Inorganica Chimica Acta, 35 (1979) 87–92
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complexes of Binucleating Ligands.
XI. Some Palladium(II) Complexes of a Ligand Containing a Bridging Thiophenoxide Component

J. G. HUGHES and R. ROBSON

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

Received November 8, 1978

*Binuclear palladium(II) complexes of the trianionic binucleating ligand (L^{3-}), formally derived from 2-mercapto-5-methylisophthalaldehyde di-2'-hydroxyanil by loss of one mercapto and two phenolic protons, appear to present a significantly larger exchangeable bridging site than earlier binucleating systems containing a bridging phenoxide component. Thus LPd_2^+ is found to incorporate at this site a range of 'three atom bridges' as in, for example, $Pd\text{–}O\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}O\text{–}Pd$, $Pd\text{–}NH\overset{\cdots}{-}C(C_6H_5)\overset{\cdots}{-}NH\text{–}Pd$ and $Pd\text{–}P(C_6H_5)_2\text{–}CH_2\text{–}P(C_6H_5)_2\text{–}Pd$ and apparently some related H-bonded three atom bridges as in, for example, $Pd\text{–}O(H)\cdots H\cdots N(H)(R)\text{–}Pd$. In one case, $Na[LPd_2(NO_2)_2]2H_2O$, it appears that two independent nitrite groups are bound at the normally bridging site (*i.e. *a 'non-bridged' system). However, LPd_2^+ will also incorporate 'two atom bridges', e.g. pyrazolate anion, neutral pyridazine, and a single nitrite ion bridging via N and O. Even 'one atom bridges' can be accommodated provided they are large enough, e.g. I^-, Br^-, but the corresponding chloro-bridged complex, LPd_2Cl, could not be obtained.*

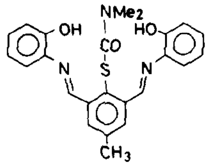
Introduction

It has been demonstrated that binucleating ligands containing a hard central phenoxide unit as the bridging component (X in I = O) fail to impose the binuclear structure, I, with the soft metals, palladium-

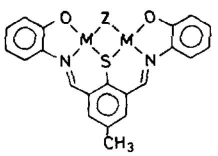
I

(II) and platinum(II), unless the additional bridging species, Z, is a 'good' donor for these metals, capable of giving the binucleating ligand substantial assitance in maintaining the binuclear structure (*e.g.* Z = RS^-, pyrazolate anion) [1]. As part of a long-term project directed towards the synthesis of binuclear systems containing two soft metal centres in close proximity, which it is hoped may show unusual and possibly useful reactivity at the bridging site, Z, we have extended our studies to include potential binucleating systems containing a bridging sulphur donor (X in I = S). It is anticipated that such systems may succeed in imposing binuclear structures such as I upon soft metals, M, whether or not the species Z is sufficiently firmly bound to assist the binucleating ligand in maintaining the structure. Presented here are the results of a broad preparative survey of the palladium(II) complexes of a ligand containing a bridging thiophenoxide component and imine-type side arms, with special regard to the range and steric requirements of the species incorporated at the exchangeable bridging site.

Results and Discussion



II



III

The *o*-aminophenol-derived Schiff base, II, provided a convenient source of the trianionic binucleating ligand (hereafter L^{3-}) in complexes of the type III, the free thiolate centre of L^{3-} being liberated, via a metal-promoted process, during the formation of the complex. Thus, for example, II smoothly afforded the crystalline pyrazolato-bridged derivative, $LNi_2(C_3H_3N_2)$, by reaction with nickel(II) bromide, lithium acetate and pyrazole in methanolic dimethylformamide.

Reaction of II with palladium(II) acetate in chloroform gave at least two products, one of which, separating from the reaction mixture in crystalline form in 15–30% yield had composition consistent with the formulation $LPd_2(CH_3CO_2)\cdot CHCl_3$. The major, more soluble product has not yet been obtained in a satisfactory state of purity. $LPd_2(CH_3CO_2)\cdot CHCl_3$ shows in its i.r. spectrum $\nu_{COO(asym)}$ at 1540 cm^{-1} and $\nu_{COO(sym)}$ at 1420 cm^{-1}, which is

TABLE I. Analytical Data.

	%C		%H		%N		%S	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$LPd_2(CH_3CO_2)\cdot CHCl_3$	38.4	38.7	2.7	2.6	3.7	3.8	4.3	4.2
$LPd_2(C_6H_5CO_2)\cdot \frac{3}{4}CHCl_3$[a]	44.1	44.0	2.7	2.8	3.6	3.8	4.1	4.3
$LPd_2[(C_6H_5)_2N_3]\cdot 2CH_3OH$	50.5	50.6	4.0	3.8	8.4	8.2	3.8	3.8
$LPd_2[C_6H_5C(NH)_2]\cdot 2H_2O$	46.2	45.8	3.6	3.2	7.7	7.6	4.4	4.3
$[LPd_2(dpm)]ClO_4$[b]	52.3	51.6	3.5	3.7	2.7	2.5	3.0	2.9
$[LPd_2(dam)]ClO_4$[c]	48.3	47.9	3.3	3.3	2.5	2.3	2.8	3.2
$LPd_2(C_5H_4N\cdot NH)\cdot 2H_2O$	44.5	45.1	3.4	3.1	8.0	7.1	4.6	4.7
$LPd_2(C_5H_4N\cdot O)\cdot H_2O$	45.6	44.9	3.1	2.9	6.1	5.9	4.7	5.5
$LPd_2(C_5H_4N\cdot C_2H_3OC_2H_5)$	49.9	49.9	3.7	3.9	5.8	5.8	4.4	4.4
$LPd_2(OH)(H_2O)(CH_3OH)$	41.3	41.3	3.4	3.2	4.4	4.2	5.0	5.2
$LPd_2(OH)(NH_3)(H_2O)$	40.4	40.5	3.4	3.0	6.7	7.2	5.1	4.8
$LPd_2(OH)(C_6H_5CH_2NH_2)(H_2O)$	47.0	46.6	3.8	3.7	5.9	5.9	4.5	5.2
$LPd_2(N_3)(H_2O)$	39.7	39.5	2.7	2.6	11.0	11.4	5.0	4.5
$Na[LPd_2(NO)_2)_2]\cdot 2H_2O$[d]	34.8	34.2	2.6	2.4	7.8	7.8	4.4	4.4
$LP_2(C_3H_3N_2)$	45.1	45.1	2.8	3.2	8.6	8.8	5.0	5.3
$[LPd_2(C_4H_4N_2)]ClO_4\cdot H_2O$	39.0	39.0	2.7	2.7	7.3	6.7	4.2	4.1
$LPd_2(NO_2)\cdot H_2O$	39.6	39.8	2.7	2.6	6.6	6.2	5.0	5.1
LPd_2I[e]	36.1	36.1	2.2	2.4	4.0	4.0	4.6	4.5
LPd_2Br[f]	38.7	38.5	2.3	2.3	4.3	4.1	4.9	4.7
$LNi_2(C_3H_3N_2)$	52.9	53.3	3.3	3.5	10.3	10.4	5.9	5.6

All compounds were dried at 80 °C under vacuum.
[a] Prepared from $Pd(C_6H_5CO_2)_2$ and II in chloroform. [b] %Cl: Calcd., 3.4; Found, 3.4. %P: Calcd., 5.9; Found, 6.3. [c] %Cl: Calcd., 3.1; Found, 2.6. %As: Calcd., 13.1; Found, 12.7. [d] %Na: Calcd., 3.2; Found, 3.4. [e] %I: Calcd., 18.2; Found, 18.2. [f] %Br: Calcd., 12.2; Found, 11.3.

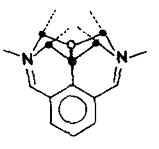


Fig. 1. Comparison of sulphur and oxygen as bridging centres in binucleating imine-type ligands. ⊗ = oxygen; ○ = sulphur.

consistent with the symmetrical bridging mode, Pd—O$\cdots$C(CH$_3$)$\cdots$O—Pd [2–4]. The acetate group in this case is one example of what we shall refer to below as "three atom bridging" species.

All our earlier binucleating systems with a bridging phenoxide component have given complexes with either a 'one atom bridge' (*e.g.* a methoxy-bridge) or a 'two atom bridge' (*e.g.* a pyrazolato bridge) at the in-plane bridging site. Molecular models indicate that, provided the system as a whole remains close to coplanar, substitution of the bridging phenoxide centre of an imine-type binucleating ligand by a bridging thiophenoxide unit leads, as a result of sulphur's having a covalent radius 0.3–0.4 Å larger than oxygen, to the following consequences, represented diagrammatically in Fig. 1.

a) the angle subtended by the two metal centres at the bridging sulphur atom is markedly increased beyond the 100–110° observed in the phenoxide systems; b) the metal–metal separation is considerably increased beyond the 2.8–3.4 Å observed in the phenoxide systems; c) the imaginary preferred valencies at the two metal centres directed towards the exchangeable bridging site, represented by broken lines in Fig. 1, converge at a much greater distance from the two metals and at a much more acute angle. In contrast to the planarity at the sulphur centre and the large metal–sulphur–metal angle implicit in this model, simple aliphatic and aromatic thiolate anions seem to prefer, when they bridge two metals, a pronounced pyramidal arrangement of the sulphur and the directly attached carbon and metal atoms with much smaller metal–sulphur–metal angles [5–8]. It appears then that there will inevitably be strain in systems of the type III, either at the bridging sulphur centre or in the side-arms (*e.g.* angle strain at the imine nitrogen) especially if the side-arms twist out of their preferred coplanarity to relieve the sulphur atom, or possibly in both these regions.

The three atom bridged structure for $LPd_2(CH_3CO_2)\cdot CHCl_3$ implied by the i.r. spectrum is consistent with the sort of geometry represented in Fig. 1.

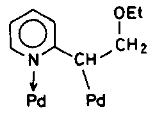
Indeed, the LPd$_2^+$ system appears to have a special affinity for potential three atom bridges in general, for LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ undergoes a number of bridge substitution reactions in which the incoming species appears to adopt this bridging mode. The products of these and other substitutions, with one or two exceptions, were electrically neutral and highly insoluble. Substitutions were generally carried out on suspensions and, although the disappearance of the strong acetate bands in the i.r. spectrum at 1420 and 1540 cm^{-1} provided a convenient means of monitoring the extent of substitution, the system was generally unsatisfactory in that the insolubility of the products precluded the observation of n.m.r. spectra, *etc.* and made purification by recrystallisation or chromatography difficult or impossible. The complexes isolated are listed in Table I.

LPd$_2$(C$_6$H$_5$CO$_2$) was obtained by reaction of LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ with sodium benzoate in boiling methanol or alternatively, in low yield by reaction in chloroform of II with palladium(II) benzoate. In the latter reaction a major, as yet unidentified, product presumed to be analogous to that formed in the corresponding reaction with palladium(II) acetate, was also formed. LPd$_2$(C$_6$H$_5$CO$_2$) showed in its i.r. spectrum $\nu_{OCO(asym)}$ at 1525 cm^{-1} and $\nu_{OCO(sym)}$ at 1400 cm^{-1}, consistent with the three atom bridged structure.

The acetate bridge of LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ could be replaced by the conjugate bases of either diphenyltriazene or benzamidine by reaction of these compounds in methanolic solution with suspended LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$. The three atom bridging modes, Pd–N(C$_6$H$_5$)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$N(C$_6$H$_5$)–Pd and Pd–N(H)$\overset{\cdots}{-}$C(C$_6$H$_5$)$\overset{\cdots}{-}$N(H)–Pd, appear likely in these cases, although the available evidence does not afford proof. Some triazenido complexes are known from crystallographic studies to involve three atom bridges [9–11]. Triazenido complexes have been reported to show, in general, i.r. bands characteristic of the N$_3$ group at 1580–1600, 1275–1290, 1200–1210 and 1155–1165 cm^{-1} but doubt has been cast upon the reliability of i.r. criteria for bonding mode [12–14]. More recently, however, it has been claimed [15] that three atom bridging triazenido groups show a characteristic band in the range 1350–1375 cm^{-1} and LPd$_2$((C$_6$H$_5$)$_2$N$_3$) does indeed show a triazenido band at 1350 cm^{-1} together with others at 1260 and 1205 cm^{-1}. Recently, examples of both bidentate [16] and bridging [17] amidinato ligands have been established. The present benzamidinato complex shows a singlet NH st. band at 3360 cm^{-1} in its i.r. spectrum consistent with the symmetrical three atom bridging mode. An amidine CN st. band appears at 1560 cm^{-1} whereas neutral amidines, monodentate neutral amidines and chelating amidinato anionic ligands [18] show CN st. bands above 1600 cm^{-1}. Again, three atom bridging appears likely but the scant evidence available is not conclusive.

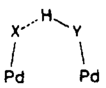
Substitution of the acetate group of LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ by bis-diphenylphosphinomethane (dpm) and by bis-diphenylarsinomethane (dam) by reaction in methanol followed by addition of lithium perchlorate afforded the crystalline salts [LPd$_2$(dpm)]ClO$_4$ and [LPd$_2$(dam)]ClO$_4$ respectively. Both derivatives were barely soluble enough in (CD$_3$)$_2$SO to allow the recording of ^{1}H n.m.r. spectra, which were of correspondingly poor quality: [LPd$_2$(dpm)]ClO$_4$, δ 4.62 (triplet, methylene of dpm), 6.58, 7.40, 8.0 (aromatic protons of dpm and *o*-iminophenol groups), 8.18 (singlet, aromatic protons of central thiophenoxide ring), ~9.0 (imine). [LPd$_2$(dam)]ClO$_4$, δ 4.10 (singlet, methylene of dam, 6.60, ~7.4, ~7.9 (aromatic protons of dam and *o*-iminophenol groups, 8.20 (aromatic protons of central thiophenoxide ring), 9.00 (imine). The free ligands, dpm and dam, show methylene resonances at δ 2.77 (triplet) and 2.60 (singlet) respectively. Coordination of the donor atoms generally causes a downfield shift of the methylene resonance, the position of which depends, among other factors, upon the coordination mode: monodentate, downfield shift of 0.1–1.5 p.p.m.; bidentate, downfield shift of 2.3–3.1 p.p.m.: bridging, shift intermediate between those for monodentate and bidentate [19]. The positions of the methylene resonances of the dpm and dam in [LPd$_2$(dpm)]ClO$_4$ and [LPd$_2$(dam)]ClO$_4$ are therefore consistent with the three atom bridging mode.

Rapid substitution of the bridging acetate group by the conjugate bases of either 2-aminopyridine or 2-hydroxypyridine occurred, even at room temperature, when LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ was stirred in suspension with a methanolic solution of the appropriate substituted pyridine. The 2-aminopyridine derivative showed an NH st. band at 3310 cm^{-1}. Simply on the basis of the nature of the bridging species, three atom bridging seems most likely. Attempts to introduce the conjugate base of α-picoline as a three atom bridging species bound through nitrogen and the α-CH$_2^-$ via reaction of LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ with α-picoline yielded only unchanged starting material. However, an alternative to simple deprotonation of a C–H unit for the generation of a formally carbanionic centre is provided by nucleophilic attack at an alkene: accordingly, we investigated the reaction, if any, between 2-vinylpyridine and LPd$_2$(CH$_3$CO$_2$)·CHCl$_3$ which, in the presence of ethanol yielded a product which appears to involve the novel bridging system IV. The i.r. spectrum of this product shows a new strong ether CO st. band at 1080 cm^{-1} and the alkene CC st. band of vinyl pyridine has disappeared.

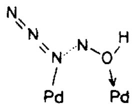


IV

Several species have been isolated which probably involve an H-bonded three atom bridging system as in V. Reaction of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with tetrabutylammonium hydroxide in methanol yields a product whose i.r. spectrum shows no acetate bands and whose composition is consistent with the formulation $LPd_2(OH)(H_2O)(CH_3OH)$. The presence of methanol, consistently suggested by the analytical data on a number of independently prepared samples, is supported by a band in the i.r. spectrum at 1040 cm^{-1} assigned to the methanolic CO st. A number of structures of the type V, consistent with this formulation can be readily conceived. Products of composition $LPd_2(RNH)(H_2O)_2$ (or $LPd_2(OH)(RNH_2)(H_2O)$) were obtained from reactions of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with either aqueous methanolic ammonia (R = H) or benzylamine (R = $C_6H_5CH_2$). Another substitution product with a bridging arrangement probably of the type V was $LPd_2(N_3)\cdot H_2O$ obtained by reaction of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with sodium azide. The three atom bridging mode, M–N=N=N–M, linear within the N_3 unit but bent at each terminal N, is known, but requires an MM separation in excess of 5 Å, unrealistically large for the LPd_2^+ system. Therefore VI appears more reasonable, but an alternative which cannot be discounted involves σ bonding of N_3^- to one palladium and π-bonding to the other. The only observable azide i.r. band was $\nu_{N_3(asym)}$ at 2040 cm^{-1} which throws no useful light on these considerations.

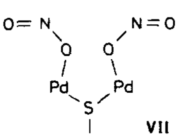


V

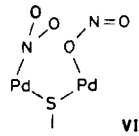


VI

In at least one case it appears that two independent entities can be introduced at the bridging site, *i.e.* a non-bridged structure. Reaction of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with sodium nitrite in methanol yields a material of composition consistent with the formulation $Na[LPd_2(NO_2)_2]\cdot 2H_2O$. This shows in its i.r. spectrum a strong $\nu_{NO_2(asym)}$ band at 1390 cm^{-1} and two shoulders, of possibly nitrite origin, on binucleating ligand bands, one at 1310 – 1320 cm^{-1} and one at 1140 cm^{-1}. The latter shoulder suggests O-bonded rather than N-bonded nitrite [20], possibly as in the non-bridged arrangement VII, which would not be inconsistent with the sort of geometry represented in Fig. 1. However, palladium(II) does seem to have a very strong preference for N-bonded over O-bonded nitrite [21] and, whilst under the present circumstances two N-bonded nitrite groups seem sterically highly unlikely (in addition to being probably inconsistent with the observed i.r. spectrum), perhaps an acceptable compromise is struck with possibility VIII which would be consistent with the observed spectrum. Not surprisingly, this compound readily loses one nitrite group (see below).



VII



VIII

The LPd_2^+ system will also accommodate two atom bridges and even one atom bridges, provided the latter are large enough. The pyrazolate-bridged material $LPd_2(C_3H_3N_2)$, produced by reaction of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with pyrazole in methanol, has an i.r. spectrum almost identical to that of the starting material except that the acetate bands have been replaced by pyrazole bands at 1055 and 750 cm^{-1}, very close to where pyrazole bands have appeared in all the two atom bridged pyrazolate derivatives of our earlier phenoxide-based binucleating ligands. When pyridazine is added to a suspension of $LPd_2(CH_3CO_2)\cdot CHCl_3$ in methanol the suspended solid rapidly dissolves presumably to yield the cathionic species $[LPd_2(C_4H_4N_2)]^+$ which can be precipitated either as the iodide or as the perchlorate by adding the appropriate lithium salt. The perchlorate was only just sufficiently soluble in $(CD_3)_2SO$ to permit the ^1H n.m.r. spectrum to be recorded and the quality of the spectrum was poor: δ 8.90 (2 imine protons), 8.12 (2 aromatic protons of central ring), 7.60–6.35 (12 aromatic protons of two *o*-iminophenol rings and pyridazine). It is difficult to conceive how pyridazine could be attached except in the two atom bridging mode. A compound of composition $LPd_2(NO_2)\cdot H_2O$ can be obtained simply by washing with water the compound of formulation $Na\ LPd_2(NO_2)_2\cdot 2H_2O$ described above. The same product can be obtained alternatively by reaction of $LPd_2(CH_3CO_2)\cdot CHCl_3$ with sodium nitrite in methanol containing 5% water. This compound shows a strong $\nu_{NO_2(asym)}$ band at 1510 cm^{-1} and $\nu_{NO_2(sym)}$ at 1125 cm^{-1} which strongly supports a two atom bridging nitrite bound through nitrogen and oxygen [20].

LPd_2I and LPd_2Br, which presumably are examples involving large one atom bridges, can be obtained from $LPd_2(CH_3CO_2)\cdot CHCl_3$ by reaction with LiI and LiBr respectively in methanol. By contrast, similar reactions with LiCl failed, despite many attempts, to yield LPd_2Cl; indeed, the acetate-bridged complex could be obtained from reactions involving II, palladium(II) and acetate ion in the presence of an excess of chloride ion, indicating a striking preference of LPd_2^+ for the hard acetate over the soft chloride, presumably for reasons associated with geometrical fit.

Simply on the basis of i.r. spectra we were able to show that a wide range of other potentially unusual and interesting species could be incorporated at the bridging site, but we were unable to isolate the products in a satisfactory state of purity because of the problems associated with insolubility. These problems, in addition, have severely limited the information available on the bridging species present in the complexes which could be isolated. The apparent preference of LPd_2^+ for three atom bridging species offers the possibility of novel reactions promoted by pairs of metals, *e.g.* it may be possible to devise systems in which a diatomic functional group and a monoatomic functional group are condensed under the influence of the metallic pair, the driving force for the condensation being provided, in part, by the favourable fit of the three atom bridged species produced. With metal centres more prone than palladium(II) to participate in redox processes the scope for unusual chemistry at the bridge site appears correspondingly wider. For all these reasons we consider it worthwhile building systems related to L^{3-} with peripheral substituents intended to increase the general solubility of the derived complexes and this work is presently underway.

Experimental

2-(NN-dimethylthiocarbamato)-5-methylisophthalaldehyde-di-2'-hydroxyanil, (II)

o-Aminophenol (0.23 g, 2.1 mmol) and 2-(NN-dimethylthiocarbamato)-5-methylisophthalaldehyde (0.25 g, 1 mmol) prepared by the method of Newman and Karnes [22] were heated in solution in methanol (20 ml). After a few minutes boiling the deep red solution deposited an orange-yellow precipitate of the dianil, which, after the suspension had been cooled, was collected, washed with methanol and dried at 80 °C under vacuum. Crude yield, 75–80%. M.p., 203–206 °C. The material in this form contained half a mol of methanol but was suitable for the preparation of complexes. Found: C, 65.3; H, 5.4; N, 9.3; S, 7.8%. Calculated for $C_{24}H_{23}N_3O_3S\cdot\frac{1}{2}CH_3OH$: C, 65.5; H, 5.6; N, 9.4; S, 7.1%. The material could be recrystallised from chloroform yielding lemon crystals. Found: C, 66.7; H, 5.3; N, 9.1; S, 7.4%. Calculated for $C_{24}H_{23}N_3O_3S$: C, 66.5; H, 5.3; N, 9.7; S, 7.4%. I.r. (KBr disc), 1670 (carbamate C=O st.), 1615 (imine C=N st.), 3400 cm^{-1} (OH st.). ^1H n.m.r. ($CDCl_3$/TMS) δ 2.45 (singlet, $-CH_3$), 3.1 (broad, $N(CH_3)_2$), 6.85–7.25 (multiplet, *o*-iminophenolic protons), 8.10 (singlet, protons of central aromatic ring), 9.15 (singlet, imine).

$LNi_2(C_3H_3N_2)$

Nickel(II) bromide trihydrate (0.31 g) in dimethylformamide (5 ml) was added to a solution of II (0.24 g) in dimethylformamide (1 ml). To the resulting solution at approximately 80 °C was added with stirring a near boiling solution of lithium acetate dihydrate (0.1 g) and pyrazole (0.1 g) in methanol (10 ml). The solution turned dark brown immediately and on cooling deposited black crystals of $LNi_2(C_3H_3N_2)$ which were collected, washed with methanol and dried at 80 °C under vacuum. Yield, 0.09 g (30%).

$LPd_2(CH_3CO_2)\cdot CHCl_3$

Upon heating to the boiling point a suspension of palladium(II) acetate and II in 2:1 molar proportions in chloroform (1 ml $CHCl_3$ per 0.1 g of each component) the solids dissolved to give a very dark brown solution from which dark brown crystals of $LPd_2(CH_3CO_2)\cdot CHCl_3$ separated after a minute or two. After the mixture had been heated at the boiling point for 5 minutes it was cooled and the crystalline precipitate was collected, washed with chloroform and then dried in vacuum at 80 °C. Yield, 15–30%. The chloroform of solvation was retained even after prolonged heating at 80 °C under vacuum. The product was insoluble in all common solvents and we were unable to devise a satisfactory recrystallisation procedure. Attempts to improve yields by using more concentrated solutions led to the separation of material contaminated with the major, as yet unidentified, product of the reaction, which was characterised by a strong band at 1670 cm^{-1} in the i.r. spectrum. The 2:1 proportions of the reactants appeared to be optimum, for variation of the proportions led to the lowered yields or to contaminated products. Solvents such as dimethylformamide and alcohols were less satisfactory than chloroform.

Bridge Substitution Reactions

Bridge substitution reactions were generally conducted in suspension in a boiling methanolic solution (exceptions below) of an excess (exceptions below) of a source of the entering bridging species. Generally, both starting LPd_2 $CH_3CO_2)\cdot CHCl_3$ and the product were insoluble in the reaction medium and the progress of the substitution was followed by removing from time to time an aliquot of the suspended solid and observing the i.r. spectrum. Generally substitution was complete within 2 hours at the boiling point of methanol. In the cases of 2-amino- and 2-hydroxo-pyridines and benzamidine the substitution proceeded rapidly at room temperature. The reaction with vinylpyridine was conducted in boiling ethanol. Excess entering species had to be avoided with dpm and dam which appeared to remove palladium from LPd_2^+ and which, therefore, were used in equimolar proportions. In the reaction with tetrabutylammonium hydroxide excess of the reagent caused decomposition. With the neutral entering species dpm, dam and pyridazine the complex dissolved as the substitution proceeded and the cationic complex so formed was then precipitated by addition of an excess of lithium perchlorate in methanol. The dpm and dam complexes were exceptional in that they alone could be successfully recrystallised (from dimethylformamide–methanol).

Physical Measurements

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer as KBr discs. N.m.r. spectra were recorded on a Varian HA-100 Spectrometer.

Analyses

Analyses were carried out by the Australian Microanalytical Service, Melbourne.

Acknowledgement

We thank the Australian Research Grants Committee for support for J. G. H. and for a grant for chemicals.

References

1 W. D. McFadyen, R. Robson and H. A. Schaap, *J. Coord. Chem., 8,* 59 (1978).
2 T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.,* 3632 (1965).
3 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 29,* 2122 (1967).
4 S. J. Betts, A. Harris and R. N. Haszeldine, *J. Chem. Soc. A,* 3699 (1971).
5 R. Mason and D. M. P. Mingos, *J. Organometal. Chem., 50,* 53 (1973).
6 P. J. Vergamini and G. J. Kubas, *Progr. in Inorg. Chem., 21,* 261 (1976).
7 J. P. Fackler, *Progr. in Inorg. Chem., 21,* 55 (1976).
8 I. G. Dance, *Chem. Comm.,* 762 (1975); 68 (1976); 103 (1976).
9 I. D. Brown and J. D. Dunitz, *Acta Cryst., 14,* 480 (1961).
10 J. E. O. Connor, G. A. Janusonis and E. R. Corey, *Chem. Comm.,* 445 (1968).
11 M. Corbett, B. F. Hoskins, N. J. McLeod and B. P. O'Day, *Aust. J. Chem., 28,* 2377 (1975).
12 W. H. Knoth, *Inorg. Chem., 12,* 38 (1973).
13 K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc. Dalton,* 1205 (1974).
14 S. Candeloro De Sanctis, L. Toniolo, T. Boschi and G. Deganello, *Inorg. Chim. Acta, 12,* 252 (1975).
15 J. Kuyper, P. I. Van Vliet and K. Vrieze, *J. Organometal. Chem., 105,* 379 (1976).
16 M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc. Dalton,* 2611 (1975).
17 F. A. Cotton, T. Inglis, M. Kilner and T. R. Webb, *Inorg. Chem., 14,* 2023 (1975).
18 J. D. Wilkins, *J. Organometal. Chem., 80,* 349 (1974)
19 R. Colton, *Coord. Chem. Rev., 6,* 269 (1971).
20 K. Nakamoto, 'The Infrared Spectra of Inorganic and Coordination Compounds', 2nd Ed., Wiley (1970), p. 160.
21 F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers (1973) p. 211.
22 M. S. Newman and H. A. Karnes, *J. Org. Chem., 31,* 3980 (1966).