Nuclear Magnetic Resonance Studies (^{31}P and ^{199}Hg) of Complexes [Hg$_2$X$_4$(PBu$_3^n$)$_2$] (X = Cl, Br and I) and their Reactions with [NBu$_4^n$]X

P. L. GOGGIN, R. J. GOODFELLOW, D. M. McEWAN and K. KESSLER

*Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.*

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In their studies of ^{31}P n.m.r. spectra of tertiary phosphine complexes of mercury(II) halides, Grim *et al.* [1] noted that whilst complexes of the type [Hg$_2$X$_4$(PR$_3$)$_2$] (PR$_3$ = PBu$_3^n$, PBu$_2^n$Ph or PEt$_2$Ph) gave a single resonance with ^{199}Hg satellites for X = Cl or Br, the iodides showed two resonances each with mercury satellites. They concluded that the sole or major component was the *trans* dimer (*I*), a structural element identifiable in crystals (although secondary association with a neighbouring dimer unit
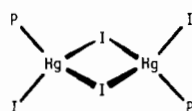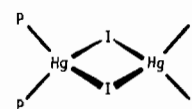

(I)

also occurs) [2, 3]. They suggested that the second component for the iodides might be either the *cis* dimer (*II*) or the unsymmetrical dimer (*III*), and favoured the latter on the grounds of similarity of
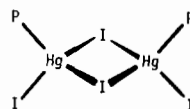
(II)   (III)

^{31}P chemical shifts and ^{1}J(HgP) coupling constants to those of the corresponding complexes [HgI$_2$(PR$_3$)$_2$]. Observation of the ^{199}Hg-{^{1}H} F.t. n.m.r. spectrum provides a method of determining the number of phosphine ligands attached to the metal, through the HgP coupling pattern. For [Hg$_2$L$_4$(PBu$_3^n$)$_2$] (0.5 *M* in CDCl$_3$), three features, a singlet, a doublet and a triplet are observed in order of increasing frequency (Table I). The doublet is the most intense and has a separation equal to ^{1}J(HgP) of the major species seen in the ^{31}P spectrum. The splitting of the triplet corresponds to ^{1}J(HgP) of the minor species in the ^{31}P spectrum and the triplet and singlet appear of approximately equal intensity.

The above results in keeping with structure (*III*) for the minor component, and the ^{199}Hg shifts are close to the values for [HgI$_2$(PBu$_3^n$)$_2$] (see Table I) and [NBu$_4^n$]$_2$[HgI$_4$] [−3510 p.p.m. (CH$_2$Cl$_2$) or

TABLE I. N.m.r. Parameters of Some Mercury Complexes with Tri-n-butylphosphine.

Complex[a]		$\delta(^{199}$Hg)[b]	$\delta(^{31}$P)[b]	^{1}J(HgP)/Hz
[Hg$_2$Cl$_4$(PBu$_3^n$)$_2$]		−741	34.1	7414
[Hg$_2$Br$_4$(PBu$_3^n$)$_2$]	major species	−1020	27.7	6633
	minor species		30.4	4851
[Hg$_2$I$_4$(PBu$_3^n$)$_2$]	major species	−1729[c]	6.2	5195
	minor species	−3507[c]		
		−572[c]	19.1	4375
[Hg$_2$Cl$_4$(PBu$_3^n$)$_2$] + 4[NBu$_4^n$]Cl	major species	−647[d]	28.6	7321
	minor species	−1142[d]		
		−402[d]	29.9	5155
[Hg$_2$Br$_4$(PBu$_3^n$)$_2$] + 4[NBu$_4^n$]Br	major species		18.8	5950
	minor species		23.5	4792
[Hg$_2$I$_4$(PBu$_3^n$)$_2$] + 4[NBu$_4^n$]I	major species		−4.0	4077
	minor species		9.0	4058
[HgCl$_2$(PBu$_3^n$)$_2$]		−404	28.9	5125
[HgBr$_2$(PBu$_3^n$)$_2$]		−471	24.0	4829
[HgI$_2$(PBu$_3^n$)$_2$]		−716	8.8	4101

[a]0.5 *M* in CDCl$_3$.   [b]In p.p.m. to high frequency of HgMe$_2$ (^{199}Hg) or H$_3$PO$_4$ (^{31}P).   [c]*ca.* 1 *M* in CH$_2$Cl$_2$.   [d][Hg$_2$Cl$_4$(PBu$_3^n$)$_2$] + 2[NBu$_4^n$]Cl, *ca.* 1 *M* in CH$_2$Cl$_2$.

−3548 in the presence of $2[NBu_4^n]I$ to suppress dissociation], as might be expected for this structure. However, this explanation appears to be too simple. The ^{31}P spectra show that whilst for a solution $1.0 M$ in Hg there are about 9 times as many Hg atoms bearing one phosphine as those bearing two, on diluting to $0.2 M$ in Hg this ratio increases to *ca.* 58 (a molecular weight determination on a dilute solution in chloroform supports the dimeric structure; observed = 1273, calc. = 1312). This change is approximately in accordance with association of two dimeric units into a tetramer at higher concentrations. An intimately bonded chain-like tetramer such as *(IV)* requires the metal to be co-ordinated to five iodides which seems unlikely on the grounds of charge distribution. Other possible explanations

(IV)
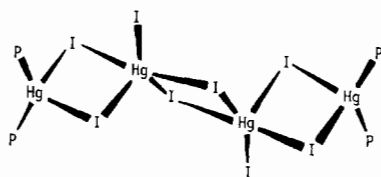
which do not require the co-ordination number about Hg to exceed four are two units of *(III)* associated by dipole pairing or close ion-pair contact in the ionised form $[Hg_2I_2(PBu_3^n)_4][HgI_3]_2$. An objection to the latter is that the ^{199}Hg chemical shift of the singlet is significantly different from that found for $[NBu_4^n][HgI_3]$ (−3257 p.p.m., in CH_2Cl_2). Whatever the form of the associated product, the association appears to be the driving force for the unsymmetrical distribution of the phosphines.

^{31}P studies with the corresponding bromide indicate that this system shows similar behaviour at high concentration, but that the extent of phosphine transfer is only about a tenth of that for the iodide. In keeping with this trend only one ^{31}P resonance with ^{199}Hg satellites was observed for the analogous chloride.

Neutral halide-bridged complexes commonly react with tetra-n-butylammonium halides in chlorinated hydrocarbons to give anionic complexes. The ^{31}P spectrum of a $CDCl_3$ solution of $[Hg_2Cl_4(PBu_3^n)_2]$ to which $2[NBu_4^n]Cl$ had been added showed two main resonances; the $^{199}Hg\text{-}\{^1H\}$ spectrum showed three, a predominant doublet and a weaker singlet and triplet of approximately the same intensity. The ^{199}Hg shifts of the last two are very close to those found for $[NBu_4^n]_2[HgCl_4]$ (−1141 p.p.m. in $CH_2 Cl_2$) and $[HgCl_2(PBu_3^n)_2]$ respectively; the main complex can be safely assumed to be $[NBu_4^n][HgCl_3(PBu_3^n)]$. The behaviour of the ^{31}P parameters on stepwise addition of $[NBu_4^n]Cl$ is illustrated in Fig. 1. The ^{31}P resonances are sharp throughout and it is evident that whilst phosphine exchange is slow,
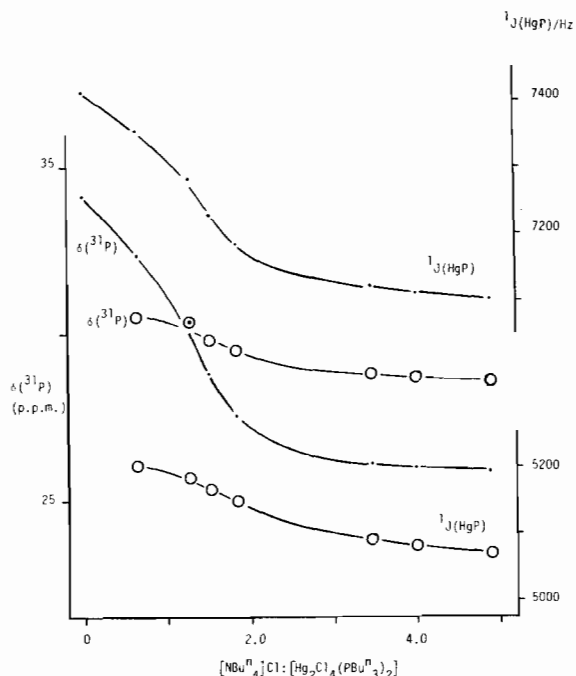

Fig. 1. Change in ^{31}P n.m.r. parameter on addition of $[NBu_4^n]Cl$. • = '$Hg(PBu_3^n)$' species. ○ = '$Hg(PBu_3^n)_2$' species.

halide exchange is fast on the n.m.r. time scale. The proportion of the minor species increases until $2[NBu_4^n]Cl$ have been added when it is *ca.* 1/6th judged from peak heights. ^{31}P spectra show that the bromide and iodide systems behave similarly and that the proportion of the second component is only little more than for the chloride, in contrast to the behaviour of $[Hg_2X_4(PBu_3^n)_2]$.

References

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2 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Chem. Comm.*, 1039 (1976).
3 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 28*, L169 (1978).