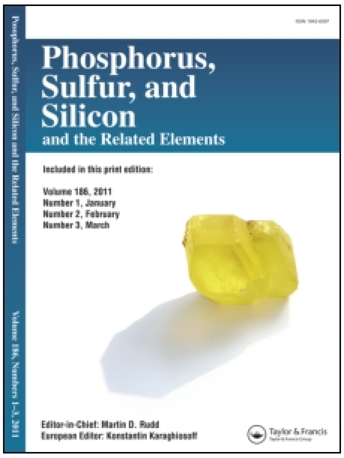

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SHORT COMMUNICATION

Polydentate Ligands Containing Phosphorus. 5. Some Derivatives of Tris(diphenylphosphino)methane.[1]

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Phosphorus-31 and proton nuclear magnetic resonance data are reported for a series of chalcogen derivatives of tris(diphenylphosphino)methane, Tdppm. Tdppm also behaves as a bidentate ligand when coordinated to Group 6 metal carbonyls in the compounds $[\text{Tdppm}]\text{M(CO)}_4$, where M is Cr or W. Five of the compounds are previously unreported.

In 1970, Issleib and Abicht[2] reported the synthesis of tris(diphenylphosphino)methane, Tdppm, as well as several of its derivatives, such as the dioxide, bis(diphenylphosphoryl)diphenylphosphinomethane, TdppmO_2, and the trisulfide, tris(diphenylthiophosphoryl)methane, TdppmS_3. These and similar compounds are inherently very interesting because of their nuclear magnetic resonance (nmr) properties and because of their potential varied behavior as ligands. Recently, the methyl analogue of Tdppm, tris(dimethylphosphino)methane, has been synthesized.[3] We report here ^{31}P and ^{1}H nmr results for some new derivatives of Tdppm, including some chalcogenides and Group 6 metal carbonyl complexes.

The synthesis of the tris-phosphorus compounds can be achieved by two routes. (1) Lithiation of the methylene group of a bis-phosphorus compound followed by reaction with a phosphinous chloride (Scheme 1) produces the desired compounds.

$$\text{R}_2\text{P(X)CH}_2\text{P(X)R}_2 \xrightarrow{\text{R}'\text{Li}} \text{R}_2\text{P(X)CHLiP(X)R}_2 \xrightarrow{\text{R}''_2\text{PCl}} [\text{R}_2\text{P(X)}]_2\text{CHPR}''_2$$

SCHEME 1

This scheme has been successfully carried out for R = Ph, R′ = n-Bu, X = electron pair or O, and R″ = Ph[2]; for R = Me, R′ = t-Bu, X = electron pair and R″ = Ph or Me.[4] (2) Or reaction of lithiomethyldiphenylphosphine sulfide[5] (in excess) with a phosphinous chloride also produces the tris-phosphorus compounds directly in reasonable yields (Scheme 2).[4,6]

$$\text{Ph}_3\text{PS} \xrightarrow{\text{MeLi}} \text{Ph}_2\text{P(S)CH}_2\text{Li} \xrightarrow{\text{Ph}_2\text{PCl}} \text{Ph}_2\text{P(S)CH}_2\text{PPh}_2 \xrightarrow{\text{Ph}_2\text{P(S)CH}_2\text{Li}} \text{Ph}_2\text{P(S)CHLiPPh}_2 \xrightarrow{\text{Ph}_2\text{PCl}} \text{Ph}_2\text{P(S)CH[PPh}_2]_2$$

SCHEME 2

Scheme 2 has been carried out successfully as shown for the hexaphenyl compound. Preliminary results indicate this scheme might also apply for Me_2PCl additions in the second and subsequent steps, although good isolated yields have not been obtained. In addition, the scheme fails when Se replaces S in the first step.

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The derivatives reported here are $Ph_2P(S)CH[PPh_2]_2$ (TdppmS), $[Ph_2P(S)]_2CHPPh_2$ ($TdppmS_2$), $[Ph_2P(S)]_3CH$ ($TdppmS_3$), $Ph_2P(Se)CH[PPh_2]_2$ (TdppmSe), $[Ph_2P(Se)]_2CHPPh_2$ ($TdppmSe_2$), $[Ph_2P(O)]_2CHPPh_2$ ($TdppmO_2$), $[Ph_2P(S)][Ph_2P(Se)][Ph_2P]CH$ (TdppmSSe), $[(Ph_2P)_3CH]Cr(CO)_4$, and $[(Ph_2P)_3CH]W(CO)_4$. TdppmS is the product of Scheme 2. $TdppmS_2$ can be produced via Scheme 1 starting with $Ph_2P(S)CH_2P(S)Ph_2$ or from TdppmS by the stoichiometric addition of one equivalent of sulfur. $TdppmS_3$ can be prepared by the addition of sulfur in boiling toluene to Tdppm,[2] TdppmS, or $TdppmS_2$. TdppmSe is formed by the addition of one equivalent of red selenium to Tdppm. Likewise $TdppmSe_2$ is synthesized by the reaction of two equivalents of red selenium with Tdppm. However, our attempts to prepare $TdppmSe_3$ via addition of three selenium atoms to Tdppm or the addition of the third selenium to $TdppmSe_2$ resulted in phosphorus-carbon bond cleavage and the recovery of $Ph_2P(Se)CH_2P(Se)Ph_2$ as the principal product. Facile phosphorus-carbon bond cleavage of this type had been noted earlier in attempted oxidation and quaternization reactions of 2 - bis(diphenylphosphino)methyl - 6 - methylpyridine.[7] Indeed, cleavage of one phosphorus-carbon bond occurred in the following attempts to prepare other TdppmXYZ compounds where X, Y, and Z are chalcogens or methyl cation:

$$\text{TdppmS}_2 \xrightarrow{H_2O_2} \text{P-C bond cleavage}$$

$$\text{TdppmSe}_2 \xrightarrow{Se} \text{P-C bond cleavage}$$

$$\text{TdppmSe}_2 \xrightarrow{S} \text{P-C bond cleavage}$$

$$\text{TdppmS}_2 \xrightarrow{MeBr} \text{P-C bond cleavage}$$

Finally, TdppmSSe was prepared by the reaction of Se with TdppmS.

Proton nmr data are given in Table I. It is interesting to note that the downfield chemical shift of the methine proton increases with the number of chalcogens in the compounds, with Se having a larger downfield influence than S. Similar results for the methylene proton chemical shifts in $Ph_2P(X)CH_2P(Y)Ph_2$, where X and Y are the various combinations of electron pair, O, S, Se, or Me^+, have been observed.[8] $^2J_{PH}$ for the phosphino groups in these compounds is small or negligible (0–3 Hz), whereas $^2J_{PH}$ for the thiophosphoryl and selenophosphoryl groups is larger (9.6–17 Hz). These are in agreement with expected coupling constants for related compounds.[8]

Phosphorus-31 nmr data are given in Table II. The assignments are all straightforward since the phosphino phosphorus atoms are shielded with respect to the thio- and selenophosphoryl phosphorus nuclei. The presence of selenium-77 (7.58 % natural abundance, I = 1/2) satellites also aids in the unequivocal assignment of the selenophosphoryl resonance. This is especially true for TdppmSSe, which has an AMX (beginning to show ABX) pattern. In the Tdppm chalcogenide complexes, $^2J_{P(X)CP}$ ranges between 40 and 70 Hz, while $^2J_{P(X)CP(X)}$ is smaller, 10.5 Hz in the case of TdppmSSe. These are in reasonable agreement with the values in the $Ph_2P(X)CH_2P(Y)Ph_2$ compounds.[8] $^2J_{P(X)CP}$ increases in the sequence $X = O < S < Se$ for both the bis and tris-phosphorus compounds.

The reaction of Tdppm with $Cr(CO)_6$ and $W(CO)_6$ produces coordination compounds in which Tdppm behaves as a bidentate ligand, forming a four-membered chelate ring, with one

TABLE I

Proton NMR data for tris-phosphorus compounds

Compound	δ_{CH} (ppm)[a]	$^2J_{PCH}$ (Hz)	$^2J_{P(X)CH}$ (Hz)	$\delta_{C_6H_5}$ (ppm)
Tdppm	4.16s	0	—	6.7–7.5
TdppmS	4.81d	0	9.6	6.8–7.9
TdppmSe	5.00d	0	10.0	6.8–8.1
TdppmSS	5.46dt	2.9	15.7	6.8–8.1
TdppmSSe	5.69[b]	3.0	14,17[c]	7.1–8.3
$TdppmSe_2$	5.98dt	3.0	16.0	7.1–8.3

[a] Chemical shifts are in ppm downfield from tetramethylsilane; s, singlet; d, doublet; t, triplet.

[b] Overlapping ddd.

[c] Double resonance experiments are necessary to determine these assignments, i.e., $^2J_{P(Se)CH}$ and $^2J_{P(S)CH}$.

TABLE II

^{31}P NMR data for tris-phosphorus compounds[a]

Compound	δ_P (ppm)[b]	$^2J_{PP}$ (Hz)	$^1J_{PSe}$ (Hz)
Tdppm	−10.4s		
TdppmS[c]	46.6t (PS) −13.2d (P)	62	
TdppmSe	42.1t (PSe) −12.4d (P)	70	743
$TdppmO_2$	31.1d (PO) −15.2t (P)	40	
$TdppmS_2^c$	43.5d (PS) −10.0t (P)	49	
TdppmSSe	43.6dd (PS) 37.8dd (PSe) −8.7dd (P)	57.1 ($J_{P(S)P}$) 43.9 ($J_{P(Se)P}$) 10.5 ($J_{P(S)P(Se)}$)	772
$TdppmSe_2^d$	37.8d (PSe) −8.0 (P)	53	780
$TdppmS_3^c$	41.9s		
$TdppmCr(CO)_4$	45.5d (PCr) −25.0t (P)	21	
$TdppmW(CO)_4^e$	−2.5d (PW) −23.0t (P)	24	

[a] Measured in CH_2Cl_2-$CDCl_3$ solutions with a Varian XL100-FT instrument at 40.5 MHz.

[b] Positive values are ppm downfield from 85% H_3PO_4; s, singlet; d, doublet; t, triplet.

[c] Ref. 6.

[d] The molecules with one ^{77}Se atom give an AA'MX spectrum from which $^2J_{P(Se)P(Se)}$ can be determined as 13.6 Hz.

[e] $^1J_{WP}$ = 210 Hz.

diphenylphosphino group uncoordinated. Presumably, the ligand does not conveniently behave as a tridentate donor since the resulting compound would contain three strained four-membered rings. The ^{31}P nmr spectrum of each coordination compound is conclusive with regard to the structure, *viz.*, there is a triplet (relative intensity, 1) upfield and a doublet (rel int, 2) downfield, corresponding to the bound phosphorus atoms. The ^{31}P coordination shifts are 55.9 and 7.9 ppm for the Cr and W compounds, respectively. This is somewhat larger than the usual coordination shifts observed in $(Ph_2PCH_2PRR')M(CO)_4$, which average +49.2 and −0.2 ppm for nine Cr and W compounds, respectively.[9] It is not clear whether this difference is due to an unusually stable chelate ring system or from the steric influence of the uncoordinated diphenylphosphino group which affects the chelate ring contribution[10,11] of the ^{31}P chemical shift. Tungsten-183 (14.4% natural abundance, $I = 1/2$) satellites are observed for the downfield ^{31}P doublet of $[Tdppm]W(CO)_4$, with $^1J_{PW}$ equal to 210 Hz. The corresponding average value for $^1J_{PW}$ in $[Ph_2PCH_2PRR^1]W(CO)_4$ is 199 Hz.[9]

The magnitudes of J_{PSe} in these tris-compounds are in the order expected, *i.e.*, as the remaining phosphorus atoms become more electronegative due to a partial positive charge resulting from bonding to chalcogen, the magnitude of J_{PSe} increases. The same order was observed[8] for the bis-phosphorus compounds of the type $Ph_2P(Se)CH_2P(X)Ph_2$, where X is an electron pair, O, S, Se, or Me.$^+$

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