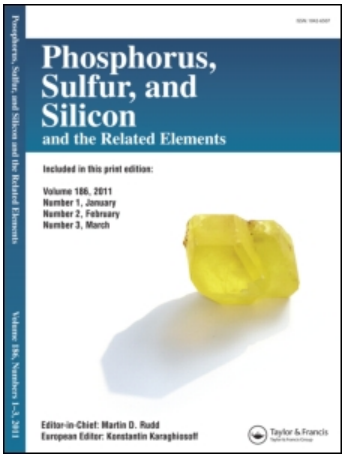

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SOME SELENIUM ANALOGUES OF THE ANIONIC TRIDENTATE TRIPODAL SULFUR LIGAND, TRIS(DIPHENYLTHIOPHOSPHINYL) METHANIDE

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SOME SELENIUM ANALOGUES OF THE ANIONIC TRIDENTATE TRIPODAL SULFUR LIGAND, TRIS(DIPHENYLTHIOPHOSPHINYL)METHANIDE.

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Abstract A new potential tridentate tripodal ligand, bis(diphenylselenophosphinyl)diphenylthiophosphinylmethanide, and its neutral protonated parent have been synthesized. The stable conformations of HTrisSSe$_2$ and its trichalcogen analogues can be determined by variable temperature ^{31}P NMR spectroscopy because of significant differences in chemical shifts for a particular chalcogenophosphinyl group in different stereochemical orientations within the sterically hindered molecules.

INTRODUCTION

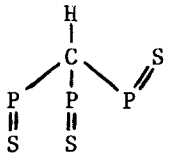
The compounds [Ph$_2$P(X)][Ph$_2$P(Y)][Ph$_2$P(Z)]CH*[1,2] where X, Y and Z are various combinations of electron pairs and the chalcogens O, S and Se form the basis for a new system of ligands. The prototype compounds (Ph$_2$P)$_3$CH* and [Ph$_2$P(S)]$_3$CH* were reported by Issleib and Abicht[3] in 1970. More recently, Karsch[4] has synthesized the hexamethyl analogue and Grim[5] and coworkers have reported the tetramethyldiphenyl analogue. Of the twenty possible HTrisXYZ compounds (with XYZ being all combinations of electron

*Abbreviations used in this work: [Ph$_2$P(X)][Ph$_2$P(Y)][Ph$_2$P-(Z)]CH is HTrisXYZ; (Ph$_2$P)$_3$CH is HTris; [Ph$_2$P(S)]$_3$CH is HTrisS$_3$; [Ph$_2$P(O)][Ph$_2$P(S)][Ph$_2$P]CH is HTrisOS. The corresponding anions obtained by proton abstraction are [TrisXYZ]$^-$, [Tris]$^-$, [TrisS$_3$]$^-$and [TrisOS]$^-$, respectively.

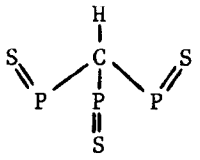
pairs, O, S and Se atoms), sixteen have already been reported. We report here the synthesis of one of the previously unreported compounds $HTrisSSe_2$ along with a discussion of its properties and the properties of its analogues.

DISCUSSION

The large steric bulk of the three diphenylphosphinyl groups attached to the same carbon atom causes restricted rotation about the P-C bonds. Space-filling molecular models indicate that the six phenyl rings must all align nearly coplanar to the methine C-H bond. As a consequence the chalcogen-phosphorus bonds must be nearly parallel or antiparallel to the C-H bond.[6] At room temperature the ^{31}P NMR spectrum of $HTrisS_3$ is a slightly broadened singlet indicating equivalence of the three phosphorus atoms on an NMR time scale. At -40°C, the NMR spectrum consists of a triplet (rel int 1) and a doublet (rel int 2) indicating a stable rotational conformation with either one P-X bond parallel (up in Fig. 1a) and two antiparallel (down in Fig. 1a) to the C-H bond or vice versa (Fig. 1b). Molecular models seem to favor the former conformation (1a) and this is confirmed in the solid state structures of $HTrisS_3$[6] and $HTrisO_2S$.[7]



1a



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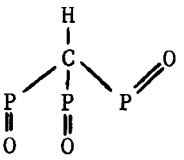

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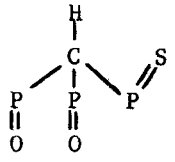

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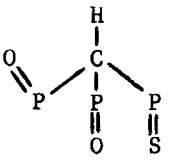

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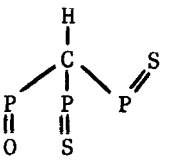

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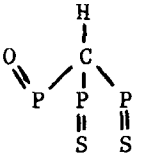
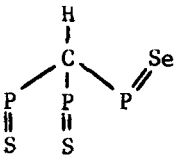
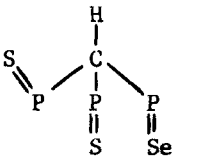


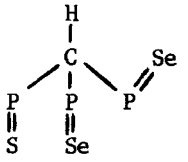
1g



1h



1i



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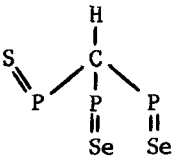

1k

FIGURE 1 Conformations of HTrisXYZ (phenyl groups omitted for clarity).

All of the trichalcogenides HTrisXYZ which have been synthesized to date show this slow rotation limit in the ^{31}P NMR spectra at moderately low (-40 to -80°C) temperatures with the adopted conformations having two chalcogenides antiparallel ("down") and the largest chalcogenide parallel ("up") to the C-H bond. The ^{31}P chemical shifts of the P(X)- group in the two stereochemically distinct positions are significant with shifts between the "up" and "down" orientations of about 13, 8 and 6 ppm for oxygen,

sulfur and selenium, respectively. The more highly shielded (upfield) phosphorus is bonded to the "down" chalcogen. The conformations of $HTrisO_2S$ and $HTrisOS_2$ can be predicted from the low temperature ^{31}P NMR spectra by comparison to the chemical shifts in $HTrisS_3$ (38.6 ppm, d, "down"; 46.8 ppm, t, "up") and $HTrisO_3$ (23.4 ppm, d, "down"; 35.9 ppm, t, "up").[1] For example the possible conformers of $HTrisO_2S$ are shown in Figs. 1d (an expected AX_2-type spectrum) and 1e (an expected AMX-type spectrum). The former is observed. For $HTrisOS_2$ the possible conformers are shown in Figs. 1f (an expected AMX spectrum) and 1g (an expected AX_2 spectrum) and the former is observed. These results give rise to the postulate that the larger chalcogen is in the "up" positions of Fig. 1. For $HTrisS_2Se$ the expected stable conformation is shown in Fig. 1h. The ^{31}P NMR results show mainly the expected AX_2-type spectrum (39.6 ppm, d, rel int 2, P(S) "down"; 39.3 ppm, t, rel int 1, (PSe) "up"). However there is also a significant but minor fraction with an integrated intensity of about 30% due to the conformer shown in Fig. 1i which is characterized by a downfield peak at 47.6 ppm indicative of a P(S) "up" group. The fact that both conformers are observed at -60°C may be due to the smaller difference in size between Se and S (117 vs 102 pm covalent radius and 190 vs 180 pm van der Waals radius, respectively) than between S and O (102 vs 73 pm covalent and 180 vs 150 pm van der Waals radius, respectively). This could result in a correspondingly smaller difference in conformational energies in the $HTrisS_2Se$ case than in the $HTrisO_2S$ and $HTrisOS_2$ cases. The energy of activation for rotation about the phosphorus-methine carbon bonds can be determined by line shape analysis of the NMR spectra and is generally larger for the larger chalcogens, viz, increasing in the order $HTrisS_2$ (29 kJ/mol) < $HTrisO_3$ (38.7) < $HTrisOS_2$ (39.6) < $HTrisS_3$ (49).[1]

HTrisXYZ can be readily deprotonated with lithium methoxide[8] to produce the anions $[TrisXYZ]^-$ which can show tridentate[9]

tripodal or bidentate[10] behavior in coordination compounds depending on the ligand and the metal. $[TrisS_3]^-$ shows both tri- and bidentate behavior whereas $[TrisO_3]^-$ generally shows the latter type chelation.[11] These ions contain a nearly planar P_3C-group with the P-C-P bond angles averaging about 120° (119.9° in the case of $[TrisS_3]^-$).[12] Upon cooling a solution of $LiTrisS_3$ to -90°C, the ^{31}P NMR spectrum remains a singlet indicating that the rotation about the P-C bonds in the anions remains unrestricted compared to the protonated parent compounds. The increase in the P-C-P angle from 115° in $HTrisS_3$ to 120° in the anion is apparently sufficient to allow free rotation in the anion. This observation suggested a possible alternate route for the synthesis of $HTrisSSe_2$.

The usual synthesis of many of the HTrisXYZ compounds is the reaction of HTris, HTrisX or HTrisXY with H_2O_2, S or red Se to produce phosphine oxide, sulfide or selenide, respectively. This reaction failed in our attempts to make $HTrisSSe_2$ and $HTrisSe_3$. These reactions generally result in phosphorus-methine carbon bond cleavage with $Ph_2(P(X)CH_2P(Y)Ph_2$ as the major decomposition product. In one case an unexpected selenium insertion occurred during the reaction of HTrisS with Se to produce $[Ph_2P(S)][Ph_2P(Se)][Ph_2P(Se)Se]CH$. It was tentatively concluded that selenium is too large to be accommodated in $HTrisSSe_2$ and $HTrisSe_3$ and that the observed selenium insertion product may have been an intermediate during the cleavage process.

Since steric effects are less in the anion, an alternate route for the synthesis of $HTrisSSe_2$ is to first form the anion $[TrisS]^-$ by deprotonation of HTrisS followed by addition of two moles of elemental selenium to form $[TrisSSe_2]^-$ and subsequent protonation to give the product $HTrisSSe_2$. This procedure is successful. The room temperature ^{31}P NMR spectrum consists of two broad singlets at 41.5 ppm (rel int 1), P(S) and 36.6 ppm (int 2) P(Se). The expected stable conformer (an expected AMX spectrum)

is shown in Fig. 1j. At -50°C the observed spectrum is consistent with the expected spectrum: 40.8 ppm [P(S) "down"], 40.4 ppm [P(Se) "up"] and 34.6 [P(Se) "down"]. A small peak also occurs at 48.7 ppm which is attributed to [P(S) "up"] of the minor (about 10%) conformer represented in Fig. 1k.

It has been shown that ^{31}P NMR spectra of HTrisXYZ compounds at low temperature can definitively determine the stable conformer in solution. This conformer is the same as that in the solid state in those two cases ($HTrisS_3$ and $HTrisO_2S$) for which the crystal structures have been determined.

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