	150.9				15.1(sh)
 IV	H9, 3.36(s), (~4/5× 3H) + 3.20(s), (~1/5× 3H); H8, H7, H5, H4, H3 and H6, as for III	Maj.		168.9	123.0	137.4	116.5	150.3	38.6	71.9	58.1	
		Min.		168.4	127.3	137.7	118.1	151.0			58.4(sh)	
 V	NH, 8.79(s,br) (1H); H7, 4.79(m) (1H); H9, either 2.38(s) (3H) or 2.22(s) (3H); H1, either 2.38, 2.2		30.5	186.7					53.0	200.6	32.4	
 VI	^{1}H nmr at 0 °C: H9, 2.32(s) (~4/5× 3H) + 2.20(s) (~1/5× 3H); H7, 5.27(s) (~4/5 H) + 5.05(s) (~1/5 H); H5, 7.01(m) (1H); H3, H4, H6, *complex*	Maj.		161.5	126.2	139.9[b] 138.9 138.0	119.2	151.4	52.8	203.8	32.2	
		Min.		164.1			118.1		47.1	204.8		
 VII	H1, 2.65(s) (3H); H9, 3.63(s) (3H); H7, 4.40(s) (1H); NH, 8.34(s, br) (1H)		29.0	191.9					40.8[c] 40.7 40.5	173.9	51.0	
 VIII	H9, 3.68 + 3.64(sh), (3H); H7, 4.78(1H); H5, 6.98(m) (1H); H3, H4, H6 complex.	Maj.		164.4	125.4	139.9[d] 138.9 137.9	117.9	150.2	36.3	175.4	51.0	
	^{1}H nmr in $C_6D_5NO_2$: H9, 3.96(s) (~4/5× 3H) + 3.75(s) (~1/5× 3H); H7, 4.68(s) (~4/5 H) + 5.22(s) (~1/5 H)	Min.		162.7	126.5		119.2	151.7				

Maj. and *min.* refer to the two species in equilibrium.
tr = triplet. m = multiplet. s = singlet. br = broad.
[a]Chemical shifts (p.p.m.) downfield of TMS. All in $CDCl_3$ at room temperature except where indicated otherwise. Approximate integrated intensities in ^{1}H spectra are given in brackets. [b]One of the peaks corresponds to C4 and the other two correspond to C_e and $C_{e'}$. [c]One of the three peaks corresponds to C7 and the other two to C_h and $C_{h'}$. [d]One of the three peaks corresponds to C4 and the other two correspond to C_e and $C_{e'}$.

TABLE II. Nmr Data[a] Relating to L.

		H_f, $H_{f'}$	$C_{g,g'}$	$C_{f,f'}$	$C_{c,c'}$	C_b	$C_{d,d'}$	C_e	$C_{h,h'}$	$C_{i,i'}$	$C_{j,j',k,k'}$	C_a
$LPd_2(C_5H_4N{\cdot}CH{\cdot}CH_2OC_2H_5)$	Maj.	8.26(~4/5 H)	185.0	149.8	139.5	135.3	133.8	123.8	41.5	31.3	26.1	20.6
		8.14(~4/5 H)	183.2	147.1	138.3		131.6		40.0	31.1	25.9	
	Min.	8.32(~1/5 H)	184.9 (sh)	147.0 (sh)	139.8	135.1 (sh)	133.7 (sh)		43.1	30.8		
		8.23(~1/5 H) (sh)	183.1 (sh)				131.3		42.1			
$LPd_2(C_5H_4N{\cdot}CH{\cdot}CH_2OCH_3)$	Maj.	8.28(~4/5 H)	185.0	149.7	139.5	135.3	133.9	123.8	41.5	31.2	26.1	20.6
		8.16(~4/5 H)	183.2	147.2	138.3		131.6		40.4			
	Min.	8.32(~1/5 H)	184.9	146.9	139.8	135.4 (sh)	133.7		42.8	30.8		
		8.23(~1/5 H) (sh)	(sh) 183.1 (sh)	(sh)	(sh)		(sh) 131.3 (sh)		42.1			
$LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COCH_3)$		8.24(1H)	184.6	149.1	139.7	135.4	133.2	123.3	41.0	31.3	26.2	20.5
		8.20(1H)	183.9	148.6	139.3		131.8		40.6	31.0		
$LPd_2(C_5H_4N{\cdot}CH{\cdot}COCH_3)$	Maj.	8.25(~4/5 H)[c]	184.8	149.4	139.9[b] 138.9	135.4	133.3	123.6	41.3	31.3	26.1	20.5
		8.13(~4/5 H)	183.6	148.4	138.0		131.7		40.2	31.1		
	Min.	8.24(~1/5 H)[c] (sh) 8.20(~1/5 H)	185.5	149.9		135.1 (sh)	133.0 (sh)		40.8	30.9		
$LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COOCH_3)$		8.26(1H)	185.1	149.4	139.7	135.7	133.7	123.2	40.8[d] 40.7	31.1 30.8	26.0	20.4
		8.15(1H)	183.9	148.3	139.2		131.6		40.5			
$LPd_2(C_5H_4N{\cdot}CH{\cdot}COOCH_3)$	Maj.	8.27	185.2	150.0	139.9[e]	135.8	133.9	123.3	41.0	31.2	26.1	20.5
		8.10	183.6	148.0	138.9 137.9		131.3		40.4			
	Min.	~8.20(sh)							41.7 39.5	30.8		

sh = shoulder. Maj. and Min. refer to the two species in equilibrium.

[a]Chemical shifts (p.p.m.) downfield of TMS. All in $CDCl_3$ at room temperature except where indicated otherwise. For labelling of protons and carbon atoms in L see structure II. Approximate integrated intensities in ^1H spectra are given in brackets. [b]Two of the three peaks correspond to C_e and $C_{e'}$ and the other to C4. [c] ^1H nmr in $CDCl_3$ at 0 °C. [d]Two of the three peaks correspond to C_h and $C_{h'}$ and the other to C7. [e]Two of the peaks correspond to C_e and $C_{e'}$ and the other to C4.

N,C bridges are also described below, which were synthesised and studied in an attempt to answer some stereochemical questions raised by the initial nmr results.

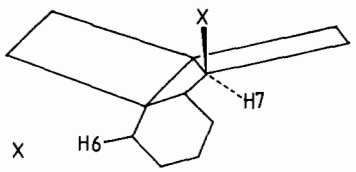
Results and Discussion

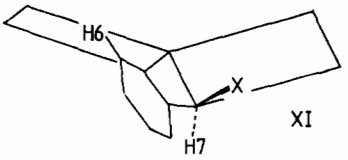
The acetate-bridged complex $LPd_2(CH_3CO_2)$ [3] reacts with 2-vinylpyridine in the presence of ethanol to generate $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OC_2H_5)$. This complex, like the related insoluble complex reported earlier [2] showed in its i.r. spectrum a strong ethereal CO stretching band at 1080 cm^{-1}. The ^1H nmr spectrum was much more complex than expected and only after the same complex spectral details were observed for several separately prepared samples did we reject our suspicion that the products were impure. Some ^1H nmr data (and also some ^{13}C nmr data, discussed later) pertaining to the bridging group in this and related complexes are presented in Table I, where the labelling schemes for protons and carbon atoms within the various bridging systems described in this paper may also be found. Table II presents similar data relating to protons and carbon atoms within L. The ^1H nmr spectrum of $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OC_2H_5)$, together with other data, discussed below, is consistent with the presence in solution at room temperature of two distinguishable forms of the complex in roughly 4:1 proportions, exchanging slowly on the nmr timescale. A very complex two proton multiplet at *ca.* 3.5 ppm was identified as arising from the ethyl methylene group, H9, by double resonance. The terminal protons, H10, appear superimposed on a broad cyclohexyl signal as two sharp overlapping triplets centred at 1.16 (the major) and 1.00 ppm (the minor), which collapsed, upon irradiation at the frequency corresponding to the H9 signal, to two singlets in these positions with intensities in roughly 4:1 proportions. A second complex two proton multiplet centred at *ca.* 4.0 ppm was identified as the methylene group, H8, coupled to the methine group, H7, which appeared as a one proton multiplet centred at *ca.* 4.5 ppm. Although these two signals were not well separated it was possible to demonstrate that the H7 signal, which approximated to two overlapping triplets, collapsed upon careful irradiation at the H8 frequency, to two singlets at 4.47 and 4.35 ppm with intensities in roughly 4:1 proportions respectively. Careful irradiation at the H7 frequency simplified the complex multiplet arising from H8 to a multiplet approximating to an AB quartet, as is consistent with the 'intrinsic inequivalence' [5] of the two H8 protons arising from the attachment of this methylene to a carbon centre carrying three other non-equivalent groups. The signals arising from the pyridine protons H3, H4 and H5 are of no special significance but the presence of two distinguishable species is again indicated by the H6 signal which consists of two approximate doublets with intensities roughly in 4:1 proportions.

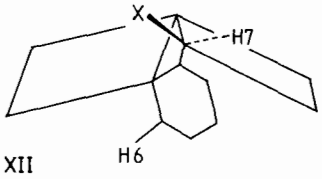
Nmr studies of a wide range of $LPd_2(Z)$ derivatives [3, 4] indicate that when Z is an asymmetric bridging species which renders the two palladium centres inequivalent, this inequivalence is apparent also within L, extending as far as the two 'imine' CH's, H_f and $H_{f'}$ (see labelling of individual protons and carbon atoms of L in structure II) and also the aromatic H_c and $H_{c'}$. In the ^1H nmr spectrum of $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OC_2H_5)$ a pair of singlets of equal intensity at 8.14 and 8.26 ppm can be ascribed to H_f and $H_{f'}$ of the major equilibrium component and a second pair, approximately one quarter as intense as the first, at 8.32 and *ca.* 8.23(sh) ppm correspond to H_f and $H_{f'}$ of the minor component. H_c and $H_{c'}$ appear as an incompletely resolved two proton multiplet at 7.30 ppm with discernible AB quartet structure.

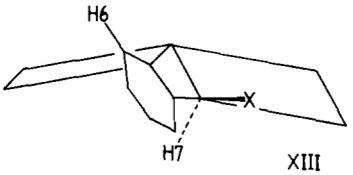
The methyl ether $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OCH_3)$ was synthesised from $LPd_2(CH_3CO_2)$, vinylpyridine and methanol in the hope of shedding further light on the above complexities. Its ^1H nmr spectrum paralleled that of the ethyl ether very closely, indicating again the presence of two relatively slowly interconverting forms in roughly 4:1 proportions. Much the same information with regards protons H8, H7, H6, H_f and $H_{f'}$ and H_c and $H_{c'}$ was provided as in the ethyl case. However, protons of the terminal methyl group, H9 (see structure IV, Table I) give rise to two singlets in roughly 4:1 proportions at 3.36 and 3.20 ppm respectively, with a total integrated intensity corresponding to three protons, in a conveniently unobstructed region of the spectrum, much more suitable for temperature dependence studies than the ethyl signals of the ethyl ether. The ^1H nmr spectrum of the methyl ether was studied as a function of temperature in deuteronitrobenzene solution at 10° intervals in the range 30° to 140 °C. All those individual features referred to above, which suggest the presence at room temperature of two slowly interconverting forms, showed coalescence behaviour in the neighbourhood of 70 °C and then very marked sharpening as the temperature was further increased, appearing as follows at 140 °C: H9, sharp singlet; H_f and $H_{f'}$, each a sharp singlet; H6, a single approx. doublet; H7, an approximate triplet.

The ^{13}C nmr spectra of both the ethyl and methyl ethers (Tables I and II) provide additional support for the presence in solution, in both cases, of two forms in equilibrium, interconverting slowly on the nmr timescale. In particular, many of the major peaks, ascribed to the major equilibrium component, could be seen to have associated with them a smaller peak or shoulder which we take to corres-



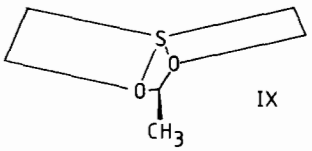






pond to the same carbon atom within the minor component. Assignments of the major peaks in the noise decoupled spectrum of the ethyl ether complex given in Table I and II are based on the off-resonance, the undecoupled and several specific decoupled spectra. Assignments of peaks corresponding to the minor component are tentative only and for some carbon atoms the peak corresponding to the minor component appears, not surprisingly, to be obscurred by that of the major component.

Before considering the possible origin of two distinguishable forms of these complexes in solution it is necessary to discuss some general stereochemical aspects of LPd_2Z complexes. We have previously [2] drawn attention to the marked preference shown by mercaptide centres which bridge two metal centres for a non planar arrangement in which the environment of the sulphur is best described as tetrahedral with a 'stereochemically active' lone pair of electrons occupying one of the tetrahedral positions. This certainly is the case in the crystal of $LPd_2(CH_3CO_2)$ which has been studied by X-ray diffraction [6], in which the bond angles at the sulphur correspond almost exactly to those of a regular tetrahedral arrangement. Framework molecular models indicate that, if the bridging mercaptide centre in L^{3-} generally has this requirement for tetrahedral geometry, then the derived binuclear palladium(II) complexes will inevitably be strained. If the sulphur is made coplanar with the aromatic ring at least one of the ligand side chains has to be bent very significantly out of that plane, thereby disrupting to some extent the conjugation and if both side chains are bent out of that plane it seems both have to be on the same side. Alternatively, if the two side chains are made coplanar with the aromatic ring the sulphur has to be very significantly bent out of that plane. In either case substantial strain is involved. In the crystal structure of $LPd_2(CH_3CO_2)$ both these deformations are apparent, the sulphur atom being located 0.40 Å on one side of the aromatic plane whilst the two side chains are bent out of the plane in the direction opposite to the sulphur, but to different extents. The bridging acetate is skewed relative to the two palladium coordination planes



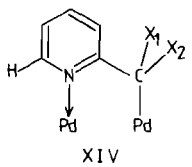
as in IX, such that the plane occupied by the acetate extends below one planar coordination set and above the other. This tendency of a 3 atom bridge to adopt a skewed orientation is clearly apparent in framework molecular models and becomes particularly pronounced when one donor atom within the 3 atom bridge is made a tetrahedral centre (like the carbon donor in the complexes described above). Models of $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot X)$ readily adopt four distinguishable skewed conformations, X–XIII, all of which seem to involve little angle strain compared with intermediate conformations. It is noteworthy that all of these conformations are, in addition, chiral. A feature of all four of these conformations, which is important in the argument which follows, is that the plane of the pyridine ring is well out of coplanarity with the associated palladium coordination plane so that in each case the pyridine α hydrogen, H6, is well above or well below the metal coordination plane.

By manipulation of the models two independent processes can be identified, combinations of which are able to convert any conformer into any other. One such process is inversion at the tetrahedral sulphur centre via a transition state or intermediate planar at sulphur. This process necessitates the two ligand side chains moving from one side of the plane occupied by the aromatic C_6 ring of L to the other. However, it is significant that during the sulphur inversion process the pyridine α hydrogen, H6, remains on the same side of the coordination plane

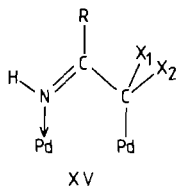
of its associated palladium, *e.g.* in X ⇄ XII, H6 remains 'below' its associated palladium coordination plane and in XI ⇄ XIII H6 remains 'above' the associated palladium coordination plane. The second process is what we shall call the 'bridge twist' process, illustrated by X ⇄ XI and XII ⇄ XIII. A crucial feature of this process is the twisting of the pyridine nucleus around the Pd–N axis through an angle of at least 90° so that H6 passes from one side of the associated palladium coordination plane to the other. The bridge twist is accompanied by only minor rearrangement within L, each individual side chain being bent out of the plane of the aromatic ring of L to slightly different extents (but in the same direction) before and after the twist.

The nmr data discussed above suggest the presence of two, not four, forms in equilibrium at room temperature. We shall present evidence below which supports the proposal that the two distinguishable forms arise because one of the above two processes, namely sulphur inversion, is rapid and the other, the bridge twist, is relatively hindered; in other words we propose that one of the forms observable by nmr at room temperature corresponds to X and XII rapidly exchanging and the other form to XI and XIII in rapid exchange. When models are manually subjected to the bridge twist process it is very apparent that the α-hydrogen atom, H6, of the pyridine unit has to squeeze past the adjacent coordinated oxygen atom at a very close distance, considerably less, it appears, than the sum of the van der Waals'radii. We believe this is the reason why the bridge twist process is relatively slow. On the other hand, we have demonstrated elsewhere [3] that in one particular case at least, namely $LPd_2((C_6H_5\text{-}CH_2)_2NO)$ where the 2 atom N,O bridging species is the conjugate base of N,N-dibenzylhydroxylamine, the sulphur inversion is rapid at room temperature on the nmr timescale and we have no reason to suspect that this is not generally true of $LPd_2(Z)$ complexes.

In an attempt to obtain further evidence for the importance (or otherwise) of this interaction between H6 and the adjacent oxygen atom we have tried to generate closely analogous pairs of complexes of the



XIV

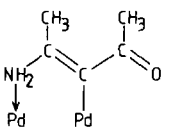


XV

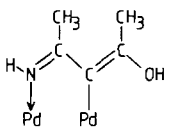
type XIV and XV, in which, as far as possible, all features of the bridging species are kept common, except that in one case, XV, the interaction in question has been eliminated.

We have been unable to generate XIV, $X_1 = X_2 = H$, from reaction between $LPd_2(CH_3CO_2)$ and either α picoline (with or without added base) or the pre-formed conjugate base, $C_5H_4N{\cdot}CH^{2-}$, as its lithium derivative; indeed all attempts at bridge substitutions using pre-formed carbanionic entering groups (*e.g.* Grignard reagents, alkyl lithiums) appear to lead to rapid breakdown of the complex, the nature of which we have not identified. However, bridge substitution upon $LPd_2(CH_3CO_2)$ in which the outgoing acetate serves as a base to deprotonate the incoming species appears to afford ready access to systems XIV and XV provided X_1 or X_2 has electron withdrawing properties. In this way we have successfully generated XIV/XV pairs in which $X_1 = H$, $X_2 = COCH_3$ and $X_1 = H$, $X_2 = COOCH_3$.

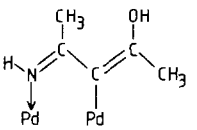
The mono-imine of acetylacetone, one tautomer of which is $CH_3CO{\cdot}CH{=}C(CH_3)NH_2$, reacts with $LPd_2(CH_3CO_2)$ in refluxing benzene-ethanol to yield $LPd_2(C_5H_8NO)$. However, some L_2Pd_3 is also formed under these conditions, the formation of this by-product always being a risk when a 'good' ligand for palladium(II) (in this case a chelating ligand) is provided as a potential bridging species [3]. A cleaner synthetic method is the room temperature reaction in chloroform in the presence of aqueous carbonate. All attempts to introduce the N-phenyl analogue of this bridging species via N-phenyl-acetylacetone-imine under similar and other conditions have failed, presumably for steric reasons. The acetylacetoneimine-derived complex can be obtained solvent-free by recrystallisation from chloroform–hexane or as a benzene solvate, in which the benzene is tenaciously held, by recrystallisation from benzene–petrol. The i.r. spectra of these two solids showed ν_{NH} at 3200 cm^{-1} and most features of the spectra were identical; however there were significant differences in the pattern of bands at 1670, 1655 and 1645 cm^{-1}. Any one of the tautomeric bridging modes, XVI–XVIII, at first sight would appear



XVI



XVII



XVIII

a feasible alternative to the desired bridging mode V (Table I). The variability of the i.r. spectra in the 1600–1700 cm^{-1} range suggests some possible complexity with regard to these tautomeric alternatives in the solid state but nmr data leave no doubt that the only significant complex in solution involves bridging mode V (Table I). In the ^1H nmr spectrum the NH appears as a broad one proton signal at 8.79

ppm and the coordinated methine, H7, as a somewhat broadened one proton signal at 4.79 ppm. Double resonance reveals that this broadening of the H7 signal arises from coupling to both the NH and the methyl protons, H1, for irradiation of the NH leads to marked sharpening, whilst irradiation of the methyl (H1) produces a doublet (coupling constant 1.2 Hz). A ketone carbon atom is apparent at 200.6 ppm in the ^{13}C nmr spectrum which was assigned by off-resonance. All other features of both the ^{1}H and ^{13}C nmr spectra (Tables I and II) are entirely consistent with the formulation $LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COCH_3)$ as in V. In particular, no feature of either the ^{1}H spectrum or the ^{13}C spectrum suggests the presence of more than one form of the complex in solution.

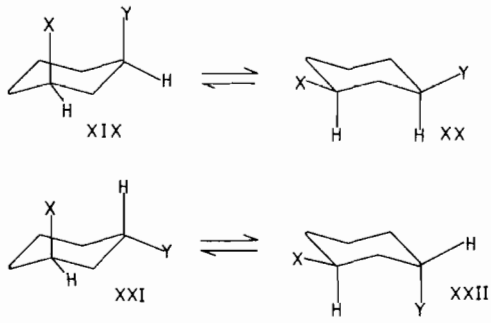
The second member of the desired XIV/XV pair with X_1 = H and X_2 = $COCH_3$, namely $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COCH_3)$, was obtained by reaction at room temperature of $LPd_2(CH_3CO_2)$ with (2-pyridyl)-acetone in chloroform in the presence of aqueous carbonate. As in the case of the acetylacetoneimine-derived complex above, the KBr disc i.r. spectrum showed the ketonic carbonyl stretching frequency below 1700 cm^{-1}, with bands at 1670, 1660 and 1650 cm^{-1}. The ^{1}H and ^{13}C nmr spectra of $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COCH_3)$ (Tables I and II) show many features which parallel those observed for the vinyl pyridine-derived complexes, $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}CH_2OR)$, (but which are in marked contrast to those observed for $LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COCH_3)$), indicating the presence of two distinguishable forms in solution at room temperature, in roughly 4:1 proportions, exchanging slowly on the nmr timescale. The ^{1}H nmr spectrum of $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COCH_3)$ in $CDCl_3$ at 0 °C shows a) the ketonic methyl protons, H9, as two well resolved sharp singlets at 2.32 (the major) and 2.20 ppm (the minor), b) the coordinated CH, H7, as two sharp singlets at 5.27 (the major) and 5.05 ppm (the minor) and c) the imine protons, H_f, $H_{f'}$, as two pairs of singlets, the major pair at 8.25 and 8.13 ppm and the minor pair at 8.24 and 8.20 ppm. The temperature dependence of the ^{1}H nmr spectrum was studied at 10° intervals in $CDCl_3$ solution in the range 0–40 °C and in deuteronitrobenzene solution in the range 30–100 °C. The individual spectral features described above, indicating the presence of two slowly exchanging forms at 0 °C, coalesced at approximately 50 °C, the onset of this coalescence being apparent in the room temperature spectrum which was significantly broadened in the appropriate regions. At 100 °C these features appeared as follows: H9 (ketonic methyl), sharp singlet; H7 (coordinated CH), sharp singlet; H_f and $H_{f'}$, each a sharp singlet. Peaks in the ^{13}C nmr spectrum of $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COCH_3)$ (Tables I and II) were assigned by off resonance studies. The general features of the spectrum closely paralleled those of the ^{13}C spectra of the $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}CH_2OR)$ derivatives, with many major peaks showing an associated minor peak or shoulder approximately one quarter as intense, ascribed to the minor equilibrium component. Assignment of resonances to particular carbon atoms in the minor component are tentative only.

The complex with bridging group XV where X_1 = H, X_2 = $COOCH_3$ and R = CH_3 was obtained from reaction of $LPd_2(CH_3CO_2)$ with methyl β-aminocrotonate in chloroform at room temperature in the presence of aqueous carbonate. In contrast to this preparation, all attempts to generate XV in which X_1 = X_2 = $COOC_2H_5$ and R = H from reactions of $LPd_2(CH_3CO_2)$ with $NH_2CH{=}C(COOC_2H_5)_2$ under similar and other conditions were unsuccessful, presumably for steric reasons. The solid state i.r. spectrum (KBr disc) of $LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COOCH_3)$ shows bands associated with the ester group at 1730 cm^{-1} ($\nu_{C=O}$) and 1150 cm^{-1}. All aspects of the ^{1}H and ^{13}C nmr spectra of this complex (Tables I and II) are consistent with bridging mode VII (Table I) and eliminate the various tautomeric alternatives analogous to those discussed earlier for the acetylacetoneimine-derived complex. In the ^{1}H nmr spectrum of $LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COOCH_3)$ the signal corresponding to H7 of the coordinated methine appears sharper than that in the spectrum of $LPd_2(HN{=}C(CH_3){\cdot}CH{\cdot}COCH_3)$ where significant coupling to both NH and the methyl protons, H1, was demonstrable. As in the case of the acetylacetoneimine-derived complex there was no evidence whatsoever for the presence in solution of more than one form of the complex.

The incorporation of the bridging group XIV, with X_1 = H and X_2 = $COOCH_3$, by the reaction of $LPd_2(CH_3CO_2)$ with methyl 2-pyridylacetate under the usual conditions in chloroform at room temperature in the presence of aqueous carbonate was very much slower than analogous bridge substitutions described above. A more convenient synthetic procedure was to use an excess of the ester in refluxing benzene–methanol. $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COOCH_3)$ shows, in its KBr disc i.r. spectrum, ester derived bands at 1720 cm^{-1} ($\nu_{C=O}$) and 1125 cm^{-1}. The presence of two relatively slowly exchanging forms of the complex in $CDCl_3$ solution at room temperature was less immediately apparent (but nevertheless was undoubtedly the case) in the ^{1}H nmr spectrum of $LPd_2(2\text{-}C_5H_4N{\cdot}CH{\cdot}COOCH_3)$ than in the spectra of the other complexes with pyridine-derived bridging groups described above. Thus there appeared to be only one sort of coordinated methine, H7 (structure VIII, Table I) which gave rise to a one proton singlet at 4.78 ppm and only close inspection revealed the presence of a shoulder (corresponding to the minor component

of the equilibrium mixture) on the peak corresponding to the ester methyl group H9. A clearly defined shoulder on one of the pair of singlets arising from H_f and $H_{f'}$ of the major component can be ascribed to H_f or $H_{f'}$ of the minor component. The ^{13}C nmr spectrum was assigned by off resonance (Tabels I and II) and provides very similar support for the presence of two distinguishable forms as was obtained for the other complexes with pyridine-derived 3 atom bridges. The ^1H nmr spectrum in deuteronitrobenzene at 20 °C reveals the presence of two forms undergoing slow exchange much more clearly than does the $CDCl_3$ spectrum. In the $C_6D_5NO_2$ spectrum the proton of the coordinated methine, H7, appears as two very well separated singlets, the major at 4.68 ppm and the other at 5.22 ppm and the ester methyl protons, H9, as two singlets, the major at 3.96 ppm and the other at 3.75 ppm. Presumably the coordinated methine protons, H7, of the two forms present in $CDCl_3$ coincidentally have the same chemical shift. The temperature dependence of the ^1H nmr spectrum of $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot COOCH_3)$ in deuteronitrobenzene was studied at 10 °C intervals in the range 20–120 °C. Coalescence of the pairs of singlets corresponding to H7 and H9 took place in the vicinity of 60 °C and at 120 °C both H7 and H9 gave rise to very sharp singlets.

The contrasting nmr evidence for the above XIV/XV pairs together with that relating to the ether derivatives, $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OR)$, provides very strong support for the proposal that in complexes with pyridine-derived 3 atom N,C bridges of the type XIV the bridge twist processes, X ⇄ XI and XII ⇄ XIII, are slow at room temperature on the nmr timescale because they require that, as the pyridine ring twists around the Pd–N bond, the pyridine α hydrogen atom, H6, passes from one side of the associated palladium coordination plane to the other and in doing so it has to squeeze past the very closely adjacent oxygen donor atom. Thus, one of the forms observable at room temperature corresponds to the pair of conformers, X ⇄ XII, rapidly exchanging by the sulphur inversion process, which together could loosely be described as the syn configuration with respect to protons H6 and H7 and the other form corresponds to the rapidly exchanging pair of conformers, XI ⇄ XIII, which could be said to have the anti configuration with respect to these two protons. By contrast, both the bridge twist and the sulphur inversion are rapid in systems of the type XV and in this case the one observed form corresponds to all four conformers rapidly interchanging. The inter-relationship between the four conformers, X–XIII, parallels that between the four conformers of disubstituted cyclohexanes, *e.g.* the 1,3-disubstituted cyclohexane conformers, XIX–XXII, which similarly fall into two pairs; the rapidly exchanging pair, XIX ⇄ XX, constitutes the *cis*



configuration and the pair, XXI ⇄ XXII, the *trans* configuration. However, the energy barrier separating the *cis* and *trans* disubstituted cyclohexane configurations is much higher than that separating the *syn* and *anti* configurations of the complexes above.

Experimental

$LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OR)$, R = Me or Et

A mixture of $LPd_2(CH_3CO_2)$ (0.20 g) and 2-vinylpyridine (0.075 g) in the appropriate alcohol, ROH (R = Me or Et) (5 ml) and tetrahydrofuran (1 ml) was stirred vigorously at room temperature for 2 days. The suspended yellow product was collected and recrystallised from dichloromethane and the appropriate alcohol to give pale yellow needles of $LPd_2(2\text{-}C_5H_4N\cdot CH\cdot CH_2OR)$ which were dried at 80 °C under vacuum. Yields of recrystallised material, Et ether, 0.155 g; Me ether, 0.152 g. *Anal.* Found for Me ether: C, 48.2; H, 5.3; N, 8.9; S, 3.9; Pd, 27.6. Calcd. for $C_{31}H_{39}N_5O_3SPd_2$: C, 48.1; H, 5.1; N, 9.0; S, 4.1; Pd, 27.5. Found for Et ether: C, 48.6; H, 5.3; N, 8.8; S, 4.5; Pd, 26.5. Calcd. for $C_{32}H_{41}N_5O_3SPd_2$: C, 48.7; H, 5.2; N, 8.9; S, 4.1; Pd, 27.0.

$LPd_2(HN{=}C(CH_3)\cdot CH\cdot COCH_3)$

A mixture of $LPd_2(CH_3CO_2)$ (0.248 g) and acetylacetoneimine [7] (0.038 g) in chloroform (6 ml) was stirred vigorously with saturated aqueous sodium carbonate (1 ml) at room temperature for 2 days. The two phases were separated and the aqueous phase was washed with chloroform (10 ml). The combined chloroform layers were dried over sodium sulphate and the filtrate obtained after filtration of the sodium sulphate was evaporated under vacuum. The residue was recrystallised from chloroform–hexane and dried under vacuum at 80 °C. Yield, 0.237 g, *Anal.* Found: C, 45.7; H, 5.4; N, 9.3; S, 4.1; Pd, 28.6. Calcd. for $C_{28}H_{37}N_5O_3SPd_2$: C, 45.6; H, 5.1; N, 9.5; S, 4.3; Pd, 28.9. $LPd_2(HN(=C(CH_3)\cdot CH\cdot COCH_3)$ could be recrystallised from benzene–petrol as a hemi-benzene solvate in which the benzene was tenaciously held even after drying at 80 °C in vacuum.

Anal. Found: C, 48.0; H, 5.2; N, 9.0; S, 4.2; Pd, 27.0. Calcd. for $C_{31}H_{40}N_5O_3SPd_2$: C, 47.9; H, 5.2; N, 9.0; S, 4.1; Pd, 27.5.

$LPd_2(2\text{-}C_5H_4N\cdot CH\cdot COCH_3)$

$LPd_2(CH_3CO_2)$ (0.30 g) and (2-pyridyl)acetone [8] (0.068 g) in chloroform (9 ml) was stirred vigorously at room temperature with saturated aqueous potassium carbonate (1 ml) 18 hr. The two layers were separated and the aqueous phase extracted with chloroform (10 ml). The combined chloroform layers were dried over sodium sulphate. The sodium sulphate was removed by filtration and the filtrate was evaporated to small volume at atmospheric pressure. Boiling methanol (12 ml) was added to the hot chloroform solution which, upon being cooled, deposited fine yellow needles, which were collected and dried in vacuum at 80 °C. Yield, 0.316 g. *Anal.* Found: C, 47.9; H, 4.5; N, 9.3; S, 3.9; Pd, 27.1. Calcd. for $C_{31}H_{37}N_5O_3SPd_2$: C, 48.2; H, 4.8; N, 9.1; S, 4.1; Pd, 27.6.

$LPd_2(HN{=}C(CH_3)\cdot CH\cdot COOCH_3)$

A mixture of $LPd_2(CH_3CO_2)$ (0.200 g) and methyl β-aminocrotonate (0.033 g) (prepared by procedure analogous to Steck's preparation of the ethyl ester [9]) in chloroform (5 ml) was stirred vigorously with saturated aqueous potassium carbonate (1 ml) at room temperature for 2 days. The two layers were separated and the aqueous phase extracted with chloroform (10 ml). The combined chloroform layers were dried over sodium sulphate. The chloroform filtrate obtained by filtration of the sodium sulphate was evaporated to small volume at atmospheric pressure and boiling 100/120 °C petrol was added. Upon being cooled the solution deposited $LPd_2(HN{=}C(CH_3)\cdot CH\cdot COOCH_3)$ as fine yellow needles, which were collected, washed with chloroform-petrol and were dried in vacuum at 80 °C. Yield, 0.156 g. *Anal.* Found: C, 44.4; H, 4.9; N, 9.3; S, 4.2; Pd, 27.9. Calcd. for $C_{28}H_{37}N_5O_4SPd_2$: C, 44.7; H, 5.0; N, 9.3; S, 4.3; Pd, 28.3.

$LPd_2(2\text{-}C_5H_4N\cdot CH\cdot COOCH_3)$

A solution of methyl(2-pyridyl)acetate (0.49 g) in boiling methanol (3 ml) was added to a solution of $LPd_2(CH_3CO_2)$ (0.240 g) in boiling benzene (2 ml) and the resulting solution was heated under reflux for 1.5 hr. The solvents were removed under vacuum and the residue, dissolved in chloroform (10 ml), was extracted with aqueous potassium hydrogen sulphate, then washed with water, then aqueous sodium bicarbonate. After being dried over sodium sulphate, which was then filtered off, the chloroform solution was evaporated under vacuum. The residue was recrystallised from chloroform –100/120 °C petrol and was dried under vacuum at 80 °C. Yield, 0.22 g. *Anal.* Found: C, 47.4; H 4,8; N, 8.8; S, 4.2; Pd, 26.7. Calcd. for $C_{31}H_{37}N_5O_4SPd_2$: C, 47.2; H, 4.7; N, 8.9; S, 4.1; Pd, 27.0.

Physical Measurements

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

Acknowledgements

We are grateful to the Australian Research Grants Committee for a maintenance grant.

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