Phosphorus-31, Selenium-77, and Mercury-199 Nuclear Magnetic Resonance Studies of Bis(tributylphosphine selenide)mercury(II) Complexes

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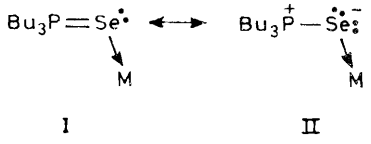
Fourier-transform ^{31}P, ^{77}Se, and ^{199}Hg n.m.r. spectra and heteronuclear multiple-resonance experiments involving these nuclei have been used to determine the signs and magnitudes of $^1J(^{199}Hg-^{77}Se)$, $^1J(^{77}Se-^{31}P)$, and $^2J(^{199}Hg-^{31}P)$ in $HgX_2(PBu_3Se)_2$ (X = Cl, Br, I, or SCN) at −100 °C. The first coupling constant is negative and *relatively* small (−751 Hz for X = Cl), and the trends in it and the other coupling constants are interpreted in terms of changes in the hybridisation of the mercury atom and the electronegativity of the HgX_2 fragment.

COMPLEXES, $HgX_2(PBu^n{}_3Se)_2$ (X = Br, Cl, or I), of tri-n-butylphosphine selenide with mercury(II) halides have been reported by Grim *et al.*,[1] who used ^{31}P n.m.r. spectroscopy including observations of ^{77}Se ($I = \frac{1}{2}$; natural abundance, 7.1%) and ^{199}Hg ($I = \frac{1}{2}$; natural abundance, 16.8%) satellites for their characterisation, and also to assess changes in the strength of the P=Se bond and to study their lability in solution. In this note we report multinuclear studies of this type of complex using both direct observation of ^{31}P, ^{77}Se, and ^{199}Hg with proton decoupling, and also using indirect detection *via* $^{31}P-\{^{77}Se, ^1H\}$ and $^{31}P-\{^{199}Hg, ^1H\}$ multiple-resonance experiments.

RESULTS AND DISCUSSION

The complexes were made by reacting stoicheiometric amounts of tributylphosphine selenide with the mercury(II)salt, and had physical properties which coincided with those reported by Grim *et al.*[2] They were examined as concentrated solutions in dichloromethane at −100 °C in order to slow ligand exchange sufficiently for the ^{31}P n.m.r. spectra to display sharp ^{199}Hg satellites and for the ^{199}Hg spectrum to be a 1 : 2 : 1 triplet as a result of coupling to ^{31}P. Although the *magnitude* of $^1J(^{199}Hg-^{77}Se)$ was available by observing the appropriate satellites (arising from 2.3% abundant species) in either the ^{199}Hg or the ^{77}Se spectrum, it was necessary to perform selective heteronuclear triple-resonance experiments upon satellites of satellites in the ^{31}P spectrum to determine the sign relative to that of $^1J(^{77}Se-^{31}P)$. This coupling constant is known [3] to be negative in tertiary phosphine selenides, and its behaviour [2] in our complexes in the presence of excess of ligand at temperatures at which chemical exchange is rapid indicates that no change of sign occurs when the complex is formed. These $^{31}P-\{^{199}Hg, ^1H\}$ and $^{31}P-\{^{77}Se, ^1H\}$ experiments were performed upon a modified JEOL FX-60 spectrometer using a GenRad model 1061 frequency synthesizer and a tuned radio-frequency power amplifier; a typical set of results is shown in the Figure. Direct ^{199}Hg and ^{77}Se spectra were recorded on a JEOL FX-90Q multinuclear instrument, and the results for all the species examined are collected in the Table.

It is of considerable interest that $^1J(^{199}Hg-^{77}Se)$ [and hence the reduced coupling constant $^1K(HgSe)$†] is negative and of *relatively* small magnitude in these species. Compare $^1K(HgSe)$ *ca.* −200 nm^{-3} with $^1K(HgP)$ *ca.* 500 nm^{-3} in $HgX_2(PR_3)_2$ [4] and recall that the valence *s*-electron density at the nucleus for selenium is more than twice that for phosphorus, which would normally lead to a larger reduced coupling constant in the case of the heavier element. In some platinum complexes of dimethyl selenide the coupling constant $^1J(^{195}Pt-^{77}Se)$ is also relatively small and can be negative when the platinum atom has electronegative substituents,[5] behaviour which can be attributed to the presence of a remaining electron lone pair upon selenium in the complex itself. Depending upon the relative importance of the canonical forms I and II in the resonance hybrid, the selenium atom in our complexes will effectively retain from one to two electron lone pairs which will have most of the selenium *s* character, and thus the valence *s*-electron overlap integral for the mercury–selenium bond will be small. The treatment of



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Pople and Santry [6] then shows that this may lead to a negative sign for the mutual polarizabilities of mercury and selenium, and hence to a negative Fermi-contact contribution to the coupling constant. Similar considerations apply to the selenium–phosphorus coupling constant which is also negative,[3] and it has been established [7] that selenium–carbon coupling constants can change sign when the selenium atom loses its last electron lone pair.

Protonation of tertiary phosphine selenides to form

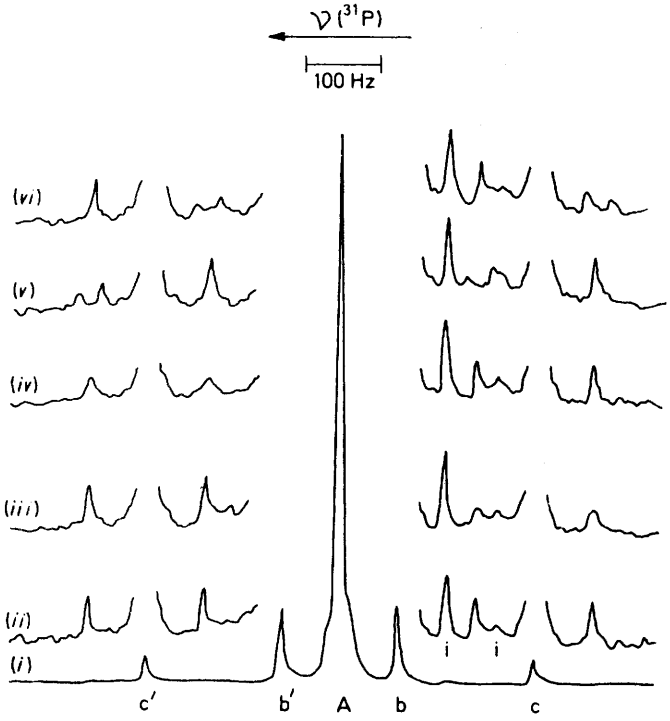
† $K(AB) = J(AB) \cdot 4\pi^2/h\gamma(A)\gamma(B)$.

R_3PSeH^+ is accompanied by a reduction in the *magnitude* of $^1J(^{77}Se-^{31}P)$.[8] That is, the coupling becomes less negative, and hence the correlation noted by Grim *et al.*[1,2] between the reduction in $^1J(^{77}Se-^{31}P)$ and the Lewis acidity of the HgX_2 fragment is to be expected. It can be seen as a consequence of donation of a selenium electron lone pair to another atom leading to an increase in the *s* character of the selenium hybrid orbital used for the selenium–phosphorus bond, and so to an increase in the Se–P overlap integral with a concomitant *algebraic* increase in the coupling constant. For the progression X = Cl ⟶ I the electron-withdrawing ability of the HgX_2 group decreases, and the reduction in $^1J(^{77}Se-^{31}P)$ produced by co-ordination becomes less, so that the coupling constant more nearly approaches its value in the unco-ordinated ligand. Much larger variations occur in the other two coupling constants as X changes, since the mercury hybrid orbitals are directly involved in the coupling. In the case of $^1J(^{199}Hg-^{77}Se)$ the increasing *s* character of the mercury orbitals used for the Hg–X bonds in the sequence X = Cl, Br, or I will lead to correspondingly reduced *s* character for the Hg–Se bond and so to a smaller *s*-overlap integral and a more negative coupling constant as is observed. The changes in $^2J(^{199}Hg-^{31}P)$ will also depend upon the mercury hybridisation, but are in the opposite direction, as is commonly found when one- and two-bond couplings are compared.

N.m.r. parameters of tributylphosphine–chalcogenide mercury complexes at −100 °C [a]

Compound	δ(^{199}Hg)	δ(^{77}Se)	δ(^{31}P)	$^1J(^{199}Hg-^{77}Se)$	$^1J(^{77}Se-^{31}P)$	$^2J(^{199}Hg-^{31}P)$
$HgCl_2(PBu_3Se)_2$	−970 ± 1	−284.6	46.6	−751 ± 10	−522.5	−160.0
$HgBr_2(PBu_3Se)_2$	−1 336 ± 2	−280.0	45.9	−823 ± 10	−531.3	−143.0
$HgI_2(PBu_3Se)_2$	−2 162 ± 2	−276.6	44.8	−950 ± 20	−548.3	−115.2
$Hg(SCN)_2(PBu_3Se)_2$	− 725 ± 1	−289.0	46.5	−962 ± 15	−527.3	−141.0
$Hg(SCN)_2(PBu_3S)_2$	−508 ± 1		58.8 [b]			(−)106.4 [c]
PBu_3Se [d]		−384.6	37.0		−693.0	

[a] Chemical shifts are in p.p.m. (±0.2 p.p.m. unless otherwise stated) to high frequency of the reference: 85% H_3PO_4 for ^{31}P, $SeMe_2$ for ^{77}Se, and $HgMe_2$ for ^{199}Hg. Coupling constants are in Hz (±0.2 Hz for those involving ^{31}P) and their signs are based upon $^1J(^{77}Se-^{31}P)$ being negative (ref. 3). [b] δ(^{31}P) for PBu_3S is 48.0 p.p.m. [c] Minus sign assigned by comparison with similar compounds rather than by direct determination. [d] At 21 °C.



Proton-decoupled pulsed Fourier-transform ^{31}P spectra of $HgCl_2(PBu_3Se)_2$ in CH_2Cl_2 at −100 °C. Each trace was obtained by Fourier transforming 1 000 transients obtained at 1-s intervals. (*i*) Normal spectrum; line A is from species without ^{77}Se or ^{199}Hg, lines b and b′ are from species containing ^{199}Hg, lines c and c′ are from species containing one ^{77}Se nucleus; (*ii*) normal spectrum at higher gain showing the four ' satellites of satellites ' from species containing ^{199}Hg and one ^{77}Se nucleus (the lines marked i are impurities); (*iii*) and (*iv*) with irradiation of the ^{199}Hg lines from the doubly substituted species at lowest and highest frequency respectively, showing $^1J(^{31}P-^{77}Se)$ and $^1J(^{199}Hg-^{77}Se)$ to be of like sign; (*v*) and (*vi*) with irradiation of the ^{77}Se lines from the doubly substituted species at highest and lowest frequency respectively, showing $^1J(^{199}Hg-^{77}Se)$ and $^2J(^{199}Hg-^{31}P)$ to be of like sign

The pattern of chemical shifts in the complexes is much as expected. Thus the reduction in electron density at selenium leads to an increase in δ(^{77}Se) of *ca.* 100 p.p.m. compared with PBu_3Se in which the substantial negative value has been attributed [3] to a significant contribution from the canonical form II. The minor variations in δ(^{77}Se) probably reflect long-range shielding effects of the group X. The values of δ(^{199}Hg) are clearly dominated by the changes in the bulk and polarizability of X, whilst the small sizes of the changes in δ(^{31}P) reflect the remoteness of this site from the point of variation.

This study provides an opportunity to compare the merits of different ways of obtaining the same n.m.r. data. The direct measurement of $^1J(^{199}Hg-^{77}Se)$ to ±10 Hz required *ca.* 3 h using ^{199}Hg observation, and would have required *ca.* 20 h using ^{77}Se observation because although its sensitivity (not receptivity since species containing both ^{199}Hg and ^{77}Se are of concern here) is somewhat greater than that of ^{199}Hg, its relaxation time in these species was much longer. The multiple-resonance experiments of the Figure using ^{31}P observation required only *ca.* 0.3 h per trace even though owing to its lower field strength and lack of quadrature detection the spectrometer used had only about one third of the sensitivity (corresponding to a

time factor of one ninth). However, against this must be set the large number of search experiments needed if the magnitude of $^{1}J(^{199}Hg–^{77}Se)$ had been unknown, as would commonly be the case.

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