Preparation and Nuclear Magnetic Resonance Study of Salts of the Platinum(I) Anions $[Pt_2X_4(CO)_2]^{2-}$ (X = Cl, Br, or I)

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Reactions of the anions $[PtX_3(CO)]^-$ (X = Cl, Br, or I) with controlled amounts of formic acid and tri-n-propylamine in tetrahydrofuran lead to high yields of salts of $[Pt_2X_4(CO)_2]^{2-}$ if appropriate cations are chosen. For Cl and Br derivatives with ^{13}C-enriched CO (75%) ^{195}Pt and ^{13}C n.m.r. studies are reported and values of $^1J(PtPt)$ established. At 300 K there is exchange of CO between adjacent platinum atoms. Studies of ^{195}Pt Fourier-transform n.m.r. spectra of the mixed halide species $[Pt_2X_nY_{4-n}(CO)_2]^{2-}$ (X,Y = Cl,Br; Cl,I; or Br,I) are interpreted on the basis of a marked preference for isomers with the higher atomic number halide on the Pt–Pt axis. For the Cl,Br system comparison between spectra obtained at 220 and at 300 K shows that at the higher temperature halide site exchange occurs on a given Pt atom, but is synchronised between both Pt atoms in the anion; this is interpreted in terms of the interplatinum atom exchange of the CO groups *via* CO bridging. Studies of the mixed halide species derived from $[PtX_3(CO)]^-$ establish ^{195}Pt shifts for fourteen of the eighteen possible species, and show that species with lower atomic number halide *trans* to CO are preferred.

The previously reported preparation of salts of the platinum(I) anions $[Pt_2X_4(CO)_2]^{2-}$ (X = Cl or Br) involved stirring a solution of PtX_2 in aqueous HX under an atmosphere of carbon monoxide for several days.[1] Whilst this procedure leads to good yields of $[NPr^n_4]_2[Pt_2Cl_4(CO)_2]$, it is less successful for the bromo-analogue. Further, it is inefficient in its use of CO, making it unsuitable for the preparation of the ^{13}C-enriched complexes which we particularly desired for n.m.r. study. We have, therefore, investigated an alternative route to these anions.[2]

The previous study[1] demonstrated the reversible reaction (i) and that a similar reaction (ii) involving dihydrogen occurred. This suggests that the hydrido-carbonyl anion

$$[PtCl_2H(CO)]^- + [PtCl_3(CO)]^- \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} [Pt_2Cl_4(CO)_2]^{2-} \quad \text{(i)}$$

$$2[PtCl_2H(CO)]^- \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} [Pt_2Cl_4(CO)_2]^{2-} \quad \text{(ii)}$$

$[PtCl_2H(CO)]^-$ might be a useful intermediate. Cortese and Heck[3] have proposed the formation of a palladium hydride by elimination of CO_2 from a formate in palladium-catalysed reductions by formic acid plus tertiary amines, and recently Roberts *et al.*[4] have demonstrated the insertion of CO_2 into a Re–H bond to give a co-ordinated formate. We have investigated the possibility of using formate to form the hydrido-carbonyl anion *via* equation (iii).

$$[PtCl_3(CO)]^- \xrightarrow[-Cl]{+HCO_2^-} [PtCl_2(HCO_2)(CO)]^- \xrightarrow{-CO_2} [PtCl_2H(CO)]^- \quad \text{(iii)}$$

Results

The reaction of $[NBu^n_4][PtCl_3(CO)]$ (ν_{CO} 2 098 cm^{-1}) with one equivalent of $[NBu^n_4]HCO_2$ (prepared *in situ* in dichloromethane) was followed by i.r. measurements of the C–O stretching region. This showed the ready conversion into $[Pt_2Cl_4(CO)_2]^{2-}$ (ν_{CO} 2 047 and 2 027 cm^{-1}), but as the reaction reached completion (*ca.* 1 h) rapid decomposition occurred. Although the Pt^I anion might result from the hydrido-carbonyl *via* reaction (ii), it could also be formed *via* reaction (i) with unchanged formate assisting in the removal of hydrogen chloride (iv). This function may be replaced by trimethylamine and the same base used to release formate from formic acid. Thus we find the reaction still goes to completion if half an equivalent of formic acid with a ten-fold excess of trimethylamine is used, following the overall reaction (v). Rapid decomposition did not occur but there

$$HCl + HCO_2^- \rightleftharpoons Cl^- + HCO_2H \quad \text{(iv)}$$

$$2[PtCl_3(CO)]^- + HCO_2H + 2NMe_3 \longrightarrow [Pt_2Cl_4(CO)_2]^{2-} + CO_2 + 2[NMe_3H]Cl \quad \text{(v)}$$

was some darkening of the solution and isolation of the product proved difficult. The reaction of trimethylamine with dichloromethane could produce undesirable reactive species, so we have explored the use of other solvents.

Satisfactory conversion occurred in acetone solution using only a slight excess of NMe_3 [with respect to equation (v)], and although there was some darkening of the solution, a good yield of $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ was obtained after separation from $[NMe_3H]Cl$. However, i.r. measurements on the reaction medium show the presence of an additional species with C–O stretching at 2 066 cm^{-1}; this complex predominates if the mixture is left for several days. We have been unable to characterise this by-product fully but believe it to be of the type $[PtCl_2R(CO)]^-$ where R is an organic fragment derived from the action of trimethylamine on acetone. The by-product is not formed when tetrahydrofuran (thf) is used as the solvent. Being sparingly soluble in thf, $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ crystallises out as the reaction proceeds and its isolation is further facilitated if NPr^n_3 is employed as the base. As a preparative procedure (see Experimental section for details) it regularly gives yields of more than 70%.

The bromo-anion can be similarly obtained in good yield but the reaction is slower. The rate is increased when more base is used; we used the ratio (Pt : HCO_2H : NPr^n_3) 2 : 1 : 3.2.

The previous route to Pt^I carbonyl anions did not lead to an iodo-derivative. This is produced by the new formate route but the reaction is very slow if only a slight excess of amine is used. A three-fold excess of amine increased the rate, and conversion of $[NBu^n_4][PtI_3(CO)]$ into $[NBu^n_4]_2[Pt_2I_4(CO)_2]$ (CO stretch 2 032 and 2 016 cm^{-1}) was almost complete after 3

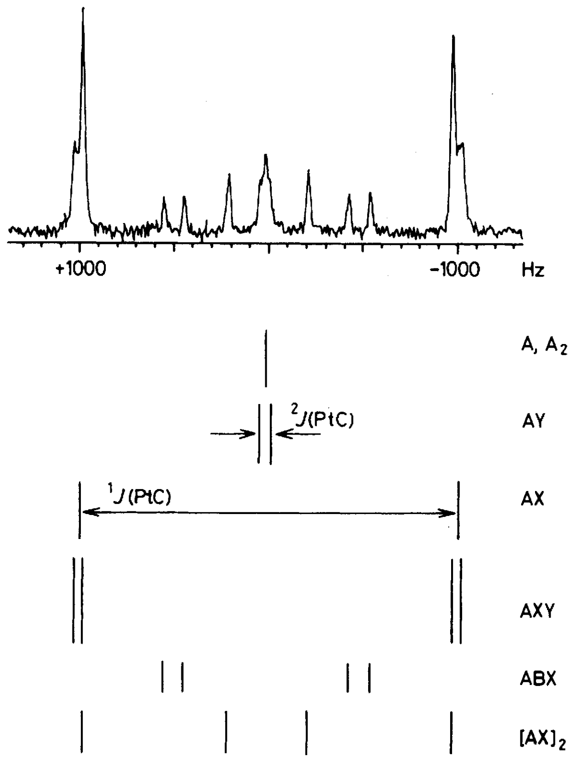


Figure 1. ^{195}Pt Fourier-transform n.m.r. spectrum of $[NBu^n{}_4]_2[Pt_2Br_4(CO)_2]$ (^{13}CO-enriched; *ca.* 75%) at *ca.* 220 K, made up of the following spin systems: A($-^{195}$Pt$-$ $-$), A$_2$($-^{195}$Pt$-$ ^{195}Pt$-$), AY ($-^{195}$Pt$-$ $-^{13}$C), AX (^{13}C$-^{195}$Pt$-$ $-$), AXY (^{13}C$-^{195}$Pt$-$ $-^{13}$C), ABX (^{13}C$-^{195}$Pt$-^{195}$Pt$-$), and [AX]$_2$ (^{13}C$-^{195}$Pt$-^{195}$Pt$-^{13}$C); for further details of analysis see Experimental section

Table. N.m.r. parameters of $[NBu^n{}_4]_2[Pt_2X_4(CO)_2]$ (X = Cl or Br) [a]

	$[Pt_2Cl_4(CO)_2]^{2-}$	$[Pt_2Br_4(CO)_2]^{2-}$
$\delta(^{13}C)$ (p.p.m.)	159.2	159.8
$\delta(^{195}Pt)(Pt-^{12}C)$ [b]	371	192
^1J(PtC)/Hz	$\pm 2\,000 \pm 2$	$\pm 2\,007 \pm 2$
^2J(PtC)/Hz	$\mp 48 \pm 2$	$\mp 48 \pm 2$
^1J(PtPt)/Hz	$5\,250 \pm 50$	$4\,770 \pm 50$

[a] In CD_2Cl_2–CH_2Cl_2 at *ca.* 220 K. [b] In p.p.m. to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz.

days. However it was accompanied by some decomposition to platinum metal, and we were unable to isolate the product from such solutions. With the tetra-n-propylammonium salt, a pale green precipitate began to form in half an hour, and after 4 days a good yield of $[NPr^n{}_4]_2[Pt_2I_4(CO)_2]$ was isolated. Unfortunately, this salt is too insoluble for n.m.r. studies.

N.M.R. Measurements.—For the anions $[Pt_2X_4(CO)_2]^{2-}$, where all the halogen ligands X are the same, ^1J(PtPt) can only be evaluated from isotopomers containing two ^{195}Pt nuclei and one or (preferably) two ^{13}C nuclei; this is only practicable for ^{13}C-enriched samples. Salts $[NBu^n{}_4][PtX_3(CO)]$ may be prepared by reaction of CO with $[NBu^n{}_4]_2[Pt_2X_6]$,[5] a reaction which is quantitative with respect to both reactants; thus, the new procedure for preparing $[NBu^n{}_4]_2[Pt_2X_4(CO)_2]$ (X = Cl or Br) is highly efficient in its use of ^{13}C-enriched CO. To obtain well resolved ^{13}C or ^{195}Pt spectra, the temperature had to be reduced to *ca.* 220 K. In practice, the ^{195}Pt spectra gave the more satisfactory results for the isotopomers of interest.

Figure 1 shows how signals from the various isotopomers go to make up the ^{195}Pt spectrum of $[Pt_2Br_4(CO)_2]^{2-}$ with *ca.* 75% ^{13}C. There is an isotope shift of *ca.* 0.8 p.p.m. between ^{195}Pt bound to ^{13}C and ^{195}Pt bound to ^{12}C (the latter to high frequency). Values of ^1J(PtPt) which were derived from the [AX]$_2$ spin system ^{13}C$-^{195}$Pt$-^{195}$Pt$-^{13}$C (see Experimental section) and other parameters are given in the Table.

At ambient temperature, the ^{13}C n.m.r. spectra show only very weak features in the region $\pm^1J$(PtC)/2. The main signals due to species containing ^{195}Pt appear as broad features at *ca.* $\pm^1J$(PtC)/4, in keeping with intramolecular exchange of CO groups. The appearance of the room temperature ^{195}Pt spectra can be similarly interpreted.

The difficulties we encountered in isolating soluble salts of $[Pt_2I_4(CO)_2]^{2-}$ deterred us from preparing any ^{13}C-enriched material. However, some indication of the effect of iodide on ^1J(PtPt) can be judged from the values that can be directly observed for mixed halide species where the platinum atoms are inequivalent. Solutions containing such species can be readily prepared by treating $[NBu^n{}_4]_2[Pt_2X_4(CO)_2]$ (X = Cl or Br) in acetone with sodium iodide for a few minutes and then evaporating off the solvent under vacuum and replacing it with dichloromethane. The spectra were run at *ca.* 220 K to reduce decomposition; this would also have reduced the rate of any equilibration of isomers (*cf.* the mixed Cl,Br anions; see later).

Convenient solutions to use are those with ratios of chloride or bromide (X) to iodide of 3 : 1 or 1 : 3, since the predominant species should be $[Pt_2X_4(CO)_2]^{2-}$, $[Pt_2X_3I(CO)_2]^{2-}$, and $[Pt_2X_2I_2(CO)_2]^{2-}$ in the first case and $[Pt_2X_2I_2(CO)_2]^{2-}$, $[Pt_2XI_3(CO)_2]^{2-}$, and $[Pt_2I_4(CO)_2]^{2-}$ in the second. Each spectrum has a similar format (*e.g.* Figure 2). There are two resonances which do not have ^{195}Pt satellites, *i.e.* of species with equivalent Pt atoms; one of these is common to both X : I ratios and can therefore be assigned to $[Pt_2X_2I_2(CO)_2]^{2-}$; the others correspond to $[Pt_2X_4(CO)_2]^{2-}$ and $[Pt_2I_4(CO)_2]^{2-}$. The remaining resonances in each spectrum correspond to an inequivalent pair of Pt nuclei with ^{195}Pt satellites forming an [AB] pattern, and are therefore assigned to $[Pt_2X_3I(CO)_2]^{2-}$ and $[Pt_2XI_3(CO)_2]^{2-}$. Although several isomers are possible for the mixed halide species, one isomer is dominant for each of the mixed Cl,Br anions (see later). As this discrimination between isomers should be greater for those containing I and X, we believe that the resonances observed for the mixed X,I anions correspond essentially to a single isomer for each composition. The particular structure cannot be identified from the n.m.r. results, but the two types of platinum–halide bond can be easily distinguished by i.r. measurements.[1] For a mull of $[NPr^n{}_4]_2[Pt_2Cl_4(CO)_2]$, the stretching vibrations of Pt–Cl *trans* to CO occur at 315m (sym) and 310s (asym) cm^{-1}; $[NPr^n{}_4]_2[Pt_2I_4(CO)_2]$ has an analogous band at 198s cm^{-1}. The Pt–Cl vibrations *trans* to Pt occur at 269w (sym) and 240vs (asym) cm^{-1}, and the iodo-analogue shows the counterpart of the last at 147s cm^{-1}. Now the ^{195}Pt n.m.r. spectrum of the product of reaction of $[NBu^n{}_4]_2[Pt_2Cl_4(CO)_2]$ with 2 mol equiv. of sodium iodide showed it to consist almost entirely of $[Pt_2Cl_2I_2(CO)_2]^{2-}$. The far-i.r. spectrum of the isolated solid has only three major features: 314s, 309s, and 149s cm^{-1}, which clearly should be assigned to Pt–Cl *trans* to CO and Pt–I *trans* to Pt. We therefore conclude that the preferred isomers have the heavier halide on the Pt–Pt axis, and Scheme 1 shows the structures deduced on this basis with their ^{195}Pt chemical shifts.

Solutions containing mixed Cl,Br anions were produced by dissolving mixtures of $[NBu^n{}_4]_2[Pt_2Cl_4(CO)_2]$ and $[NBu^n{}_4]_2$-

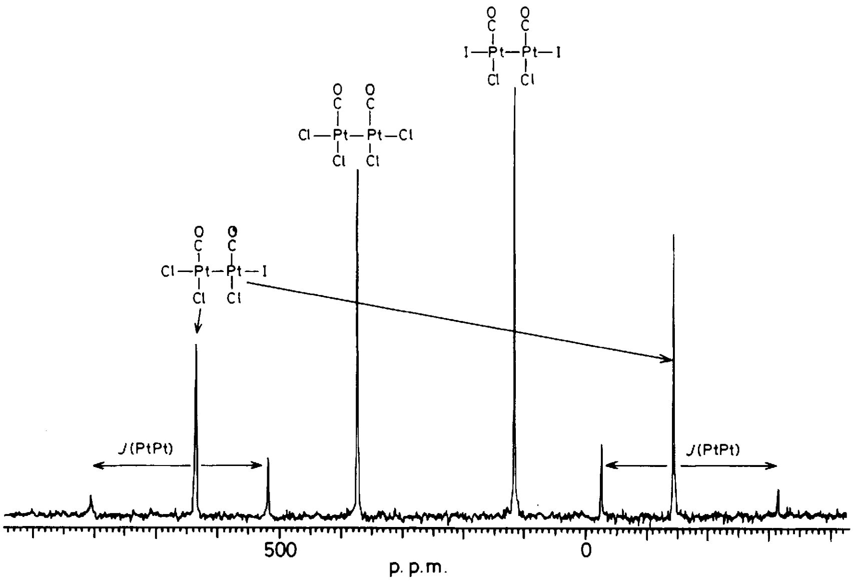
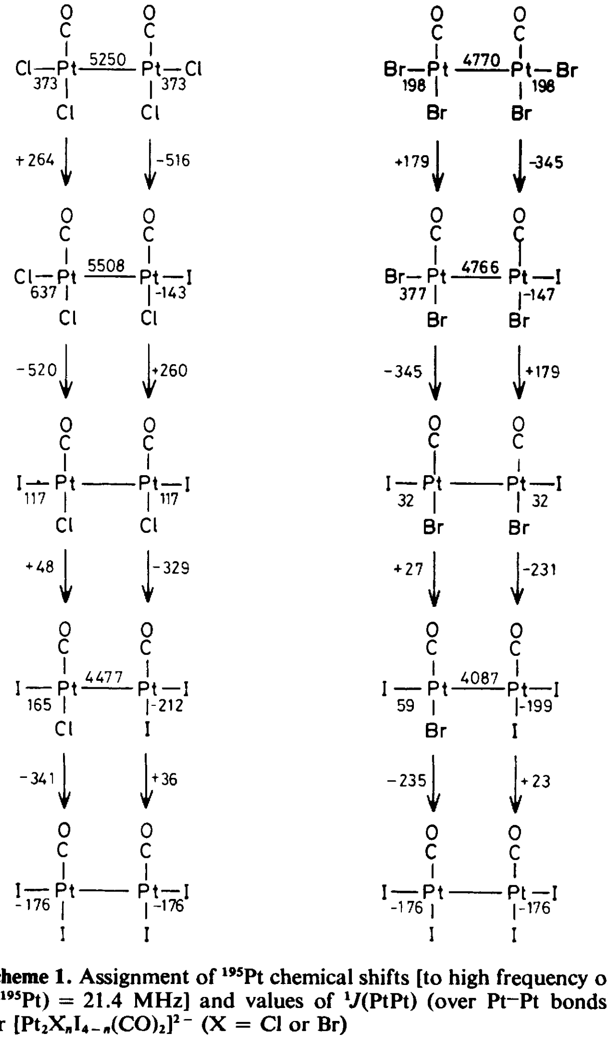


Figure 2. ^{195}Pt Fourier-transform n.m.r. spectrum of $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ + NaI at *ca.* 220 K



Scheme 1. Assignment of ^{195}Pt chemical shifts [to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz] and values of $^1J(PtPt)$ (over Pt–Pt bonds) for $[Pt_2X_nI_{4-n}(CO)_2]^{2-}$ (X = Cl or Br)

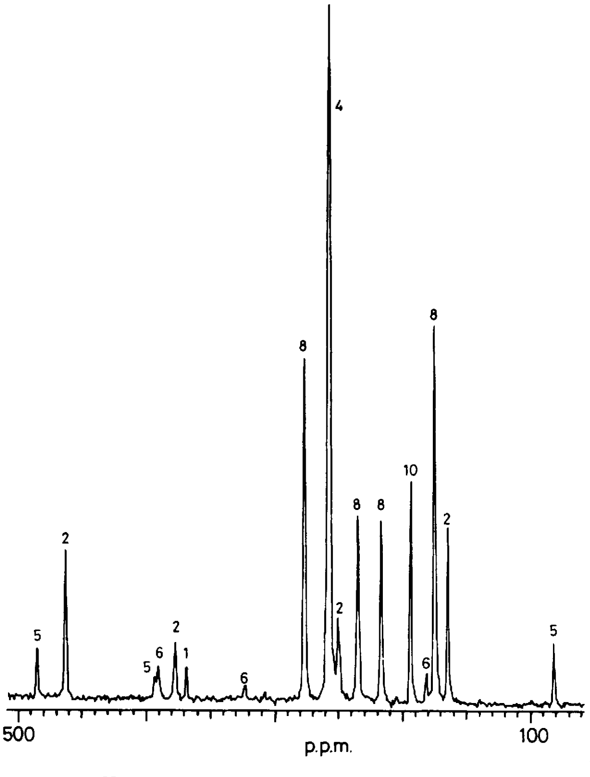
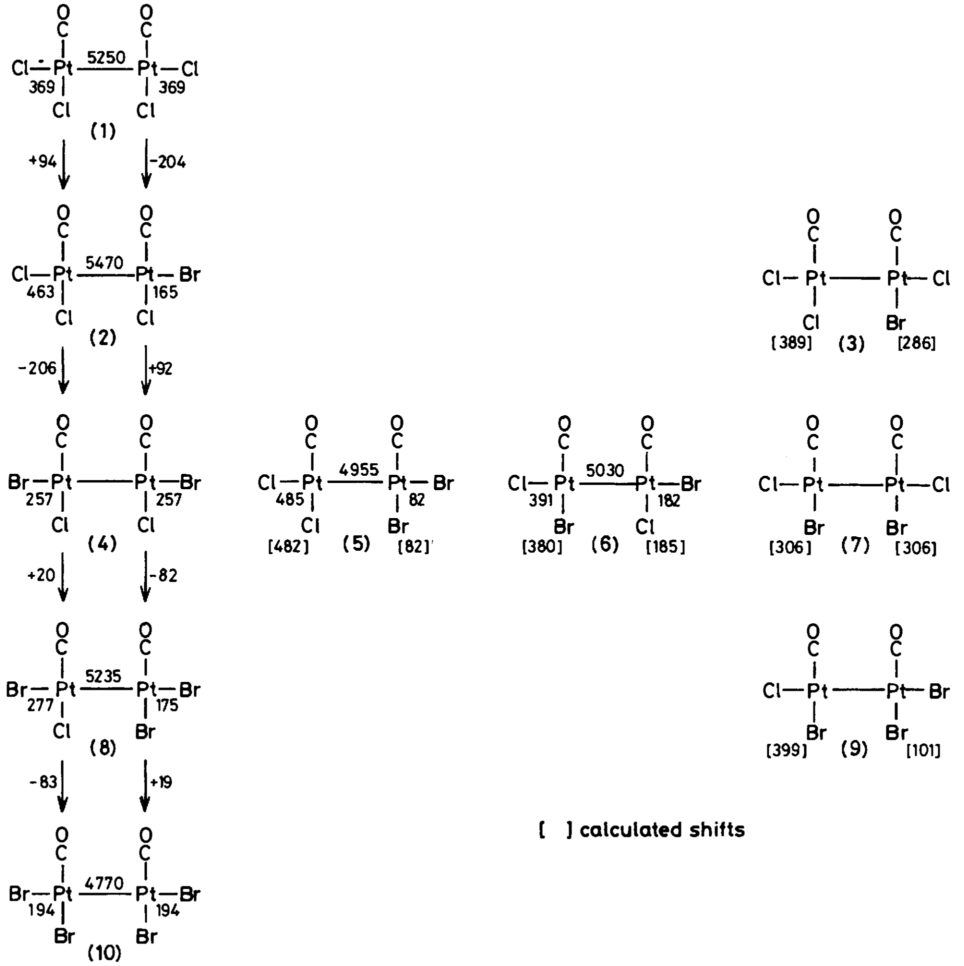


Figure 3. ^{195}Pt N.m.r. spectrum of $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ + $[NBu^n_4]_2[Pt_2Br_4(CO)_2]$ at *ca.* 220 K (central area only; numbers correspond to species as in Scheme 2)

$[Pt_2Br_4(CO)_2]$ in appropriate ratios. As some lines were markedly broadened at ambient temperature, these solutions were examined at *ca.* 220 K. The procedure used for the X,I anions readily yielded the parameters of the major species present but for the Cl,Br system some additional weak features were observed (*e.g.* see Figure 3). From the major species, the changes in $\delta(^{195}Pt)$ on replacing Br by Cl in various positions were evaluated, and these changes were

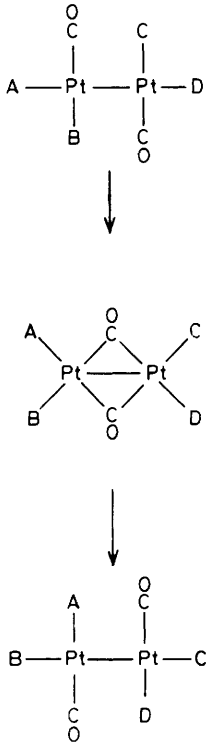


Scheme 2. Assignments of ^{195}Pt chemical shifts [to high frequency of $\Xi(^{195}\mathrm{Pt}) = 21.4$ MHz] and values of ^{1}J(PtPt) (over Pt–Pt bonds) for $[\mathrm{Pt_2Cl_nBr_{4-n}(CO)_2}]^{2-}$. From the shifts of the major species [(1), (2), (4), (8), and (10)] we obtain average changes in δ(^{195}Pt) of −205 and +93 p.p.m. for replacing Cl by Br on the Pt–Pt axis and −83 and +20 p.p.m. for replacing Cl by Br *trans* to CO [negative changes in δ(Pt) relate to the Pt nucleus on which the halide replacement occurs whilst the positive changes relate to the other Pt nucleus]. These were used to calculate shifts, given in square brackets, for the other possible isomers, *e.g.* (6) is obtained from (2) by replacing Cl by Br *trans* to CO'

then used to calculate the shifts expected for other possible isomers (see Scheme 2). In this way additional features are identified as belonging to two isomers (5) and (6) of $[\mathrm{Pt_2Cl_2Br_2(CO)_2}]^{2-}$, but no resonances assignable to the other possible isomers, (3), (7), and (9), were observed. Where a species has inequivalent platinum atoms, ^{1}J(PtPt) was obtained from the four lines of the AB pattern, except that for (5) and (6) one 'inner' line was obscured by other resonances.

In the room temperature spectrum some lines are broad and others absent. The resonances of species (1), (5), and (10), all of which have two atoms of the same halide on a particular platinum centre, are sharp whilst those of (2) and (8) are markedly broadened. That the two ends of species (2), (5), and (8) are still inequivalent shows that exchange of halides between platinum centres is still slow, and points to exchange of site on a particular platinum. Of course this will only explain the broadened lines of $[\mathrm{Pt_2Cl_3Br(CO)_2}]^{2-}$ and $[\mathrm{Pt_2ClBr_3(CO)_2}]^{2-}$ if there is a finite amount of the second isomer [(3) or (9), respectively] present, although they were not observable in the spectrum at 220 K. As is usual, all the resonances shift to high frequency at the higher temperature. However, relative to the average change for the sharp resonances [(1), (5), and (10)], the resonances of (2) and (8) alter in the way to be expected if they incorporated a small amount (*ca.* 5%) of the other isomer [(3) or (9), respectively]. The resonance of species (4) is not noticeably broadened at room temperature and, if anything, it moves (relative to the other sharp resonances) in the direction opposite to that expected if it had incorporated either isomer (6) or (7). Since isomer (7) has the unfavourable distribution of halides at both ends, its concentration is likely to be very small indeed and it would, therefore, make no significant contribution to the appearance of (4). Since isomer (6) was observed at 220 K, it might be expected to contribute to the position and linewidth of (4) if the rate of exchange was similar to that of the other species. However, if the exchange repositions the halides at both ends in the same process, then it would not convert (6) into (4); rather the ends of (6) would be interconverted. The room temperature spectrum does not show lines corresponding to those of (6) in the 220 K spectrum, but these may constitute a broad feature at the mean shift of the ends (*ca.* 314 p.p.m.) which underlies that of species (8).

A CO-bridged structure resembling that found for the palladium analogue [6] would provide a suitable intermediate [7] for the intramolecular exchange of carbonyl ligands identified



Scheme 3. Possible mechanism for site exchange of carbonyl and halide (A, B, C, and D) ligands in $[Pt_2X_4(CO)_2]^{2-}$

above. As shown in Scheme 3, such a process should result in the simultaneous exchange of the positions of the halides for both platinum atoms as implied by the room temperature spectra of the mixed Cl,Br anions.

Mixed Halide Derivatives $[PtX_3(CO)]^-$ (X = Cl, Br, *or* I).—Information on the behaviour of δ(^{195}Pt) in mixed halide derivatives of $[PtX_3(CO)]^-$ was desirable both for the interpretation of the results for $[Pt_2X_4(CO)_2]^{2-}$ and because the Pt^{II} anions are likely decomposition products of the Pt^{I} anions. Solutions containing $[PtX_3(CO)]^-$ with mixed halide ligands are readily prepared by allowing solutions containing two (or three) of the pure halogeno-species to equilibrate. In contrast to the mixed halogeno-anions of $[Pt_2X_4(CO)_2]^{2-}$, there is now no ambiguity of assignment as there are two halides *cis* to CO but only one *trans* to CO, and halide replacement for the two types of site results in very different and therefore easily distinguished changes in δ(Pt). There is a preference for the heavier halide to be *cis* rather than *trans* to CO. This is so strong for iodo-species that $[PtBrI_2(CO)]^-$ was the only mixed halide complex for which the isomer with I *trans* to CO was observed. The ^{195}Pt chemical shifts and the differences corresponding to halide exchange are given in Scheme 4. The values for the single halide species are in good agreement with those previously reported.[5]

Discussion

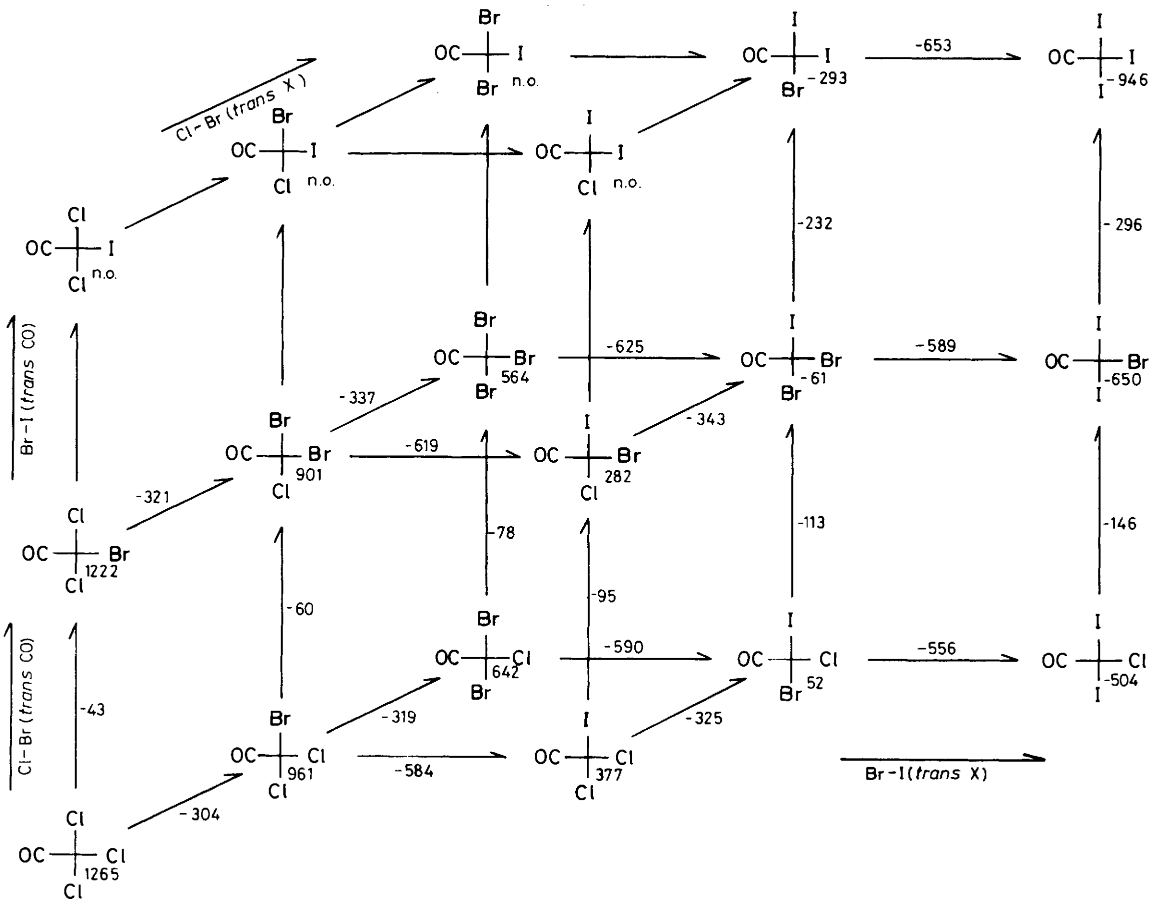
Although the square planar co-ordination about platinum in $[Pt_2Cl_4(CO)_2]^{2-}$ and other Pt^{I} complexes suggests that these compounds might be regarded as Pt^{II} compounds in which one 'ligand' happens to be platinum, the *X*-ray photoelectron spectrum of $[Pt_2Cl_2(\mu\text{-}PPh_2CH_2PPh_2)_2]$ is in keeping with an effective oxidation state similar to the formal oxidation state of +1.[8] Commonly, lowering the oxidation state reduces the chemical shift[9] of the metal nucleus, and the lowering by some 900 p.p.m. of the shift of $[PtCl_3(CO)]^-$ on reduction to $[Pt_2Cl_4(CO)_2]^{2-}$ fits this pattern. However, the change is much less for the bromo-anion and has the reverse sense for the iodide. Large changes in δ(Pt) occur on changing the atomic number of the halide ligands {*e.g.* δ(Pt) for $[PtX_3(CO)]^-$ is 1 265, 564, and −946 p.p.m. for X = Cl, Br, and I, respectively} but these do not seem to correspond to any great difference in the bonding.[10] Variations in the halide contributions to δ(Pt) between the Pt^{II} and Pt^{I} complexes mask the effect of reduction (or formation of a Pt–Pt bond). In fact it is more meaningful to consider the effect of platinum as a ligand (*i.e.* the Pt–Pt bond) on the contribution of the halide *trans* to it. Comparison of the results in Schemes 1 and 2 with those in ref. 10 show that the effect of a *trans* platinum is similar to that of $AsMe_3$, SMe_2, or $TeMe_2$ ligands associated with a medium *trans* influence. By contrast, the effect of a *trans* CO ligand in either the Pt^{I} or Pt^{II} anions is much greater and comparable with that of PMe_3, a high *trans* influence ligand. The preference for heavier halides to be *trans* to Pt rather than *trans* to CO suggests that the Pt–Pt bond has a significantly lower *trans* influence than the Pt–CO bond.

Exchanging halides on the adjacent platinum atom in these diplatinum anions results in a change in δ(^{195}Pt) in the direction opposite to that for the same halide exchange on the observed platinum atom (see Schemes 1 and 2). There are two markedly different magnitudes for this transmitted contribution to the chemical shift, in keeping with the two different sites (*trans* to CO and *trans* to Pt). The larger effect is *ca.* half that of the change in δ(^{195}Pt) caused by the equivalent change of halides directly bound to the observed platinum atom and we have assigned these to sites *trans* to the Pt–Pt bond. The smaller indirect effect which we assign to the site *trans* to CO is much less than the effect of changing halides on the observed platinum. It is, in fact, less than that of the corresponding halide replacement on the adjacent platinum of $[Pt_2X_6]^{2-}$, where the transmission occurs by halide bridges instead of a Pt–Pt bond.[11]

The values of ^1J(PtPt) in $[Pt_2X_4(CO)_2]^{2-}$ range from 4 087 to 5 508 Hz and are thus in the higher bracket of values of this coupling constant.[12] Whilst this could be interpreted as being in keeping with the relatively short Pt–Pt distance [258.4(2) pm],[13] the poor correlation of ^1J(PtPt) with Pt–Pt separation suggests that it might be better associated with the low *trans* influence of the ligands *trans* to the metal–metal bond.[12] There are sufficient values of ^1J(PtPt) for the Cl,Br system (Scheme 2) to allow some analysis of the effect of halide on this coupling constant. Replacement of Cl by Br on the Pt–Pt axis causes increases of +220, +280, and +205 Hz whereas replacement *trans* to CO results in decreases (−515, −440, and −465 Hz). It is a little surprising that the heavier halide, with an apparently greater *trans* influence, should cause an increase in *J*(PtPt), but the increase in ^1J(Pt-Pt) from 8 189 to 8 828 Hz in $[Pt_2X_2(\mu\text{-}PPh_2CH_2PPh_2)_2]$ (X = Cl or Br, respectively) is similar.[12] It is more surprising that the heavier halide *cis* to the Pt–Pt bond should produce a reduction in ^1J(PtPt), which is of greater magnitude. The comparative regularity of the effect of replacing Cl by Br on ^1J(PtPt) permits the making of rough estimates for other isomers, *e.g. ca.* 5 700 Hz for (4). When these are included it is noteworthy that the preferred isomers always have significantly greater coupling constants than those of the less favoured isomers.

Experimental

Preparation of the Complexes.—The complexes $[NBu^n_4][PtX_3(CO)]$ (X = Cl, Br, or I) were obtained by stirring a



Scheme 4. ^{195}Pt chemical shifts [to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz] and changes on halide exchange for $[NBu^n_4][PtX_3(CO)]$ (X = Cl, Br, or I) (n.o. = not observed)

solution of $[NBu^n_4]_2[Pt_2X_6]$ in CH_2Cl_2 under a CO atmosphere.[5] Tripropylamine and formic acid were used as solutions (0.45 and 0.21 mol dm^{-3}, respectively) in dry tetrahydrofuran.

$[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ was prepared by the addition of NPr^n_3 solution (2 cm^3, 0.9 mmol) and HCO_2H solution (2 cm^3, 0.42 mmol) to $[NBu^n_4][PtCl_3(CO)]$ (0.480 g, 0.84 mmol) dissolved in thf (4 cm^3). The mixture was left for *ca.* 1 day until yellow-green crystals had formed and the i.r. spectrum of the mother-liquor showed no peak for $[PtCl_3(CO)]^-$ (ν_{CO} 2 082 cm^{-1}). The crystals were collected, washed first with thf and then diethyl ether, and dried in air; yield 0.39 g (87%) (Found: C, 37.9; H, 6.85; N, 2.3. $C_{34}H_{72}Cl_4N_2O_2Pt_2$ requires C, 38.05; H, 6.75; N, 2.6%); m.p. 165 °C.

$[NBu^n_4]_2[Pt_2Br_4(CO)_2]$ was prepared similarly by the addition of NPr^n_3 solution (1.5 cm^3, 0.675 mmol) and HCO_2H solution (1 cm^3, 0.21 mmol) to a solution of $[NBu^n_4][PtBr_3(CO)]$ (0.296 g, 0.42 mmol) in thf (1.5 cm^3). The product crystallised from the reaction medium as bright yellow crystals in *ca.* 1 day. Completion of the reaction was indicated by the absence of the i.r. peak for $[PtBr_3(CO)]^-$ (ν_{CO} 2 079 cm^{-1}) in the supernatant. The product was collected as above; yield 0.20 g (76%) (Found: C, 33.0; H, 5.85; N, 2.05. $C_{34}H_{72}Br_4N_2O_2Pt_2$ requires C, 32.65; H, 5.8; N, 2.25%); m.p. 170 °C. In repeat preparations of this salt, the product sometimes formed as an oil. However, cooling of this oil to −5 °C for a few hours, followed by re-warming, always gave a crystalline product.

$[NPr^n_4]_2[Pt_2I_4(CO)_2]$ was prepared by the addition of NPr^n_3 solution (1 cm^3, 0.44 mmol) and HCO_2H solution (0.5 cm^3, 0.105 mmol) to a solution of $[NPr^n_4][PtI_3(CO)]$ (0.166 g, 0.21 mmol) in thf (0.5 cm^3). A pale green precipitate of product began to form in under 0.5 h. The solution was left for a further 4 days until the i.r. spectrum of the mother-liquor showed that only a small amount of $[PtI_3(CO)]^-$ (ν_{CO} 2 068 cm^{-1}) remained. The product was collected, washed with thf and diethyl ether, and dried in air; yield 0.10 g (72%) (Found: C, 22.35; H, 4.35; N, 2.1. $C_{26}H_{56}I_4N_2O_2Pt_2$ requires C, 23.55; H, 4.25; N, 2.1%); m.p. 172 °C; ν_{CO} 2 026 and 2 010 cm^{-1} (Nujol).

Spectroscopic Measurements.—I.r. spectra were measured in absorbance with a Perkin-Elmer 580 ratio recording spectrometer and a Nicolet 7199A Fourier-transform system. A 0.2 mm pathlength CaF_2 cell was used with a balancing cell containing pure solvent. ^{195}Pt N.m.r. spectra were measured for solutions in CH_2Cl_2–CD_2Cl_2 in 10 mm o.d. sample tubes with a JEOL FX90Q Fourier-transform spectrometer using *ca.* 90° pulses and no ^1H broad-band irradiation. Shifts were calculated *via* the ^2D lock frequency. ^{13}C N.m.r. spectra were measured with a JEOL FX 200 spectrometer.

^{195}Pt *N.m.r. spectra of* ^{13}CO*-enriched samples.* The isotopomer ^{13}C–^{195}Pt–^{195}Pt–^{13}C is an example of the $[AX]_2$ spin system; half the ^{195}Pt intensity should therefore appear as a doublet with width [$^1J(PtC)$ + $^2J(PtC)$] whilst the remainder should occur as eight lines at the positions given by equations (vi)—(ix).[14] Because of the large value of $^1J(PtPt)$ compared with L, the ' outer lines ' given by equations (viii) and (ix) are very weak and were not observed, Furthermore, lines cor-

$$\pm \tfrac{1}{2}[K - (K^2 + L^2)^{\frac{1}{2}}] \qquad \text{(vi)}$$

$$\pm \tfrac{1}{2}[M - (M^2 + L^2)^{\frac{1}{2}}] \qquad \text{(vii)}$$

$$\pm \tfrac{1}{2}[K + (K^2 + L^2)^{\frac{1}{2}}] \qquad \text{(viii)}$$

$$\pm \tfrac{1}{2}[M + (M^2 + L^2)^{\frac{1}{2}}] \qquad \text{(ix)}$$

$$K = {}^1J(\text{PtPt}) + {}^3J(\text{CC}) \qquad M = {}^1J(\text{PtP}) - {}^3J(\text{CC})$$
$$L = {}^1J(\text{PtC}) - {}^2J(\text{PtC})$$

responding to equation (vi) were not resolved from those for equation (vii) so we could not evaluate ${}^3J$(CC), although we could set an upper limit of 150 Hz for it. The separation (S_t) of the combined lines [equations (vi) and (vii)] was used to evaluate ${}^1J$(PtPt) *via* equation (x). The ^{195}Pt spectrum of the

$${}^1J(\text{PtPt}) = (L^2 - S_t^2)/2S_t \qquad \text{(x)}$$

isotopomer (^{13}C−^{195}Pt−^{195}Pt−) constitutes the AB part of an ABX system where the difference in A and B chemical shifts is due to the ^{13}C/^{12}C isotope effect. The outside lines of the four doublets [splitting ${}^1J$(PtPt)] have very low intensities and were not observed. Values of ${}^1J$(PtPt) were calculated from the positions of the inner halves of the doublets but as the errors are four times those for the values from the $[AX]_2$ system they were used merely as a check.

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