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Selenium-77–Phosphorus-31 Nuclear Spin–Spin Coupling in Tri-n-butylphosphine Selenide Complexes of Mercury(II) Halides

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The phosphorus chalcogen bond in R_3PE (where E is O, S, and Se) and their metal complexes has been thoroughly studied by classical methods such as infrared and Raman spectroscopy [1–4] and crystallographic bond length determinations [5–7]. In addition, for the uncomplexed phosphine oxides and selenides, nuclear magnetic resonance investigations, particularly studies of phosphorus-31–oxygen-17 [8] and phosphorus-31–selenium-77 [9, 10] spin–spin coupling have been performed. However, no definitive study of the variation of $^1J_{^{31}P-^{77}Se}$ or $^1J_{^{31}P-^{17}O}$ in metal complexes has been reported [11]. We report here the first such study for tertiary phosphine selenide complexes.

The important observations for tertiary phosphide selenide complexes of mercury(II) halides are: (1) at room temperature, the selenide ligands in $(n\text{-}Bu_3PSe)_2HgX_2$ are labile; *i.e.*, they exchange rapidly on the NMR time scale; (2) $^1J_{P-Se}$ decreases upon coordination, consistent with the expected weakening of the P–Se bond upon coordination; (3) the magnitude of change (decrease) of $^1J_{P-Se}$ from the value in the uncoordinated ligand is greatest for the most acidic Lewis acid, *i.e.*, $HgCl_2 > HgBr_2 > HgI_2$; (4) the ligand exchange rate slows with decreasing temperature and the change of $^1J_{P-Se}$ increases concomitantly; (5) $^1J_{P-Se}$ reaches a limiting minimum value for the bromide and chloride with decreasing temperature indicating that the ligand exchange is "frozen out" on the NMR time scale; and (6) at low temperature, two bond coupling, $^2J_{^{31}P-^{199}Hg}$, is observed. These observations are discussed below.

The uncomplexed ligand, tri-n-butylphosphine selenide, has a phosphorus-31–selenium-77 coupling constant of 693 Hz [10]. The complexes, $(n\text{-}Bu_3PSe)_2HgX_2$, when dissolved in CH_2Cl_2–$CDCl_3$ (3:1 by volume) at room temperature exhibit phosphorus selenium coupling constants of 551, 560, and 587 Hz, respectively, for X = Cl, Br, and I. The large and monotonic decrease in J_{P-Se} indicates that the phosphorus selenium bond is weakened upon coordination. This, of course, is anticipated as numerous previous data of many types on R_3PE complexes have firmly established [1–3]. However these results are in striking contrast to an earlier brief report, based on NMR studies, that the phosphorus–selenium bond remains relatively unperturbed upon complex formation [11]. Clearly, in the present complexes there is an approximate 20% decrease in $^1J_{P-Se}$. Further, the magnitude of the decrease in $^1J_{P-Se}$ upon coordination varies with the Lewis acidity of the mercury halide in a predictable fashion.

The phosphine selenide complexes show lability of the selenide ligands on the NMR time scale at room temperature. This type of lability has been noted previously in ^{31}P NMR studies with tertiary phosphine complexes of cadmium [12] and mercury(II) halides [13] and with tertiary phosphine oxide complexes of zinc, cadmium, and mercury(II) salts [14]. This lability is easily demonstrated by the addition of excess free ligand to the solution of the complex, $(n\text{-}Bu_3PSe)_2HgI_2$. No extra peak due to the free ligand appears in the ^{31}P NMR spectrum, but only a shift of the original single resonance in the spectrum to reflect the weighted average of the chemical shift in the complex and of the free ligand. More interestingly, as increasing amounts of excess ligand are added, $^1J_{P-Se}$ increases also and approaches the value of $^1J_{P-Se}$ in the free ligand, again reflecting the averaging of $^1J_{P-Se}$ among each of the species present in solution, with the free ligand value predominating with a large excess of ligand present.

Reduction of the temperature of a CH_2Cl_2–$CDCl_3$ solution of $(n\text{-}Bu_3PSe)_2HgBr_2$ causes a decrease in $^1J_{P-Se}$ for the complex until the rate of change of $^1J_{P-Se}$ is very minimal from –60° to –89 °C, at which temperature $^1J_{P-Se}$ is 535 Hz. This apparent minimum of $^1J_{P-Se}$ at low temperatures indicates that ligand exchange is slow on the NMR time scale. This "frozen out" situation was not experimentally obtained in earlier studies in the case of the tertiary phosphine complexes such as $(R_3P)_2HgX_2$ [13]. Other evidence that the selenide ligands are nonlabile in $(n\text{-}Bu_3PSe)_2HgBr_2$ at –89 °C is the appearance of another NMR peak for the uncomplexed ligand when excess ligand is added to the solution. Further, two bond phosphorus-31–mercury-199 (^{199}Hg with a nuclear spin of one-half is 16.8% naturally abundant) coupling becomes observable for the $(n\text{-}Bu_3PSe)_2HgCl_2$ and $(n\text{-}Bu_3PSe)_2HgBr_2$ compounds at reduced temperatures (Figure 1). This is the first report of such coupling, although $^2J_{WP}$ [15], $^3J_{W-P}$ [16], and $^2J_{Cd-P}$ [11] have been reported previously. The selenide in the corresponding mercuric iodide complex remains labile at the lowest temperature attainable on this system.

Experimental

The $(n\text{-}Bu_3PSe)_2HgX_2$ compounds were prepared by mixing ethanol solutions of the ligand and HgX_2

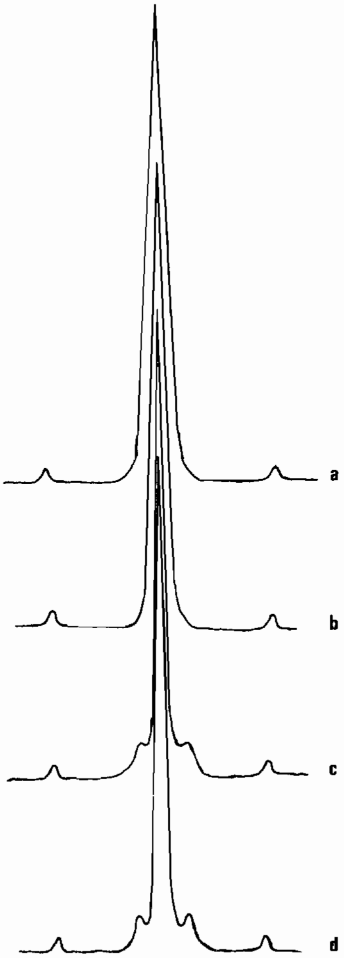

Figure 1. The ^{31}P NMR spectra of (n-Bu$_3$PSe)$_2$HgBr$_2$ at various temperatures: a) 33°; b) −30°; c) −70°; d) −89 °C. The small outer peaks are the ^{77}Se satellites for which $^{1}J_{P-Se}$ is 560 Hz, 546 Hz, 538 Hz, and 535 Hz, respectively at 33°, −30°, −70°, and −89 °C. The small inner peaks are the ^{199}Hg satellite for which $^{2}J_{P-Hg}$ is 122 Hz and 141 Hz, respectively at −70° and −89 °C.

[17]. ^{31}P NMR measurements were made on CH_2Cl_2–$CDCl_3$ (3:1) solutions in 10 mm spinning tubes with 85% H_3PO_4 as the external reference using a Varian 100 MHz FT instrument operating at 40.5 MHz. Deuterium in the solvent was used as a lock. Temperature measurements were made with a pentane thermometer inserted in the probe before and after the NMR measurements and are accurate to ±2 °C.

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