Palladium(I) Carbonyl Halide Complexes

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Salts $(R_4N)_2[Pd_2X_4(CO)_2]$ [R = Pr^n, Bu^n, or pentyl (Pn^n); X = Cl or Br] have been prepared. From their i.r., and in some cases Raman, spectra it is concluded that they have carbonyl-bridged structures. The anions appear to be essentially planar in the solid $Pr^n{}_4N^+$ salts but in solution and as the salts of the larger cations they seem to be bent about the carbonyl bridge. I.r. spectra indicate that the polymeric complex $(PdXCO)_n$ (X = Cl or Br) has CO and X bridges alternately between palladium atoms. Phases of probable molecular forms $(Pr^n{}_4N)_2[Pd_4Cl_6(CO)_4]$ and $Pd_6Cl_6(CO)_6(PhCN)_2$ have been obtained and their i.r. spectra studied. The work indicates that a previous report of $[PdCl_2(H)CO]^-$ salts and a derived complex $[PdCl_2(CO)(AsPh_3)]$ is in error.

CARBONYL halide complexes of palladium(II) were first reported by Fink[1] in 1898, but Manchot *et al.*[2] were only able to confirm the one of composition $PdCl_2CO$. Stable chloride and bromide complexes $Bu^n{}_4N[PdX_3CO]$ are readily isolated from the reaction of CO with $(Bu^n{}_4N)_2[Pd_2X_6]$ in dichloromethane.[3]

In 1942 Gel'man and Meilakh[4] reported that, over several days, a saturated solution of diammonium tetrachloropalladate(II) in concentrated hydrochloric acid reacted with carbon monoxide to yield a green-yellow compound $NH_4[PdCl_2CO]$, and also isolated a number of other salts with this anion. They suggested that the ion was probably dimeric with bridging CO groups but, because of the lack of suitable techniques at that time, there was no real evidence to support such a structural formulation. This early report of a formally palladium(I) complex seems to have been substantially ignored by subsequent workers and reviewers.

Recently we have reported the preparation of chloride and bromide complexes of platinum(I),[5] $(Pr^n{}_4N)_2[Pt_2X_4(CO)_2]$, and have concluded from vibrational spectra that the metal atoms are linked and that there are no bridging groups. We were interested, therefore, to see if we could confirm the previous report of a palladium complex of comparable stoicheiometry and to investigate its structure.

Relatively recently there has been substantial interest in a polymeric palladium(I) complex, $(PdClCO)_n$. Dent *et al.*,[6] studying the carbonylation of allyl chloride in the presence of $PdCl_2$, reported an insoluble compound of such composition. However, Fischer and Vogler[7] claimed that repeating the aforementioned experiment, or allowing the complex $[PdCl_2(PhCN)_2]$ in chloroform to react with CO, resulted in the formation of $[Pd_2Cl(CO)_2]$. They listed some i.r. frequencies of their product. Schnabel and Kober[8] then found that the last mentioned reaction led to a yellowish green product PdClCO which had the same i.r. features and properties as '$Pd_2Cl(CO)_2$;'[7] they were also able to obtain this compound by reaction of palladium powder with carbon monoxide and phosgene in *o*-dichlorobenzene at elevated temperatures and pressure. A compound of the same composition was also obtained by Treiber[9] by the reaction of the complex $[Pd_2Cl_4(CO)_2]$ with a controlled amount of water (mol. ratio 2 : 1) in air or methanol but in this case the product was red-violet. None of this work contains any significant comment about the structure of the complex. Kushnikov *et al.*[10] studied the reaction of carbon monoxide with PdX_2 (X = Cl or Br) in the presence of methanol vapour or in dioxan containing known quantities of water. The composition of the solid product obtained depended on reaction conditions but a phase $(PdXCO)_n$ could be obtained for both halides and it was shown that in no case did the product contain any palladium metal even though one of the chloride phases obtained only had a chlorine : palladium ratio of 0·75 : 1. All the phases showed strong i.r. absorptions in the 1 900—2 000 cm^{-1} range but their number, energies, and relative intensities depended on chemical composition. Their energies have been correlated with the degree of reduction from palladium(II).[11] The compounds reacted with anhydrous acetonitrile or dimethylformamide to give palladium metal and from this observation it was concluded that they were polymeric compounds containing metal–metal bonds. There has been no discussion or speculation on the question of whether the CO or X groups are terminal or bridging. Since the compounds $(PdXCO)_n$ could be regarded as neutral precursers of the anions $[Pd_2X_4(CO)_2]^{2-}$ we were also interested in reinvestigating their structures.

RESULTS

Preparation and Isolation of Palladium(I) *Complexes*.—Disodium tetrachloropalladate(II) or dipotassium tetrabromopalladate(II) in concentrated aqueous hydrochloric or hydrobromic acids respectively react slowly with carbon monoxide at atmospheric pressure. In the case of the chloride system, the colour lightens over the course of *ca.* 2

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[1] E. Fink, *Compt. rend.*, 1898, **126**, 646.

[2] W. Manchot, *Ber.*, 1925, **58**, 2518; W. Manchot and J. König, *ibid.*, 1926, **59**, 883.

[3] M. G. Norton, Ph.D. Thesis, Bristol University, 1968.

[4] A. Gel'man and E. Meilakh, *Doklady Akad. Nauk S.S.S.R.*, 1942, **36**, 171.

[5] P. L. Goggin and R. J. Goodfellow, *J.C.S. Dalton*, 1973, 2355.

[6] W. T. Dent, R. Long, and G. H. Whitfield, *J. Chem. Soc.*, 1964, 1588.

[7] E. O. Fischer and A. Vogler, *J. Organometallic Chem.*, 1965, **3**, 161.

[8] W. Schnabel and E. Kober, *J. Organometallic Chem.*, 1969, **19**, 455.

[9] A. Treiber, *Tetrahedron Letters*, 1966, 2831.

[10] Yu. A. Kushnikov, A. Z. Belina, and V. F. Vodvizhenskii, *Russ. J. Inorg. Chem.*, 1971, **16**, 218.

[11] A. Z. Belina, Yu. A. Kushnikov, and V. F. Vodvizhenskii, *Russ. J. Phys. Chem.*, 1971, **45**, 404.

days from deep brown to golden yellow. These conditions are analogous to the ones in which ions $[Pt_2X_4(CO)_2]^{2-}$ were produced in the corresponding reactions[5] with $[PtX_4]^{2-}$. The progress of the reaction was conveniently monitored by extracting the complex anions from a portion of the solution with Bu^n_4NCl in dichloromethane and observing the i.r. spectrum in the 2 300—1 700 cm^{-1} range. In the case of the chloride there was, initially, growth of a band at 2 132 cm^{-1}, corresponding to the ion $[PdCl_3CO]^-$,[3] but this subsequently decreased in intensity as two other bands at 1 966 and 1 904 cm^{-1} grew. As the carbonylation proceeded further, a black deposit began to form at which stage the 2 132 cm^{-1} band was quite weak compared to that at 1 904 cm^{-1} (relative intensities *ca.* 1 : 50). In some experiments an additional band was found at 1 712 cm^{-1} but the variability of its intensity relative to the 1 904 cm^{-1} band shows that it is related to some additional by-product.

Bulk extraction of the product was also carried out with Bu^n_4NCl in dichloromethane, excess of Bu^n_4NCl being largely retained in the aqueous phase which loses all its colour. Unfortunately, we could not find a suitable medium from which to purify the desired product by recrystallisation. No precipitation occurred when Pr^n_4NCl was added to a dichloromethane solution of the $Bu^n_4N^+$ salts, but on removal of the solvent part of the residue was almost insoluble in dichloromethane or acetone, and had the empirical composition $Pr^n_4N[PdCl_2CO]$.

The reaction sequence for the corresponding bromide was analogous but the reaction was slower. After three times the period required for complete reaction of the chloride, the relative absorbances at 1 903 and 2 121 cm^{-1} were 5 : 1 and further enhancement of the ratio was very slow. The extract of the reaction mixture with Bu^n_4NBr again frequently showed an absorption at 1 709 cm^{-1} and after prolonged reaction times this was sometimes the most intense feature in the 2 200—1 700 cm^{-1} range. An orange product $Pr^n_4N[PdBr_2CO]$ was obtained by the same method as that for the corresponding chloride.

The $Pr^n_4N^+$ salts are only very slightly soluble in dichloromethane, acetone, and nitrobenzene (the bromide somewhat more so than the chloride) and the solutions slowly decompose even at room temperature. They are practically insoluble in chloroform and totally so in carbon tetrachloride, benzene, ether, and hexane. The solubility relations between $Pr^n_4N^+$ and $Bu^n_4N^+$ salts closely parallel those of corresponding derivatives of $[Pd_2X_6]^{2-}$ anions.

In order to allow more extensive studies of vibrational spectra to be made, we used the alternative approach of preparing $Bu^n_4N^+$ and $Pn^n_4N^+$ salts by reaction (1) with

$$PdXCO + R_4NX \xrightarrow[\text{or } CHCl_3]{CH_2Cl_2} R_4N[PdX_2CO] \qquad (1)$$

stoicheiometric proportions. For this experiment it was essential that all the reagents were thoroughly dried. Addition of n-hexane to the solution caused the desired product to separate out as a waxy solid or oil in the case of $Bu^n_4N[PdCl_2(CO)]$ or the $Pn^n_4N^+$ salts respectively. Although these were not good crystalline samples their i.r. spectra showed only, at most, very weak traces of other CO-containing species, and the elemental analyses indicated approximate agreement with the required stoicheiometry. When the salt $Pr^n_4N[PdCl_2(CO)]$ was washed with methanol it quite quickly turned violet-red and analyses of the product corresponded fairly well to a new phase Pr^n_4N-$[Pd_2Cl_3(CO)_2]$. The corresponding bromide was, however, essentially unaltered by the same treatment except for a slight superficial darkening.

We have confirmed the observation by Schnabel and Kober[8] that CO reacts with the complex $[PdCl_2(PhCN)_2]$ in chloroform to give $(PdClCO)_n$ but we have found that it is difficult to get a pure sample of $(PdBrCO)_n$ by Kushnikov's procedure,[10] the product being contaminated with a little dioxan and containing some palladium(II) bromide impurities. A better product was obtained by the reaction of dry CO with a suspension made by adding the complex $[PdBr_2(PhCN)_2]$ to chloroform. (Under these conditions the reactant is actually very finely divided $PdBr_2$.[12])

When benzene containing a small amount of benzonitrile was used as the solvent for the reaction of CO with the complex $[PdCl_2(PhCN)_2]$, a polymeric product of approximate composition $(PdClCO)_3PhCN$ was obtained. The i.r. spectrum of the product obtained from the complex $[PdBr_2(PhCN)_2]$ under the same conditions was similar in frequency and intensity pattern to that of the chloride but showed considerable contamination from $PdBr_2$ and thus an approximate composition could not be deduced by elemental analysis.

Vibrational Spectra and Molecular Structure.—$(R_4N)_2$-$[Pd_2X_4(CO)_2]$. I.r. and, where obtainable, Raman spectra of the ionic complexes $R_4N[PdX_2CO]$ are presented in Table 1. Measurements of Raman spectra in the carbonyl-stretching region were difficult because reduced laser power of long wavelength was generally necessary to avoid sample decomposition. For the ion $[PdCl_2CO]^-$ in hydrochloric acid, we were able to detect two features, 1 973m,p and 1 922vvw, and these correspond to i.r. bands, 1 972 and 1 922 cm^{-1}, in the same medium. In all other Raman measurements, we were only able to detect the stronger of these two bands. All other i.r. measurements in solution simply showed the corresponding two bands although they were always at somewhat lower energies for dichloromethane or chloroform solutions than for aqueous-acid solution.

CO-stretching bands in palladium(II) anions $[PdX_3CO]^-$ are some 30 cm^{-1} higher than in platinum analogues.[3] The platinum(I) chlorocarbonyl anion $[Pt_2Cl_4(CO)_2]^{2-}$ with terminal CO *cis* to the Pt–Pt bond has CO-stretching features at 2 047 and 2 027 cm^{-1} in dichloromethane[5] and we would certainly not expect a palladium complex of comparable structure to display CO bands at substantially lower wavenumbers. The polymeric platinum(0) carbonyl $[Pt(CO)_2]_n$ has CO-stretching bands at 2 068 and 1 891 cm^{-1} which must relate to terminal and bridging groups respectively.[13] Considering the balance of the effects (*a*) number of carbonyl groups around a metal atom, (*b*) oxidation number, and (*c*) ionic charge on the complex, the range 1 900—1 980 cm^{-1} is consistent with the CO groups in our complex being in a bridging position. This is higher than the wavenumber range normally associated with bridging carbonyls but CO-stretching energies are generally rather higher for complexes of the end members of the transition series.

In view of the stoicheiometry of the complex, the bridging role of the carbonyl groups, and the occurrence of only two CO-stretching features coincident between i.r. and Raman spectra it seems probable that the species is dimeric. In the large number of complexes which obey the 18-electron rule, a bridging-carbonyl group effectively

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[12] H. Frye, E. Kuljian, and J. Viebrock, *Z. Naturforsch.*, 1965, **20b**, 269.

[13] G. Booth, J. Chatt, and P. Chini, *Chem. Comm.*, 1965, 639.

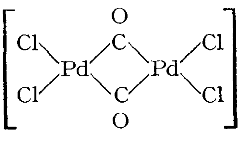
TABLE 1

Vibrational spectra (2 300—1 700 and below 700 cm^{-1}) of the ions [Pd$_2$X$_4$(CO)$_2$]$^{2-}$ (X = Cl or Br)

	(Pr$^n_4$N)$_2$[Pd$_2$Cl$_4$(CO)$_2$]				(Bu$^n_4$N)$_2$[Pd$_2$Cl$_4$(CO)$_2$]		(Pr$^n_4$N)$_2$[Pd$_2$Cl$_4$(CO)$_2$]	(Pr$^n_4$N)$_2$[Pd$_2$Br$_4$(CO)$_2$]			(Pr$^n_4$N)$_2$[Pd$_2$Br$_4$(CO)$_2$]
	I.r.$_{\text{mull}}$	I.r.$_{\text{CH}_2\text{Cl}_2}$	R$_{\text{Solid}}$	R$_{\text{conc.HCl}}$	I.r.$_{\text{mull}}$	I.r.$_{\text{CH}_2\text{Cl}_2}$	I.r.$_{\text{oil}}$	I.r.$_{\text{mull}}$	I.r.$_{\text{CH}_2\text{Cl}_2}$	R$_{\text{solid}}$	I.r.$_{\text{oil}}$
CO str. $A_g(A_1)$ †	1 963vw	1 969m	1 962s	1 973s,p	1 960s	1 966m	1 964m	1 958w	1 966m		1 963m
B_{2u} (B_2)	1 905vs	1 907vs		1 922vvw	1 898vs	1 904vs	1 907vs	1 903vs	1 905vs		1 905vs
PdCO bend	663w,sh				656w,sh			655wm			
	638vs			636vvw	629s		623s	604s			628sh
	620vs			604vvw	606ms						590vs
PdC str. A_g (A_1)			406s	419vs,p							
B_{1g} (A_2)			425m								
B_{2u} (B_2)	404wm,bd				394w			388w			378w,bd
B_{3u} (B_1)	467m				455wm		453wm	458w			443w
Pd**X** str. A_g (A_1)			*314*m	*308*s,p	*315*wm		*315*w	*256*w		*264*m	*243*ms
B_{1g} (A_2)			*229*m							*186*m *	
B_{2u} (B_2)	*260*vs				*260*ms		*261*sh	*186*s			*194*s
B_{3u} (B_1)	*272*vs			*286*vw,dp	*272*s		*273*s	*197*s			
Other CO-region bands	1 952vw				2 137vvw ‡		2 123w ‡	1 872m			2 115w ‡
	1 948vw				2 120vw ‡		1 880sh	1 832w,bd			2 055vw
	1 876m				1 948vw		1 847w,bd				2 040vw
					1 939vw						1 875w,sh
					1 874wm						1 835vw,bd
					1 866wm						
Other anion bnads	144w		457w		195w		198vvw	99vw		*140m* *	147vw
	108m		190wm		145w		144vvw	90w			113vw
	ca. 50m,bd		134s		117w		112w,bd				*ca.* 90m,bd
			123sh		104m						
Other bands	519w §			522vw §	535vw §		581w,bd §	518vw §			540sh §
	513w §			473w,dp §	523vw §		473w,bd §	360vw §			475wm §
	360vw§			378vw,p §	481w §			240vvw			463w ‡
	343vw §			337vw,dp	360vw §						360vvw
											264w,sh ‡
Limit of study	(40)	(1 700)	(100)	(260)	(40)	(1 700)	(40)	(40)	(1 700)	(120)	(40)

* Alternative assignments. † Descriptions based on Pd–Pd as *x* direction, C–C as *y*. ‡ Pd^{II} impurity. § Cation.

contributes a total of two electrons to the metal atoms; accordingly, if our dimeric anions contain four terminal halides and two bridging carbonyl groups, each palladium atom carries 15 valence-shell electrons. 16-Electron complexes of Pd^{II}, Pt^{II}, Rh^{I}, and Ir^{I} always display square-planar co-ordination about the metal atom. Thus the simplest structure likely for $[Pd_2X_4(CO)_2]^{2-}$ would appear to be D_{2h}, (I). The complex is diamagnetic and thus the odd electrons on each palladium atom must spin pair (= Pd–Pd bond). On a simple crystal-field picture for a square-planar complex, the odd *d* electrons would be in the in-plane interaxial *d* orbitals which are of space and symmetry appropriate for such Pd–Pd bonding. The CO-stretching region spectra of solutions are not compatible with D_{2h} symmetry but dimeric complexes of this type can display square-planar geometry about the metal without being planar overall {*e.g.* $[Rh_2Cl_2(CO)_4]$ [14]}. Indeed, the overlap of *d* orbitals on the adjacent palladium atoms might be optimised by bending the structure about the bridging CO groups.



(I)

A notable feature of the i.r. spectra is the strong absorption around 600 cm^{-1}. This region is free of activity in the complexes $[PdX_3CO]^-$, $[PtX_3CO]^-$, $[PtX_2(CO)_2]$, and $[Pt_2X_4(CO)_2]^{2-}$ which contain only terminal CO groups. Noack,[15] in a temperature study of $[Co_2(CO)_8]$ in hexane, showed that the CO-bridged form displayed strong bands near 600 cm^{-1}, presumably arising from CoCO bending modes, but that these are absent from the Co–Co bonded form for which the nearest band is 529 cm^{-1}. In comparison with the platinum(I) complex this is further evidence that the CO groups in the palladium(I) complex are bridging.

For the solid $Pr^n_4N^+$ salts, the i.r. feature near 1 960 cm^{-1} is exceedingly weak relative to that near 1 900 cm^{-1}, about 1 : 100 for the chloride and 1 : 70 for the bromide. We presume that in this state the anions must approximate quite closely to a D_{2h} structure; indeed had these been the only derivatives studied and had we not measured solution spectra, we would almost certainly have argued that the higher-frequency band and the other, mostly weak, bands observed in the carbonyl region were simply lattice effects since it is quite common to observe a multitude of weak CO bands in i.r. spectra of mulls of metal carbonyls. We will consider the low-frequency spectra of these complexes on the D_{2h} basis.

For the chloride (Figure 1) there are only two i.r. bands in the region that could be associated with Pd–Cl stretching, 271 and 260 cm^{-1}, and two Raman bands, 314 and 229 cm^{-1}. All these are absent from spectra of the bromide, for which the i.r. shows new bands at 197 and 185 cm^{-1}, and the Raman spectrum, 264, 186, and 140 cm^{-1}, the middle or lowest band of which could correspond to the feature at 190 cm^{-1} in the chloride.

In the complex $[Pt_2X_4(SMe_2)_2]$, which has SMe_2 as a bridging group,[16] the total Pt–X stretching energy spread is 15 and 11 cm^{-1} respectively for chloride and bromide,[17] and it seems common that in dimeric complexes with bridging groups between the metal atoms there is very little energy difference between terminal MX vibrations which only have 180° phase difference in the nature of the motion at the two metal atoms.[18,19] For the ions $[Pt_2X_4(CO)_2]^{2-}$ the stretching vibrations associated with the two Pt–Cl bonds separated by a Pt–Pt bond are 268 and 240 cm^{-1} for the chloride and 218 and 172 cm^{-1} for the bromide. The symmetric mode is the higher energy but the spread in these cases could just be the result of coupling of this mode with Pt–Pt bond stretching. In view of this, the difference of 85 cm^{-1} between the A_g and B_{1g} vibrations in the ion $[Pd_2Cl_4(CO)_2]^{2-}$ seems extraordinarily large; if the assignment is correct, this may be the result of the rather different relative displacements of the palladium atoms during the vibrations and their effects on the Pd–Pd bond.

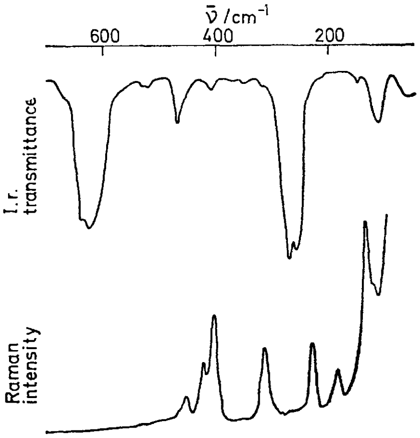


FIGURE 1 I.r. and Raman spectra (below 700 cm^{-1}) of the salt $(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$

M–C Stretching features are generally more intense than MCO bending ones in Raman spectra, suggesting that 425 and 406 cm^{-1} should be assigned as the former. The i.r. bands at 467 and 404 cm^{-1} seem to be the most probable counterparts and show a shift to lower wavenumbers in the corresponding bromide.

Figure 2 shows the CO-stretching region of the i.r. spectra of the solid $Pr^n_4N^+$, solid $Bu^n_4N^+$, and oily $Pn^n_4N^+$ salts of $[Pd_2Cl_4(CO)_2]^{2-}$. It is evident from the relative intensities of the bands near 1 900 and 1 960 cm^{-1} that the deviation from planarity is greatest in the $Bu^n_4N^+$ salt; the situation is reminiscent of the complex $[Rh_2Cl_2(CO)_4]$ in which the totally symmetric vibration, which would have been i.r. inactive in a planar structure, shows similar i.r. intensity to the other two vibrations which would have been active even in a D_{2h} structure.[20] The $Pn^n_4N^+$ oil is intermediate in intensity behaviour, which is the same as that of solutions. The $Bu^n_4N^+$ salt also showed i.r. bands below 400 cm^{-1} (315, 195, and 117 cm^{-1}) which were absent in the $Pr^n_4N^+$ salt but had counterparts in its Raman spectrum. There was no

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[14] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

[15] K. Noack, *Helv. Chim. Acta*, 1964, **47**, 1555.

[16] P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

[17] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1974, in the press.

[18] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

[19] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc.* (*A*), 1971, 2031.

[20] C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, 1962, **45**, 1094.

i.r. feature near 230 cm^{-1}. Transformation from a D_{2h} to a C_{2v} state causes A_g and B_{1g} vibrations to become A_1 and A_2 respectively, only the former thus becoming i.r. active. This evidence reinforces the assignments proposed for the PdCl vibrations in the Raman spectrum of the $Pr^n_4N^+$ salt. The intensity of the 315 cm^{-1} feature relative to the 273 cm^{-1} band is lower for the $Pn^n_4N^+$ salt than for the $Bu^n_4N^+$ salt, in keeping with the interpretation from the CO-stretching region. Parallel comparisons can be made between solid $Pr^n_4N^+$ and oily $Pn^n_4N^+$ bromide salts.

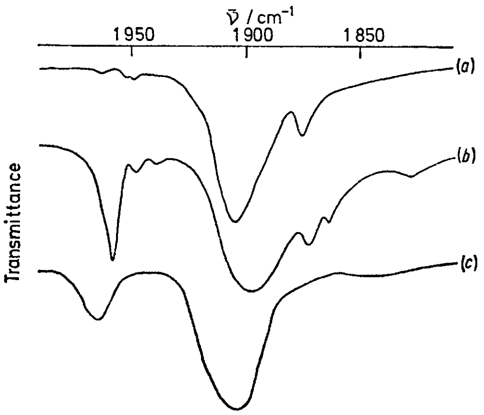


FIGURE 2 I.r. spectra of the ion $[Pd_2Cl_4(CO)_2]^{2-}$ in the CO-stretching region: (a) $Pr^n_4N^+$ (mull); (b) $Bu^n_4N^+$ (mull); (c) $Pr^n_4N^+$ salt (oil)

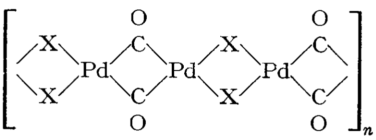
$(PdXCO)_n$. I.r. frequencies of $(PdXCO)_n$ are listed in Table 2, those of the chloride being in good agreement with the ones previously reported for that range of the spectrum studied in common.[7,8] Unfortunately the complexes were so readily decomposed by the laser beam that Raman spectra could not be recorded. The spectra are free from any features of PhCN, or any Pd^{II} carbonyl complexes. The CO-stretching region is dominated in each case by an extremely intense, broad band which is some 50—70 cm^{-1} higher than in the derived $Pr^n_4N^+$ salts, as would be expected for closely related structures differing in overall negative charge {*cf.* the i.r.-active CO feature in $[Pt_2Cl_4(CO)_2]$ is 2 146 cm^{-1} (ref. 21) and in $[PtCl_3CO]^-$ it is 2 096 cm^{-1} (ref. 3)}.

TABLE 2

I.r. spectra (above 40 cm^{-1}) of $(PdXCO)_n$ mulls

$(PdClCO)_n$	
CO str.	2 023vvw, 2 002vw, 1 978vs,bd, 1 951vvw,sh, 1 936vw
PdCO def.	668sh, 620vs,bd, 585s,bd
PdC str.	433m, 385m; PdCl str. 304vw,sh, 262vs, 221s
Other bands	859vvw, 808w, 768vvw,bd, 492vvw,bd, 362vw,sh, 116w, 90m
$(PdBrCO)_n$	
CO str.	2 008vvw,sh, 1 996vw, 1 987w, 1 953vs,bd, 1 938sh, 1 922wm
PdCO def.	644m, 588vs,bd, 544sh
PdC str.	425m, 378m, PdBr str. 194vs, 179sh
Other bands	847w, 791wm, 740w, 478wm,bd, 362vw,sh, 263vw, 229m, 80m

The overwhelming dominance of one feature in this region suggests a structure, (II), in which all bridges are planar. In keeping with the higher CO energies, the two most-intense bands assigned as Pd–C stretching energies are correspondingly lower than in the anions. The strong bands near 600 cm^{-1} are an additional indication that the CO groups are still bridging. The polymeric structure differs most from the anions in having bridging instead of terminal halide. For the chloride there are two strong bands at 262 and 221 cm^{-1}, and it seems that a band near 220 cm^{-1} is a good indication of bridging chloride in these palladium(I) systems. For the bromide, the strong band at 194 cm^{-1} with its low-energy shoulder seem the natural relatives of the two strong bands in the chloride since there are no other bands between these and 80 cm^{-1}. The band at 229 cm^{-1} seems too high in energy and too low in intensity to relate to either of the two strong bands in the chloride.



(II)

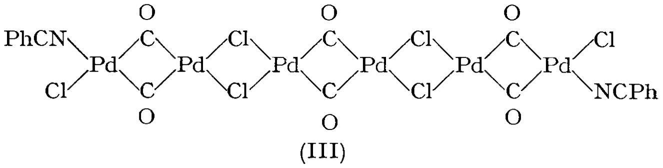
The polymeric structure of these relatively reactive complexes is likely to be periodically terminated by some foreign end-group and, whatever its nature, this should lead to different activities around the terminus. It seems probable that at least some of the additional very weak CO features arise from such a cause. An interesting aspect of the proposed structure is that the singly occupied *d* orbitals are aligned such that a degree of Pd–Pd bond delocalisation is possible along the chain, albeit with alternate short and long spacings.

$(PdClCO)_3PhCN$. The i.r. bands of the phase approximating to this composition are listed in Table 3. The simplest structure based on full square-planar co-ordination is (III). The three strongest CO bands seem reasonably compatible with such a structure with probable assignments: 1 979m as the central asymmetric stretch [*cf.* $(PdCOCl)_n$]; and 1 954s and 1 948s as those near the end of the chain, *trans* to Cl and to PhCN.

TABLE 3

I.r. spectrum (below 2 500 cm^{-1}) of the complex $[Pd_6Cl_6(CO)_6(PhCN)_2]$

CO str.	1 979m, 1 954s, 1 948s, 1 917wm
PdCO bend	642sh, 620s, 592sh
PdC str.	445w, 412vw, 391w
PdCl str.	317vw, 283w, 260sh, 250s, 221s
PhCN	2 296s, 1 596m, 1 491m, 1 449s, 1 348vw, 1 292w, 1 203wm, 1 180wm, 1 168w, 1 093vw, 1 067w, 1 028wm, 999w, 976vw, 932w, 759s, 682s, 550m 357wm, 331wm
Other bands	880vw, 820w, 137vw, 114w



(III)

$(Pr^n_4N)_2[Pd_4Cl_6(CO)_2]$. The i.r. bands observed for the phase approximating to this composition are listed in Table 4. The sharpness of the three CO bands suggest that

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[21] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1958, 2283.

it is a single compound and not a mixture of $(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$ and $(PdClCO)_n$. The band pattern is not consistent with a totally planar structure or with a C_{2h} centrosymmetric corregated structure. To judge from the complex $[Rh_2Cl_2(CO)_4]$,[20] a C_{2h} boat structure should show three CO features but with the close pair of CO bands being higher than the third, single, one rather than as observed. A structure in which one of the carbonyl bridges is planar whilst the other is bent would best fit the observation since, although a C_s system should display four CO features, that associated with symmetric stretching in the planar bridge is still probably fairly weak in the i.r. spectrum; this suggested structure must be regarded as somewhat speculative.

TABLE 4

I.r. spectrum (2 300—1 700 and 700—40 cm^{-1}) of the salt $(Pr^n_4N)_2[Pd_4Cl_6(CO)_4]$

CO str.	1 995vw, 1 964vs, 1 918vs, 1 906vs, 1 876w, 1 855vw, 1 845sh
PdCO bend	636sh, 619s, 584sh
PdC str.	483vw, 467vw, 437w, 390w,bd
PdCl str.	272m, 257m, 243sh, 223m
Other bands	310vvw, 180sh, 144vw, 108wm

DISCUSSION

Kingston and Scollary[22] have reported that CO reacted with palladium(II) chloride in acidified 2-methoxyethanol to give a yellow solution from which a $AsPh_4^+$ salt could be precipitated by addition of $AsPh_4Cl$. They concluded from the presence of a weak i.r. band at 1 960 and a strong one at 1 900 cm^{-1} that the complex was $AsPh_4[PdCl_2(H)CO]$, with the former band being the Pd–H stretch. However, we recently observed the platinum analogue of such a species[5] in which ν(CO) appeared at 2 070 and ν(PtH) at 2 208 cm^{-1} and this demonstrates that a band at 1 900 cm^{-1} is far too low for such a palladium(II) complex. Clearly, they had obtained the salt $(AsPh_4)_2[Pd_2Cl_4(CO)_2]$ and the conductivity evidence which supported the 1 : 1 electrolyte formulation would also be in keeping with the 2 : 1 electrolyte structure. We have checked both the reaction medium (*ca.* 1M in Pd) and a $Bu^n_4N^+$ extract in CH_2Cl_2 (*ca.* 1M in Pd) and find no trace of ^1H resonance in the range τ 10—40 (for $[PtCl_2(H)CO]^-$ it occurs at τ 25·12).[5] They also reported that the salt formed a red derivative $[PdCl_2(CO)AsPh_3]$ with CO-stretching bands at 1 900s and 1 870w in chloroform; again, these seem too low for such a compound in comparison with *cis*-$[PtCl_2(CO)AsEt_3]$ for which it occurs[21] at 2 111 cm^{-1}. We have found that reaction of $AsPh_3$ in methanol with the salt $(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$ gives a brown complex with the CO region dominated by an i.r. absorption at 1 861vs cm^{-1} for the solid, and 1 896vs and 1867m for a dichloromethane solution. It is clearly the same product as that reported previously but its stoicheiometry corresponds to $PdCl(CO)AsPh_3$. We do not feel able to propose a structure for this species on the basis of the i.r. spectra, which we cannot reconcile with a CO-bridged dimeric structure.

It has been pointed out[23] that where metal carbonyl halide species are dimeric or polymeric they are invariably halogen- and *not* carbonyl-bridged. The anions $[Pd_2X_4(CO)_2]^{2-}$ therefore appear to be the first examples of a new mode of bonding. The reason for this is almost certainly that the previously documented dimeric or polymeric carbonyl halides are derivatives of metals in oxidation states where there are no odd electrons to be spin paired, except of course for $[Pt_2Cl_4(CO)_2]^{2-}$ which is Pt–Pt bonded. In the ions $[Pd_2X_4(CO)_2]^{2-}$, the palladium atoms would be separated by about 340 and 350 pm for chloride[24] and bromide[15] bridges respectively but for CO bridges the separation would be *ca.* 260 pm to judge from $\{Rh(C_5H_5)CO\}_3$.[25] The direct Ru–Ru bond in $[Ru_3(CO)_{12}]$ is 285 pm[26] and the Hg–Hg bond in Hg_2F_2 is 243 pm.[27] It is clear, therefore, that carbonyl bridging provides a much more suitable metal-atom separation for Pd–Pd bonding than halide bridging would.

The distinction between the structures adopted by the palladium and platinum complexes is a further example of the greater tendency to direct metal–metal bonding as a group is descended in the Periodic Table (ref. 23, p. 691). The difference may arise either because the *d*-orbital radius is more suitable for metal–metal bonding in the heavier element [platinum(II) 5*d* orbitals act as better π-electron donors than palladium(II) 4*d* orbitals], or because with the lower nd–$(n + 1)s$ orbital energy separation in platinum an appropriate hybridised orbital is more favourable.[28] The tendency is also well reflected by the lower stability of Cd_2^{2+} compared to Hg_2^{2+}, the force constant of the former being only about half that of the latter.[29]

The present work adds considerably to the knowledge of palladium(I) chemistry. The only other complexes which appear to contain this state are $[PdAl_2Cl_7(C_6H_6)_2]$,[30] $[Pd(C_6H_6)(H_2O)ClO_4]_n$,[31] and $[Pd_2X_2(Bu^tNC)_4]$[32] (X = Cl, Br, or I). The last complexes are believed to be halide bridged, but we regard the spectroscopic evidence as not necessarily conclusive on this point.

EXPERIMENTAL

Details relevant to the measurement of the vibrational spectra have been presented previously.

Preparation of Complexes.—$(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$. Hydrated disodium tetrachloropalladate(II) (4 g) and conc.

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[22] J. V. Kingston and G. R. Scollary, *Chem. Comm.*, 1969, 455.

[23] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 707.

[24] J. N. Dempsey and N. C. Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4987.

[25] O. S. Mills and E. F. Paulus, *Chem. Comm.*, 1966, 815.

[26] R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1968, 778.

[27] D. Grdenic and C. Djordjevic, *J. Chem. Soc.*, 1956, 1316.

[28] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[29] J. D. Corbett, *Inorg. Chem.*, 1962, **1**, 700; T. G. Spiro, *Progr. Inorg. Chem.*, 1970, **11**, 1.

[30] G. Allegra, A. Immirzi, and L. Parri, *J. Amer. Chem. Soc.*, 1965, **87**, 1394; G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Parri, and G. Vitulli, *ibid.*, 1970, **92**, 289.

[31] J. M. Davidson and C. Triggs, *J. Chem. Soc. (A)*, 1968, 1324.

[32] S. Otsuka, Y. Tatsuno, and K. Ataka, *J. Amer. Chem. Soc.*, 1971, **93**, 6705.

hydrochloric acid (20 cm^3) were stirred together in a flask (3 l) filled with carbon monoxide. Over 2—3 days in winter daylight (the reaction was virtually complete after only 1 day in summer) the solution turned a yellowish brown colour and a small amount of a black deposit started to form. The reaction mixture was filtered and shaken with two portions of Bu^n_4NCl (2 g) in dichloromethane (50 cm^3) and the organic phase was separated and dried over dry $MgSO_4$. After filtration, Pr^n_4NCl (3 g) in dichloromethane (30 cm^3) was added and the solvent removed on a rotary evaporator at room temperature. All readily soluble material was extracted from the residue with 80, 10, 10, and 10 cm^3 aliquot portions of acetone leaving the bright greenish yellow *solid* (2·7 g) (Found: C, 40·25; H, 7·35; Cl, 18·25; N, 3·6. Calc. for $C_{26}H_{56}Cl_4N_2O_2Pd_2$: C, 39·85; H, 7·2; Cl, 18·1; N, 3·6%). The product darkens above 155 °C and melts at 170 °C with decomposition. The salt $(Pr^n_4N)_2[Pd_2Br_4(CO)_2]$ was similarly prepared from K_2PdBr_4 over 3—4 days in 45% yield. The orange *product* darkens above 145 °C and melts with decomposition at 180 °C (Found: C, 32·4; H, 6·1; Br, 33·55; N, 2·85. Calc. for $C_{26}H_{56}Br_4N_2O_2Pd_2$: C, 32·5; H, 5·85; Br, 33·25; N, 2·9%).

$(R_4N)_2[Pd_2X_4(CO)_2]$ (R = Bu^n *or* Pn^n). Solid $[PdXCO]_n$ (0·2 g) was added in small portions to a stirred, dry dichloromethane (20 cm^3) solution containing the equivalent quantity of R_4NX (0·5 h). Only small traces of a black solid remained undissolved, and the solutions became yellow (Cl) or yellow-orange (Br). The solution was filtered into dry n-hexane (80 cm^3) and an oily film covered the walls of the flask. The supernatant liquid was poured off and replaced by a fresh portion of n-hexane, and the flask shaken. Replacing the liquid a number of times and repeated shaking caused the Bu^n_4N salts to turn to a waxy yellow *solid* which was dried *in vacuo* {Found: C, 46·35; H, 8·3; Cl, 15·15; N, 3·4. $(Bu^n_4N)_2[Pd_2Cl_4(CO)_2]$ requires C, 45·6; H, 8·1; Cl, 15·85; N, 3·15%}, 83% yield. The $Pn^n_4N^+$ salts remained as *oils* but were pumped to remove most of the included solvent {Found: C, 48·8; H, 8·3; N, 2·7. $(Pn^n_4N)_2[Pd_2Cl_4(CO)_2]$, deep yellow, requires C, 50·05; H, 8·8; N, 2·8. Yield 78%. Found: C, 42·1; H, 7·15; N, 2·35. $(Pn^n_4N)_2[Pd_2Br_4(CO)_2]$, yellow-brown, requires C, 42·55; H, 7·5; N, 2·35. Yield 91%}.

$[PdClCO]_n$. This complex was prepared by the reaction of carbon monoxide with $[PdCl_2(PhCN)_2]$ in dry chloroform.[8] The yellow-green *product* decomposes at *ca.* 230 °C (Found: C, 7·45; Cl, 20·65. Calc. for CClOPd: C, 7·05; Cl, 20·85%).

$[PdBrCO]_n$. This complex was prepared by passing CO through a stirred suspension made by adding $[PdBr_2(PhCN)_2]$ (0·7 g) to dry chloroform (250 cm^3). Over 1·5 h the colour of the suspended solid lightened from brown to yellow. The very finely divided solid was separated with a centrifuge, washed with dry benzene, and dried *in vacuo*. The yellow *compound* darkens above 145 °C and turns black at 200 °C. Yield 57% (Found: C, 5·65; Br, 37·4. Calc. for CBrOPd: C, 5·6; Br, 37·25%).

$(Pr^n_4N)_2[Pd_4Cl_6(CO)_4]$. A quantitative yield of this phase was obtained by soaking the salt $(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$ in methanol (10 min), decanting the solvent, and drying *in vacuo* (Found: C, 28·75; H, 5·1; Cl, 17·95; N, 2·7. Calc. for $C_{28}H_{56}Cl_6N_2O_4Pd_4$: C, 29·9; H, 5·0; Cl, 18·9; N, 2·5%).

$[PdCl(CO)]_6(PhCN)_2$. The complex $[PdCl_2(PhCN)_2]$ (1·5 g) was dissolved in benzene (80 cm^3) containing benzonitrile (1 cm^3) and allowed to react with carbon monoxide for 5 h. The yellow precipitate was washed with hexane and dried *in vacuo* (Found: C, 19·6; H, 1·15; Cl, 19·2; N, 2·7. Calc. for $C_{18}H_{10}Cl_6N_2O_6Pd_6$: C, 19·6; H, 0·8; Cl, 17·3; N, 2·5%).

$[PdCl(CO)(AsPh_3)]_2$. An equivalent amount of $AsPh_3$ was dissolved in the minimum volume of methanol. Solid $(Pr^n_4N)_2[Pd_2Cl_4(CO)_2]$ was covered with a little methanol and the $AsPh_3$ solution added dropwise over 1 h with constant stirring. The colour of the solid changed to chocolate brown. The insoluble product was collected, washed with methanol, and dried. It was purified by dissolving in dichloromethane and filtering into n-hexane from which the product precipitated. Yield 84%. The *compound* decomposes at 110 °C (Found: C, 47·9; H, 3·2; Cl, 7·45. Calc. for $C_{19}H_{15}AsClOPd$: C, 47·3; H, 3·5; Cl, 8·0%). I.r. spectrum: (mull, 2 200—1 750 and 700—40 cm^{-1}) 1 963m, 1 918w; 1 890vw; 1 861vs; 1 816vvw; 688vs; 673sh; 635vw; 615w; 541w; 472vs; 463vs; 436sh; 423vw; 398vw; 362vw; 345wm; 332s; 329s; 317m; 297w; 275w; 240vw; 214w; 205vw; 186vw; 96vw; (in CH_2Cl_2, 2 200—1 700) 1 976vw; 1 896vs; 1 867m; and 1 815vw cm^{-1}.

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