Inorganica Chimica Acta, 47 (1980) 87–96

Complexes of Binucleating Ligands. XIV. Some Chloroform-Soluble Palladium(II) Complexes

M. LOUEY, P. D. NICHOLS and R. ROBSON

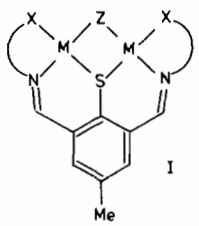
Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia

Received June 3, 1980

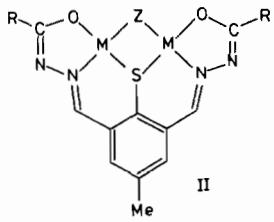
A series of chloroform-soluble complexes of general formulation $LPd_2(Z)$ is reported, where L^{3-} is a new binucleating ligand bearing a bridging thiophenoxide and solubility-enhancing cyclohexyl side chain substituents and where Z^- represents a range of mono anionic bridging units derived from the following protonic acids by deprotonation: formic acid, acetic acid, propionic acid, benzamide, maleimide, benzamidine, urea, 2-hydroxypyridine, 2-aminopyridine, N,N'-diphenyltriazine and its di-para-nitro derivative, pyrazole, acetone-oxime, cyclohexanone-oxime, N,N-dibenzylhydroxylamine, nitrous acid, hydrazoic acid and methanol. ^1H and ^{13}C NMR spectra were generally observable and provided useful structural information, e.g. the bridging nitrite in $LPd_2(NO_2)$ was shown to be present in the two atom N,O bridging mode rather than the three atom O,O bridging mode and $LPd_2((CH_3)_2CNO)$ was shown to contain the acetone-oxime anion in the two atom, N,O bridging mode rather than the C,N two atom or C,O three atom modes. ^1H and ^{13}C NMR spectra of the maleimide-derived complex $LPd_2(C_4H_2NO_2)$ indicated an N,O three atom bridge with inequivalent alkene protons which became equivalent by exchange upon addition of DMSO, indicating that the LPd_2^+ unit is capable of incorporating at the normally bridging site two independent species as bulky as the maleimide anion and DMSO; such information has relevance to the potentiality of LM_2 systems for promoting intramolecular reactions at the binuclear site.

Introduction

A series of binuclear complexes of the type I was reported recently [1], in which M = Pd(II) and the side chains, $\widehat{NX}$ = ortho $N{\cdot}C_6H_4O^-$. Members of this series are represented below as $L'Pd_2(Z)$. The intention of these exploratory studies was to lay the foundations upon which could be built procedures for the generation of complexes containing a wide range of pairs of soft metal centres. Such complexes are of interest because of the possibilities they



I



II

offer for new types of reactivity at bridging sites such as that occupied by Z in I.

Although it was possible to isolate complexes incorporating a variety of species at the bridging site of the $L'Pd_2^+$ unit, work with this particular system was severely hindered by the general insolubility of the complexes. Efforts to generate related complexes showing better solubilities in organic solvents, using the side chain $\widehat{NX}$ = $N{-}N{=}C(SC_8H_{17})S^-$, were successful with M = Ni(II) and Cu(II), but with Pd(II), a cation more relevant to our long term objectives, the binucleating ligand had a pronounced tendency to bind more than two metal centres [2]. This undesirable behaviour, no evidence for which was found with the above ligand L', was ascribed to the presence of the terminal sulphur functions. The present report is concerned with attempts to produce complexes of the type I with side chains offering scope for the ready introduction of a variety of solubility-enhancing substituents and carrying terminal oxygen donors, in the hope of avoiding the above-mentioned problems presumed to be associated with sulphur termini. With these considerations in mind, systems of the type II, based on acyl hydrazide side chains, were chosen for study.

Results and Discussion

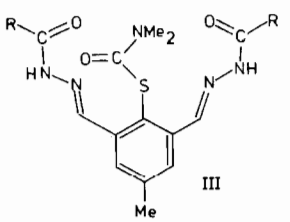
Initial approaches to systems of the type II were made with R = C_6H_5 mainly for the purpose of checking the binucleating capacity of the donor system rather than in the expectation of useful solubilities. Benzoyl hydrazine readily condensed with 2-(N,N-dimethylthiocarbamato)-5-methyliso-

TABLE 1. Analytical Data.

	%C		%H		%N		%S		%Metal	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$L''Cu_2(C_3H_3N_2)$[a]	51.4	51.1	3.3	3.3	13.8	13.7	5.3	5.4	20.9	20.0
$L''Ni_2(C_3H_3N_2)$[a]	52.2	52.0	3.3	3.3	14.1	14.0	5.4	5.4	19.6	18.9
$L''Pd_2(CH_3CO_2)$	43.8	43.5	2.9	3.2	8.2	8.0	4.7	4.4		
III ($R = C_6H_{11}$)	62.5	62.1	7.5	7.6	14.1	13.9	6.4	6.5		
$LNi_2(C_3H_3N_2)$[a]	51.1	51.2	5.3	5.3	13.8	13.3	5.3	5.2	19.3	18.3
$LPd_2(HCO_2)$	42.1	42.5	4.4	4.5	8.2	8.0	4.7	4.6	31.1	30.9
$LPd_2(CH_3CO_2)$	43.0	43.1	4.6	4.6	8.0	8.0	4.6	4.8	30.5	30.9
$LPd_2(C_2H_5CO_2)$	43.9	43.6	4.8	4.7	7.9	8.0	4.5	4.4	29.9	29.6
$LPd_2(C_6H_5 \cdot CONH)$	47.5	47.5	4.6	4.5	9.2	9.2	4.2	4.0	28.0	28.3
$LPd_2(C_6H_5 \cdot C(NH)_2)$	47.6	47.3	4.8	4.7	11.1	10.9	4.2	4.0	28.1	29.0
$LPd_2(CN_2OH_3)$[b]	41.4	41.7	4.5	4.5	12.1	11.5	4.6	4.3	30.1	31.0
$LPd_2(C_5H_4N \cdot O) \cdot C_6H_6$[c]	50.4	50.0	4.8	4.8	8.6	8.5	4.0	3.9	26.3	26.6
$LPd_2(C_5H_4N \cdot NH) \cdot C_6H_6$[d]	50.4	50.0	5.0	4.7	10.4	10.2	4.0	4.0	26.3	25.8
$LPd_2((C_6H_5)_2N_3)$	50.4	50.2	4.7	4.7	11.8	12.0	3.8	3.8	25.5	24.4
$LPd_2((p\text{-}NO_2 \cdot C_6H_4)_2N_3)$	45.4	45.6	4.0	4.1	13.6	13.3	3.5	3.8	23.1	23.0
$LPd_2(C_3H_3N_2)$	44.3	44.6	4.6	4.7	11.9	11.6	4.5	4.7	30.2	29.9
$LPd_2((C_6H_5CH_2)_2NO)$	52.2	52.2	5.1	5.1	8.2	8.3	3.8	3.6	25.1	25.1
$LPd_2((CH_3)_2CNO)$[e]	43.9	44.1	5.0	4.8	9.8	9.8	4.5	4.4	30.0	29.6
$LPd_2((C_6H_{10})NO)$[f]	46.4	46.1	5.2	5.2	9.3	9.3	4.3	4.0	28.4	28.8
$LPd_2(NO_2)$	40.3	40.1	4.3	4.3	10.2	10.1	4.7	4.4	31.2	31.0
$LPd_2(N_3)$	40.6	40.5	4.3	4.5	14.4	14.4	4.7	4.8	31.3	30.7
$LPd_2(CH_3O)$	43.1	42.7	4.8	4.6	8.4	8.3	4.8	4.6	31.8	31.5
$LPd_2(C_4H_2NO_2) \cdot C_6H_6$[g]	48.7	48.8	4.6	4.9	8.6	8.7	4.0	4.1	26.2	27.0
L_2Pd_3	47.2	46.8	5.0	4.8	9.6	9.5	5.5	5.3	27.3	26.9
$(LH)Pd_2Cl_2 \cdot DMF$[h]	39.9	39.2	4.8	4.6	8.9	8.5	4.1	4.1	27.2	27.0
$(LH)Pd_2Cl_2$[i]	38.9	39.1	4.3	4.1	7.9	7.4	4.5	4.6	30.0	29.6

[a] $C_3H_3N_2^-$ = pyrazolate anion. [b] $CN_2OH_3^-$ = conjugate base of urea. [c] $C_5H_4NO^-$ = conjugate base of 2-hydroxypyridine. [d] $C_5H_4N \cdot NH^-$ = conjugate base of 2-aminopyridine. [e] $(CH_3)_2CNO^-$ = conjugate base of acetone-oxime. [f] $(C_6H_{10})CNO^-$ = conjugate base of cyclohexanone-oxime. [g] $C_4H_2NO_2^-$ = conjugate base of maleimide. [h] %Cl: Calcd.: 6.1; Found: 6.9. [i] %Cl: Calcd.: 10.0; Found: 9.9.

phthalaldehyde to give III ($R = C_6H_5$) which, in turn, by reaction in DMF at approximately 90 °C with the



III

appropriate metal salt and a source of bridging species, yielded complexes of the type II in which M = Cu(II) or Ni(II) and Z^- = pyrazolate anion or M = Pd(II) and Z^- = acetate, represented respectively as $L''Cu_2(C_3H_3N_2)$, $L''Ni_2(C_3H_3N_2)$ and $L''Pd_2(CH_3CO_2)$. These complexes showed only marginal solubility in common solvents.

The ligand precursor III with R = n-C_8H_{17} was obtained similarly but attempts to produce complexes of the type II ($R = C_8H_{17}$) gave only gummy materials which were, however, very soluble in chloroform. The difficulty encountered in isolating these complexes in crystalline form probably stems from the disordered C_8 chains. Systems incorporating the somewhat more ordered side chain substituent, R = cyclohexyl, appear to offer a workable compromise giving complexes, hereafter $L(M(II))_2(Z)$, which are both readily crystallisable and sufficiently soluble in solvents such as chloroform and benzene to allow solution studies. The ligand precursor III (R = cyclo-C_6H_{11}) was obtained by condensation of cyclohexane carboxylic acid hydra-

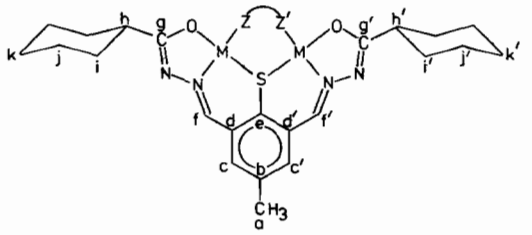


Fig. 1. Labelling of carbon centres in binucleating ligand.

zide, $C_6H_{11}\cdot CO\cdot NH\cdot NH_2$, and 2-(N,N-dimethylthiocarbamato)-5-methylisophthalaldehyde. Reaction of this precursor with nickel(II) acetate and pyrazole in DMF gave crystalline $LNi_2(C_3H_3N_2)$ which showed encouraging solubility in chloroform.

Reaction of III (R = cyclo-C_6H_{11}) with palladium(II) acetate in chloroform gave $LPd_2(CH_3CO_2)$ in good yield and this readily underwent a number of bridge substitution reactions, providing thereby a convenient starting material for the preparation of a range of complexes, $LPd_2(Z)$. Complexes were isolated in which Z^- = the anionic conjugate bases of the following protonic acids: formic acid, acetic acid, propionic acid, benzamide, maleimide, benzamidine, urea, 2-hydroxypyridine, 2-aminopyridine, N,N'-diphenyltriazine and its di-*para*-nitro derivative, pyrazole, acetone-oxime, cyclohexanone-oxime, N,N-dibenzylhydroxylamine, nitrous acid, hydrazoic acid and methanol. Analytical data are presented in Table I.

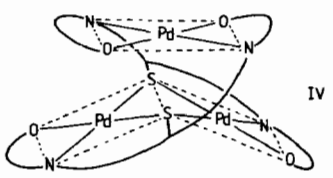
Attempts to replace the acetate in $LPd_2(CH_3CO_2)$ by novel N,C donor bridging species derived from amines such as allylamine and benzylamine gave an amine-free product of formulation L_2Pd_3. It was subsequently discovered that several 'good' donors for palladium(II) (*e.g.* primary amines in general, ammonia, NO_2^-, N_3^-, pyridine and substituted derivatives) with $LPd_2(CH_3CO_2)$ gave L_2Pd_3, at least in part. Fortunately L_2Pd_3 was characterised by strong bands in the IR spectrum (1620, 1170, 1190 cm^{-1}) not present in the common IR pattern observed for $LPd_2(Z)$ derivatives in general, so that it was readily apparent when L_2Pd_3 formation was a complication in the preparation of certain $LPd_2(Z)$ complexes. NMR data and a possible structure for L_2Pd_3 are discussed below.

Reaction of III (R = cyclo-C_6H_{11}) with $PdCl_2(C_6H_5CN)_2$ in DMF in the absence of added base gave a complex of the S-deprotected but incompletely deprotonated ligand $(LH)^{2-}$, namely $(LH)Pd_2Cl_2$, which showed $\nu_{NH(st)}$ of the protonated side arm at 3120 cm^{-1}.

With only one or two exceptions the $LPd_2(Z)$ complexes were sufficiently soluble in chloroform to allow the observation of ^1H and ^{13}C NMR spectra. In the case of $LPd_2((CH_3)_2CNO)$, in which the bridging group is the conjugate base of acetone-oxime, all the lines in the noise-decoupled ^{13}C NMR spectrum were assigned by consideration of a combination of the off-resonance decoupled spectrum, several specific proton decoupled spectra and the undecoupled spectrum. The noise-decoupled ^{13}C spectrum of the maleimide derived complex, $LPd_2(C_4H_2NO_2)$, was assigned by off-resonance and specific decoupling and that of $LPd_2(C_2H_5CO_2)$ by off resonance decoupling. Lines in all other ^{13}C spectra were satisfactorily assigned empirically by comparison with these three spectra. ^1H and ^{13}C NMR data relating to the binucleating ligand component of the complexes are presented in Table II. The carbon atoms of L^{3-} are labelled as in Fig. 1 and directly attached protons are labelled with the same subscripts, *e.g.* the aromatic protons of L^{3-} are labelled H_c and $H_{c'}$. NMR data relating to the bridging component, Z, in $LPd_2(Z)$ are presented in Table III.

In those cases where the two palladium centres within the binuclear unit were rendered inequivalent by attachment to bridging units carrying two distinguishable donors (Z and Z' in Fig. 1) the inequivalence of the two halves of L^{3-} was apparent in both the ^1H and the ^{13}C NMR spectra, generally extending as far as carbons c and c', hydrogens c and c' and carbons i and i'. Thus, in such cases, in the ^1H spectra two separate 'imine' resonances (H_f and $H_{f'}$) were apparent and the aromatic resonances (H_c and $H_{c'}$) appeared broadened, sometimes showing discernible quartet structure, whilst in the ^{13}C spectra a single line could be seen for each of the carbons, c, c', d, d', f, f', g, g', h, h', and sometimes i and i'. By contrast complexes containing bridging species with two equivalent donor centres showed a single resonance for the two H_f protons, a single resonance for the two H_c protons and single lines for the pairs of carbons of the type c, d, f, g, h and i.

An example of extreme side chain inequivalence is provided by L_2Pd_3 (see C_g and $C_{g'}$ and C_f and $C_{f'}$ in Table II). The molecular weight of this material observed by osmometry in chloroform (1150) was close to that expected for L_2Pd_3 (1170). Molecular models indicate that the arrangement IV, in which the two ligand units are equivalent but in which the two side chains of a given L^{3-} unit are in very differ-



IV

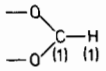
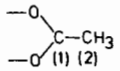
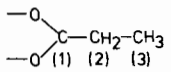
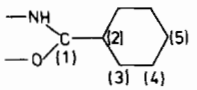
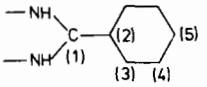
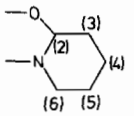
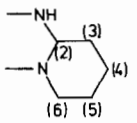
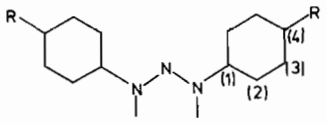
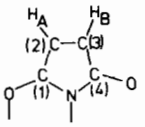
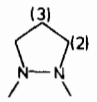
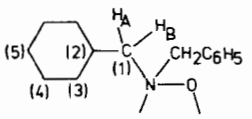
ent environments, can be achieved without undue strain. We have been unable to imagine any other way in which the two L^{3-} and the three Pd^{2+} components could be realistically assembled.

TABLE II. NMR Data[a] Relating to the Binucleating Ligand Component (see Fig. 1 for labelling of atoms).

	H_f	H_c	C_g	C_f	C_c	C_b	C_d	C_e	C_h	C_i	$C_{j,k}$	C_a
$LPd_2(HCO_2)$	8.05	7.45	183.9	149.5	140.3	136.8	131.9	120.9	40.1	31.1	26.1	20.5
											25.8	
$LPd_2(CH_3CO_2)$	8.04	7.42	184.0	149.5	140.1	136.8	132.0	–	40.4	31.4	26.2	20.6
											25.9	
$LPd_2(C_2H_5CO_2)$	7.93	7.38	183.7	149.2	140.2	136.8	131.7	120.5	40.2	31.2	26.1	20.5
											25.8	
$LPd_2(C_6H_5{\cdot}CO{\cdot}NH)$	8.04	7.44	183.6	148.8	140.3	136.1	132.2	121.5	40.5	31.2	26.2	20.5
	7.93			148.6	140.1		131.9		40.3		26.0	
$LPd_2(C_6H_5{\cdot}C(NH)_2)$	8.20	7.43	183.3	148.2	140.2	135.1[b] or	132.2	122.0	40.4	31.1	26.1	20.4
						138.8					25.9	
$LPd_2(C_5H_4N{\cdot}O)$	7.84	7.38	184.5	149.5	139.8[c]	136.8[d]	133.6	122.2	40.5	31.2	26.2	20.5
	8.21		183.6	147.9	139.6		131.2		40.1	31.1	26.0	
					139.5							
$LPd_2(C_5H_4N{\cdot}NH)$	8.06	~7.3	184.2	149.4[e]	139.5	136.3[f]	133.9	123.1	40.9	31.2	26.1	20.5
	8.26		183.4	148.7	139.1	136.1	131.9		40.2			
$LPd_2((C_6H_5)_2N_3)$	8.17	7.37	183.9	149.2	139.1	136.9	133.3	121.9	39.6	30.4	25.8	20.6
$LPd_2((p{\cdot}NO_2{\cdot}C_6H_4)_2N_3)$	8.19	7.48	183.9	149.6	139.4	137.6	133.1	121.0	39.3	30.5	25.6	20.6
$LPd_2(C_3H_3N_2)$	7.93	7.47	184.7	149.2	140.5[g]	137.2	133.2	–	40.5	31.2	26.2	20.8
					139.2							
$LPd_2((CH_3)_2CNO)$	8.03	~7.3[j]	184.7	149.9	138.5	137.5	134.2	122.7	40.9	31.0	26.2	20.9
	7.81		183.8	148.6	138.2		132.3		40.3		26.1	
$LPd_2((C_6H_{10})NO)$	8.00	~7.3[j]	184.6	149.8	138.6	137.6	134.2	–	40.9	31.0	26.2[h]	20.9
	7.80		183.7	148.7	138.2		132.2		40.1		26.1	
$LPd_2((C_6H_5CH_2)_2NO)$	7.78	~7.3	183.9	149.6	137.4	136.1	132.8[i]	124.0	40.6	31.1	26.2	20.6
	7.71		183.4	147.3					40.4	30.8	26.1	
$LPd_2(N_3)$	7.91	~7.3	~185	~149	~139.1	137.1	~133.7	123.3	39.6	30.6	26.0	20.5
$LPd_2(NO_2)$	8.00	7.44	–	150.8	139.2	–	133.3	–	40.6	31.2	26.1	20.9
	7.96			149.4	139.0				40.1	31.0	25.9	
$LPd_2(C_4H_2NO_2)$	8.19	7.42	184.5	150.8	140.2	136.9	132.6	121.2	40.1	31.2	26.1	20.5
	7.94		183.6	148.3			131.6				25.9	
L_2Pd_3	8.21	7.50	185.0	167.0	139.9	137.2	133.3	124.9	45.0	31.1	26.1	20.7
	8.19	7.43	177.8	148.5	139.4		131.9		40.5	30.0		

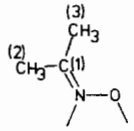
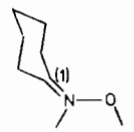
[a]Chemical shifts (ppm) downfield of TMS. All in $CDCl_3$. [b]One corresponds to C_b, the other to a C_6H_5 carbon (see Table III). [c]Two of the three correspond to C_c and C_c', the third to a pyridine ring carbon (see Table III). [d]Unusually intense. Probably a pyridine carbon superimposed (see Table III). [e]Pyridine carbon superimposed on C_f resonance at 148.7 ppm. [f]One of the two corresponds to C_b, the other to a pyridine C (see Table III). [g]One of the two corresponds to C_c, the other to the ∝C's of pyrazole. [h]Cyclohexyl carbons of bridging group superimposed. [i]C_6H_5 carbons superimposed. [j]Discernible splitting into pseudo quartet, with $CHCl_3$ at 7.26 ppm superimposed on upfield component.

TABLE III. NMR Data[a] Relating to the Bridging Species Z in LPd_2Z.

	Z	^{1}H NMR	^{13}C NMR
V		H(1), 7.29(s)	C(1), 167.4
VI		H(2), 2.26(s)	C(1), 178.0; C(2), 23.7
VII		H(3), 1.12(t); H(2), 2.31(qu)	C(1), 180.6; C(2), 20.5; C(3), 10.6
VIII		NH, 5.37	C(1), 169.3; C(2), 134.3; C(3), 127.5; C(4), 128.3; C(5), 130.8
IX		NH, 5.04	C(1), 163.3; C(2), 138.8 or 135.1[b], C(3), 126.2; C(4), 128.6; C(5), 129.7
X			C(2), 168.8; C(3), 112.7; C(4), 136.8; C(5), 119.8; C(6), 139.8 or 139.6 or 139.5[c]
XI		NH, 4.66 (broad)	C(2), 163.7; C(3), 109.5; C(4), 136.3 or 136.1[d]; C(5), 116.9; C(6), 148.7[e]
XII	 R = H		C(1), 152.1; C(2), 123.9; C(3), 127.9; C(4), 125.1
XIII	R = NO_2	Quartet, 8.02, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 42.2 Hz	C(1), 156.7; C(2) + C(3), 123.8; C(4), 149.6
XIV		H_A, H_B, quartet, 6.73, J_{AB} = 5.5 Hz, $\Delta\nu_{AB}$ = 33.3 Hz	C(1), (4), 186.0, 179.1[i]; C(2), (3), 137.0, 136.0[j]
XV		H(2), 7.20; H(3), 6.13	C(2), 140.5 or 139.2[f], C(3), 104.4
XVI		H_A, H_B, quartet, 4.28 J_{AB} = 11.7 Hz, $\Delta\nu_{AB}$ = 51.2 Hz	C(1), 71.9; C(2) 135.3; C(3), 132.8[g]; C(4), 128.2; C(5), 127.7

(continued overleaf)

TABLE III. *(continued)*

	Z	^{1}H NMR	^{13}C NMR
XVII		Oxime Me's, 2.28(s) and 2.07(s)[h]	C(1), 165.1; C(2), (3), 22.8, 19.3[h]
XVIII			C(1), 170.7

[a]Chemical shifts (ppm) downfield of TMS. All in $CDCl_3$. [b]One corresponds to C(2) the other to C_b (see Table II). [c]One of the three corresponds to C(6), the other two to C_c and $C_{c'}$ (see Table II). [d]One of the two corresponds to C(4), the other to C_b. [e]Superimposed on C_f ($C_{f'}$). [f]One of the two corresponds to C(2), the other to C_c. [g]Superimposed on C_d (or $C_{d'}$). [h]Uncertain which resonance corresponds to which Me. [i]Uncertain which corresponds to C(1) and which to C(4). [j]Uncertain which corresponds to C(2) and which to C(3).

The evidence available supports 'three atom bridging' [1] (V–XIV, Table III) in the complexes incorporating at the bridging site the conjugate bases of the following species: formic acid, acetic acid, propionic acid, benzamide, benzamidine, maleimide, 2-hydroxypyridine, 2-aminopyridine, and diphenyltriazine and its di-*p*-nitro derivative.

All three carboxylate derivatives show equivalent binucleating ligand side chains (Table II), consistent with symmetrical three atom bridging. Carboxylate bands in the IR spectrum of $LPd_2(CH_3CO_2)$ at 1420 cm^{-1} ($\nu_{OCO(sym)}$) and 1550 cm^{-1} ($\nu_{OCO(asym)}$) are consistent with this bridging mode [3–5], which has been confirmed by X-ray crystallography [6]. Similar carboxylate IR bands are observed for $LPd_2(C_2H_5CO_2)$ ($\nu_{OCO(sym)}$, 1410 and $\nu_{OCO(asym)}$, 1540 cm^{-1}) and for $LPd_2(HCO_2)$ ($\nu_{OCO(sym)}$, 1355 and $\nu_{OCO(asym)}$, 1560 cm^{-1}).

The closely related complexes derived from benzamide and benzamidine both showed a single N–H st. band in the IR spectrum at 3370 cm^{-1} and an NH resonance in the ^{1}H NMR spectrum at 5.37 (1H) and 5.04 ppm (2H) respectively. The ^{1}H and ^{13}C NMR spectra (Table II) indicated binucleating ligand side chains which were equivalent in the benzamidine case and inequivalent in the benzamide case. In general inequivalence of the side chains in $LPd_2(Z)$ derivatives was most readily apparent in well separated resonances due to C_g and $C_{g'}$ in the ^{13}C NMR spectra, but in the case of the benzamide complex only a single resonance, presumably arising from accidental superimposition was observed at 183.6 ppm. However, the side chains undoubtedly were inequivalent in this case as was indicated by the inequivalent H_f and $H_{f'}$, C_f and $C_{f'}$, C_c and $C_{c'}$ and C_d and $C_{d'}$ (Table II). The benzamidine complex shows a CN st. band at 1560 cm^{-1}, like the earlier reported $L'Pd_2(C_6H_5C(NH)_2)$, and in both cases the absence of amidine CN st. bands above 1600 cm^{-1} supports the proposed symmetrical three atom bridging mode [1].

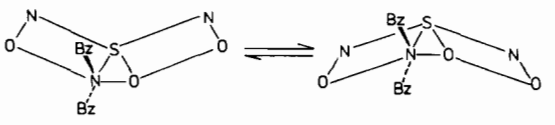
$LPd_2(CH_3CO_2)$ underwent a rapid reaction with urea in benzene solution to give $LPd_2(CN_2OH_3)$, the high insolubility of which precluded any solution measurements. However, IR bands at 3320 and 3340 cm^{-1} (NH st.) and at 3420 (OH st.) tend to support N,N bridging, Pd–NH···C(OH)···NH–Pd, rather than N,O bridging, as would be consistent with the general preference of palladium(II) for nitrogen over oxygen donors. There was no evidence for the incorporation into LPd_2^+ of either N,N'-dibenzylurea or N,N'-diphenylurea after several hours with $LPd_2(CH_3CO_2)$ in boiling benzene and boiling toluene respectively, unchanged acetate complex being recovered in both cases.

The presence in $LPd_2((C_6H_5)_2N_3)$ and $LPd_2((NO_2C_6H_4)_2N_3)$ of equivalent binucleating ligand side chains (Table II) and also equivalent bridge aromatic substituents (Table III) supports the symmetrical three atom bridging mode, Table III. It has been claimed [7] that the three atom bridging triazenido group shows a characteristic IR band in the range 1350–1375 cm^{-1} and the earlier reported $L'Pd_2((C_6H_5)_2N_3)$ [1] did indeed show a triazenido band at 1350 cm^{-1}, but unfortunately in the present LPd_2 series strong ligand bands at 1380 and 1350 cm^{-1} obscure such bridge bands if present.

The available evidence supports two atom bridging in the complexes incorporating the conjugate bases of the following species: pyrazole, N,N-dibenzylhydroxylamine, acetone-oxime, cyclohexanone-oxime and nitrous acid.

The pyrazole-derived complex, whose ^{13}C and ^{1}H NMR spectra indicated equivalent ligand side chains, showed strong pyrazole bands in the IR spectrum at 1050 and 750 cm^{-1}, where pyrazole bands have appeared in numerous earlier two atom bridging pyrazolate derivatives.

The ^{13}C and ^{1}H NMR spectra of the N,N-dibenzylhydroxylamine complex indicated inequivalent ligand side chains (Table II) and equivalent benzyl groups (Table III). However, the two protons of each benzylic CH_2 group displayed 'intrinsic non-equivalence' [8] (AB quartet, Table III) as is consistent with coordination of the nitrogen atom. The equivalence of the two $C_6H_5CH_2$ groups suggests either that they are in indistinguishable locations above and below a planar LPd_2^+ unit or that inequivalent benzyl groups of a non-planar arrangement can rapidly exchange, as in XIX ⇄ XX. Molecular models



XIX XX

indicate considerable strain in the planar LPd_2^+ arrangement. Indeed, the X-ray crystallographic study of $LPd_2(CH_3CO_2)$ [6] reveals that the two approximately square planar donor sets are well out of coplanarity, the geometry around the hinging sulphur being pyramidal, with the attached carbon and palladium centres forming a triangular base. The proposed rapid exchange of benzyl groups, XIX ⇄ XX, would involve inversion at such a pyramidal sulphur.

The reaction of oximes with $LPd_2(CH_3CO_2)$ was investigated with the possibility in mind of the unusual C,N bridging mode, XXI. However, the ^{1}H

XXI XXII

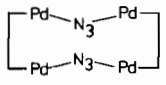
and ^{13}C NMR spectra of $LPd_2((CH_3)_2CNO)$ indicate that the oxime methyl groups are inequivalent, which supports the N,O bridging mode, XVII (Table III), since, by comparison with the N,N-dibenzylhydroxylamine complex above, the methyl groups in both XXI and the less likely XXII would be expected to be equivalent. The chemical shift of the oxime carbon in the ^{13}C spectrum, 165.1 ppm, is only very slightly greater than the range observed for neutral uncoordinated oximes, 145–163 ppm [9]. King [10] has reported a number of reactions of 2-bromo-2-nitroso-propane with metal carbonyl anions, one product of which was proposed to involve an N,O bridging species of the type, XVII. Attempts to rearrange thermally the N,O bridging oxime unit to the N,C bridging mode were unsuccessful; unchanged complex was recovered after one hour in bromobenzene at approx. 155 °C. The off-resonance decoupled ^{13}C spectrum of the acetone-oxime complex, together with several specific proton decoupled spectra and the undecoupled spectrum afforded complete assignment of the noise decoupled spectrum (Table II) and also provided the following links between carbon and proton resonances and the following coupling constants: C_f at 149.9 carries H at 8.03; $C_{f'}$ at 148.6 carries H at 7.81; C_a at 20.86 carries H at 2.38; C(oxime CH_3) at 22.76 carries H at 2.28; C(oxime CH_3) at 19.26 carries H at 2.07; $^{1}J_{C_fH_f} = {}^{1}J_{C_{f'}H_{f'}} = 173$ Hz; $^{1}J_{C_cH_c} = {}^{1}J_{C_{c'}H_{c'}} = 160$ Hz; $^{1}J_{C_3H_3} = {}^{1}J_{C_2H_2} = 130$ Hz; $^{1}J_{C_aH_a} = 128$ Hz; $^{2}J_{C_bH_a} = 6$ Hz; $^{3}J_{C_3H_2} = {}^{3}J_{C_2H_3} = 3.5$ Hz; $^{3}J_{C_aH_c} = 4$ Hz.

The earlier reported $L'Pd_2(NO_2)$ [1] showed $\nu_{NO_2(asym)}$ and $\nu_{NO_2(sym)}$ bands in the IR spectrum at 1510 and 1125 cm^{-1} respectively, which was taken as support for a two atom N,O bridge rather than a three atom O,O bridge analogous to that in $LPd_2(CH_3CO_2)$. $LPd_2(NO_2)$ likewise shows a strong $\nu_{NO_2(sym)}$ band at 1120 cm^{-1} but a very strong ligand band at 1500 cm^{-1} prevents definite assignment of $\nu_{NO_2(asym)}$, although a well defined shoulder at 1510 cm^{-1} probably has this origin. In the present case, however, the ^{1}H and ^{13}C NMR spectra (Table II) remove any ambiguity regarding the bridging mode because the ligand side chains are inequivalent, indicating two atom N,O bridging.

The isolation in the $L'Pd_2^+$ series of a complex, $[L'Pd_2(NO_2)_2]Na$ [1], was regarded as important because it appeared that two unlinked NO_2^- groups were incorporated at the site normally occupied by bridging groups, which in turn suggested that the incorporation of independent species at that site, possibly followed under appropriate circumstances by some sort of condensation under the influence of the two metal centres, was a feasible proposition. Attempts to generate analogous bis-nitrite derivatives, using excess nitrite, in the present LPd_2^+ series provided only $LPd_2(NO_2)$ or L_2Pd_3. However, evidence of a different sort for the incorporation of two unlinked species at the normally bridging site of LPd_2^+ is provided below.

The azide derivative of LPd_2^+ showed a molecular weight by osmometry in chloroform of 1340 in close agreement with the formulation $[LPd_2(N_3)]_2$ (calcd. 1361). Whilst the ^{1}H NMR spectrum showed only a single H_f resonance, side chain inequivalence was apparent in the ^{13}C spectrum. Carbons g + g′ appeared as a very broad unresolved signal, carbons f + f′ and d + d′ as broadened doublets and carbons c + c′ and h + h′ as significantly broadened singlets. By contrast the central carbons a, b and e appeared as very sharp singlets. This evidence is consistent with a tetranuclear structure, XXIII, in which there

are two different types of side chains which are able to exchange by some molecular flexing process at a rate at room temperature such that only those

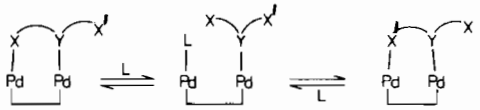


XXIII

exchanging nuclei with sufficiently well separated chemical shifts (*i.e.* carbons g + g′, f + f′, d + d′ and, to a lesser extent, c + c′ and h + h′) give rise to broadened resonances. The central carbons, a, b and e are presumably in the same environment before and after this flexing process and therefore appear as sharp singlets. The nature of the azide bridging in XXIII is uncertain; the KBr disc IR spectrum showed a strong $\nu_{N_3(asym)}$ at 2080 cm^{-1} (shoulder at 2060 cm^{-1}) which throws no useful light on this problem and $\nu_{N_3(sym)}$ which, it has been claimed [11], can be diagnostically useful, could not be located in the 1300 cm^{-1} region.

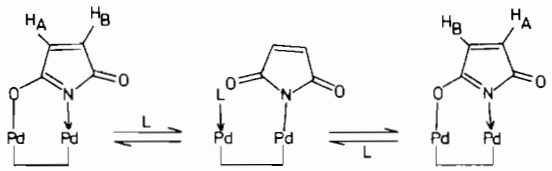
The compound $LPd_2(OCH_3)$ appears to be a very complicated species, at least in solution. The ^{13}C NMR spectrum showed at least four resonances in the g-carbon region (182–185 ppm) and at least four resonances presumed to arise from methoxy carbons in the region 50–60 ppm. The rest of the ^{13}C spectrum was very complex. The ^1H NMR spectrum was also complex and exceedingly broad. The molecular weight by osmometry in chloroform increased with increasing concentration ranging from approx. 1900 to approx. 2500 (calcd. for $LPd_2(OCH_3)$, 701) in the observable concentration range.

The importance with regard to our long term objectives of the question as to whether or not two independent species can be accommodated at the normally bridging site of LPd_2^+ prompted us to devise an NMR experiment which might throw some light on the question. If, for example, a system such as XXIV could be generated, exchange of X by X′, promoted by some monodentate ligand L, *via* the



XXIV XXV

'non-bridged' intermediate XXV might possibly be observable. With this possibility in mind attempts were made to incorporate into LPd_2^+ the conjugate base of diacetamide (*i.e.* $(CH_3CO)_2N^-$) by reaction of $LPd_2(CH_3CO_2)$ with diacetamide in benzene-methanol. However, $LPd_2(CH_3CONH)$ was isolated, formed, presumably, *via* metal-promoted solvolysis of one of the amide links. The cyclic analogue derived from maleimide shows no such sensitivity to CN fission, for $LPd_2(C_4H_2NO_2)$ is readily isolated, and the two alkene protons (XIV, Table III) are indeed inequivalent, appearing as an AB quartet in the ^1H NMR spectrum in $CDCl_3$. Addition of successive small aliquots of $(CD_3)_2SO$ to the $CDCl_3$ solution causes the quartet to collapse to a very broad band and finally to sharpen up to a singlet. Significantly the H_f and $H_{f'}$ remain inequivalent whilst the alkene protons are exchanging rapidly enough to produce a sharp singlet. Similar collapse of the quartet to a very broad signal is caused by addition of successive small aliquots of acetonitrile, but in this case precipitation of the complex and interference of the strong acetonitrile signal with the alkene signals prevented the observation of a sharp singlet. Neither saturation of the $CDCl_3$ solution with D_2O nor the addition of triethylamine affected the quartet signal. These results, implying rapid exchange of the alkene protons in the presence of dimethylsulphoxide or acetonitrile whilst the N–Pd bond remains intact, point to the rapid formation and decay of the non-bridged intermediate XXVI. Presumably triethylamine is too bulky to occupy the position of L in XXVI. The possibility does exist that the predominant species in solution in the presence of sufficient $(CD_3)_2SO$ to produce an alkene singlet is XXVI itself rather than a rapidly equilibrating mixture of the two bridged forms. However, addition of further $(CD_3)_2SO$ leads to the separation of pure crystalline maleimide complex free of any $(CD_3)_2SO$ which suggests, but does not prove, that XXVI is present in solution only as a reactive intermediate. In either case, it does appear that two unlinked species can be accommodated at the normally bridging site of LPd_2^+ provided they are not too bulky and therefore the formal possibility exists of bringing two independent species together at that site to undergo some sort of novel reaction under the influence of the metal pair.



XXVI

Experimental

The S-Protected Ligand Precursors, III (R = C_6H_5, C_6H_{11})

To a filtered boiling solution of 2-(N,N-dimethylthiocarbamato)-5-methylisophthalaldehyde (4.5 g, 18 mmol) in ethanol (70 ml) was added a solution of the appropriate acyl hydrazide (37 mmol) in hot ethanol (80 ml). After the addition of acetic acid (0.5 ml) the mixture was stirred under reflux for 2 h

during which time a colourless microcrystalline precipitate separated. After the suspension had been chilled in ice, the solid was collected, washed with ethanol and dried in vacuum. The products in this form give analytically pure complexes. Yields: R = C_6H_5, 90%; R = C_6H_{11}, 85%.

L''Cu$_2$($C_3H_3N_2$), L''Ni$_2$($C_3H_3N_2$) and LNi$_2$($C_3H_3N_2$)

A solution of pyrazole (0.020 g) and the appropriate III (0.18 g) in DMF (5 ml) at approx. 90 °C was added to a solution of the metal acetate (0.20 g) in DMF (4 ml) at approx. 90 °C. After 5 min at this temperature the mixture was cooled to room temperature whereupon the products separated as brown needles, which were collected, washed with methanol and dried in vacuum. Yields: L''Cu$_2$($C_3H_3N_2$), 65%; L''Ni$_2$($C_3H_3N_2$), 40%; LNi$_2$($C_3H_3N_2$), 60%.

L''Pd$_2$(CH_3CO_2)

III with R = C_6H_5 (0.24 g, 0.5 mmol) in DMF (2 ml) at approx. 90 °C was added to a boiling solution of palladium(II) acetate (0.24 g, 1.07 mmol) in chloroform (3 ml). After a few minutes at the boiling point the solution deposited fine yellow needles which were collected, washed with methanol and dried in vacuum. Yield, 0.129 g (60%).

(LH)Pd$_2$Cl$_2$

III (R = C_6H_{11}) (0.060 g) and $PdCl_2(C_6H_5CN)_2$ (0.067 g) in DMF (3 ml) were heated at approx. 90 °C for 1 h and the resulting reddish solution was filtered whilst hot. Boiling methanol was added to the hot filtrate until solid started to separate. Upon cooling, the mixture deposited (LH)Pd$_2$Cl$_2$·DMF as red crystals. It was impossible to remove DMF completely from this solid by heating under vacuum but suspending the solid in refluxing chloroform for 12 h gave solvent-free (LH)Pd$_2$Cl$_2$.

LPd$_2$(CH_3CO_2)

III with R = C_6H_{11} (8.00 g, 16 mmol) and palladium(II) acetate (7.38 g, 33 mmol) in chloroform (45 ml) were heated under reflux for 1 h. The deep red-brown solution so formed was filtered whilst hot and the filtrate, upon cooling deposited yellow needles, which were collected and washed with chloroform-petrol. The crystals contained chloroform of solvation which was removed by drying at 80 °C under vacuum for 4 h. Yield, 6.06 g. Further product could be obtained by partial evaporation of the mother liquors. The above product was analytically pure, but it could be satisfactorily recrystallised from either benzene-petrol or chloroform-petrol.

L$_2$Pd$_3$

(*a*) A solution of allylamine (0.010 g) in benzene (2 ml) was added to a solution of LPd$_2$(CH_3CO_2) (0.090 g) in benzene (2.5 ml) and the mixture was allowed to stand at room temperature for 2 h. The yellow precipitate of L$_2$Pd$_3$ which was separated was collected, washed with cold benzene and dried in vacuum.

(*b*) Ammonia gas was bubbled through a solution of LPd$_2$(CH_3CO_2) (0.11 g) in benzene (3.5 ml). Yellow L$_2$Pd$_3$ precipitated immediately and after 1 min was collected, washed with benzene and dried in vacuum. Yield, 0.062 g (68%).

Bridge Substitution Reactions

Bridge substitution reactions were conducted in many cases (see below) simply by heating under reflux LPd$_2$(CH_3CO_2) with an excess of the protonated form of the entering anion in the appropriate solvent as follows: – in benzene – LPd$_2$($C_2H_5CO_2$), LPd$_2$(C_5H_4N·O), LPd$_2$(C_5H_4N·NH), LPd$_2$((C_6H_5)$_2N_3$), LPd$_2$($C_3H_3N_2$); in benzene-methanol – LPd$_2$(C_6H_5CONH), LPd$_2$($C_6H_5C(NH)_2$), LPd$_2$(CN_2OH_3), LPd$_2$($C_4H_2NO_2$); in benzene-dichloromethane – LPd$_2$((CH_3)$_2$CNO); in chloroform-petrol – LPd$_2$((C_6H_{10}))NO); in dioxan – LPd$_2$(HCO_2). Generally substitution was complete with 2 h at the boiling point of the solvent used.

In the cases of LPd$_2$(($C_6H_5CH_2$)$_2$NO) and LPd$_2$((NO_2·C_6H_4)$_2N_3$) the substitution was conducted at room temperature in a stirred two-phase medium consisting of LPd$_2$(CH_3CO_2) and the protonated form of the entering group in chloroform together with excess aqueous sodium carbonate.

For substitutions by N_3^-, NO_2^- and CH_3O^- the anionic form of the entering group was used in proportions equimolar to the LPd$_2$(CH_3CO_2) used. Substitutions by N_3^- and CH_3O^- were conducted at room temperature with LPd$_2$(CH_3CO_2) suspended in methanolic solutions of NaN_3 and $LiOCH_3$ respectively. The introduction of NO_2^- was carried out at room temperature with LPd$_2$(CH_3CO_2) in tetrahydrofuran to which was added aqueous sodium nitrite.

Chloroform-petrol and benzene-petrol were generally satisfactory for recrystallisation of the substitution products except for LPd$_2$(CH_3O) which was recrystallised from chloroform-methanol and LPd$_2$(($C_6H_5CH_2$)$_2$NO) which was recrystallised from ethanol.

Physical Measurements

IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer as KBr discs. NMR spectra were recorded on a Jeol FX 100 spectrometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

Acknowledgements

We are grateful to the Chemistry Department, University of Lancaster, U.K., for making available to R. R. facilities which were used for some of this work and also to Dr. T. N. Huckerby of that Department for assistance with NMR spectra. We thank the Australian Research Grants Committee for support for P.D.N. and for a maintenance grant.

References

1 J. G. Hughes and R. Robson, *Inorg. Chim. Acta, 35,* 87 (1979).
2 P. Krautil and R. Robson, *J. Coord. Chem., 10,* 7 (1980).
3 T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.,* 3632 (1965).
4 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 29,* 2122 (1967).
5 S. J. Betts, A. Harris and R. N. Haszeldine, *J. Chem. Soc. A,* 3699 (1971).
6 B. F. Hoskins and I. McDonald, unpublished results. The analysis is presently under refinement but the gross features of the structure are clear.
7 J. Kuyper, P. I. Van Vliet and K. Vrieze, *J. Organometal. Chem., 105,* 379 (1976).
8 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon, p. 373 (1969).
9 G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists', Wiley–Interscience, p. 129 (1972).
10 R. B. King and W. M. Douglas, *Inorg. Chem., 13,* 1339 (1974).
11 J. Nelson and S. M. Nelson, *J. Chem. Soc. A,* 1597 (1969).