to the decrease in quantum yield.

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**Registry No.** 6-Me(bpy), 56100-22-2; 6,6′-$Me_2$bpy, 4411-80-7; 2-Me(phen), 3002-77-5; [Ru(6-Me(bpy))$_3$]$Cl_2$, 73396-22-2; [Ru(6,6′-$Me_2$bpy)$_3$]$Cl_2$, 73396-21-1; [Ru(2-Me(phen))$_3$]$Cl_2$, 73396-20-0; [Ru(2,9-$Me_2$phen)$_3$]$Cl_2$, 73396-19-7; [Os(6-Me(bpy))$_3$]$Cl_2$, 73396-18-6; [Os(6,6′-$Me_2$bpy)$_3$]$Cl_2$, 73396-17-5; [Os(2-Me(phen))$_3$]$Cl_2$, 73396-16-4; [Os(2,9-$Me_2$phen)$_3$]$Cl_2$, 73396-15-3; Ru(bpy)$_3$$Cl_2$, 14323-06-9; Ru(phen)$_3$$Cl_2$, 23570-43-6; Os(bpy)$_3$($ClO_4$)$_2$, 15928-87-7; Os(phen)$_3$$Cl_2$, 73466-62-3; 2,2-bipyridine, 366-18-7; 2-methylpyridine, 109-06-8; $K_2OsCl_6$, 16871-60-6.

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# Unsymmetrical Bis-Phosphorus Ligands. 12. Synthesis and Nuclear Magnetic Resonance Studies of Some Derivatives of Bis(diphenylphosphino)methane[1,2]

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The complete series of 15 compounds of the type $(C_6H_5)_2P(X)CH_2P(Y)(C_6H_5)_2$, where X and Y ($X = Y$ and $X \neq Y$) are an electron pair, O, S, Se, or $CH_3^+$, have been synthesized. In addition, several coordination compounds of the monoselenide ligand, viz., $[(C_6H_5)_2P(Se)CH_2P(C_6H_5)_2]M(CO)_4$, where M = Cr, Mo, or W, and $[(C_6H_5)_2P(Se)CH_2P(C_6H_5)_2]HgX_2$, where X = Cl, Br, or I, have been prepared. Where appropriate these compounds have been characterized by proton, carbon-13, and phosphorus-31 NMR spectrometry. From a correlation between the chemical shifts of the methylene protons and the charge on phosphorus in the $(C_6H_5)_2P(X)CH_2P(Y)(C_6H_5)_2$ derivatives, it is found that the effective positive charge on phosphorus increases in the order $(C_6H_5)_2P- < (C_6H_5)_2P(O)- < (C_6H_5)_2P(S)- < (C_6H_5)_2P(Se)- < (C_6H_5)_2PCH_3-^+$. Coupling constants of phosphorus with selenium-77, carbon-13, and phosphorus are given as are selenium–phosphorus stretching frequencies as measured by Raman spectroscopy.

Bis(diphenylphosphino)methane (dppm) has been extensively used as a ligand,[3] and the chemistry of its dioxide (dppm$O_2$) its disulfide (dppm$S_2$), and to a lesser extent its diselenide (dppm$Se_2$) is also well-known.[4–7] However, only very recently the monoxide (dppmO)[8] and monosulfide (dppmS)[9] have been examined as ligands, and it was found that they have a preference for bonding in chelated fashion via the chalcogen and phosphine to form a five-membered chelate ring. It was therefore of interest to extend these studies to include the monoselenide derivative (dppmSe) $(C_6H_5)_2P(Se)CH_2P(C_6H_5)_2$ of dppm. The selenium compounds offer the additional advantage of having another nuclear magnetic resonance (NMR) active nucleus, viz., selenium-77, of 7.58% natural abundance and a nuclear spin of one-half. From the correlations observed in the $^1H$ NMR spectra of the earlier dppm derivatives, it seemed profitable to extend the synthetic aspects of this study to include all 15 of the compounds $(C_6H_5)_2P(X)CH_2P(Y)(C_6H_5)_2$, where X and Y ($X = Y$ and $X \neq Y$) are an electron pair, oxygen, sulfur, selenium, or the methyl cation. Eight of these compounds had been synthesized and characterized previously.[10–17]

## Results and Discussion

We found the most efficient synthesis of dppmSe to be the direct stoichiometric reaction of dppm and red elemental selenium in equimolar amounts in refluxing toluene or benzene. The progress of the reaction can be followed visually by the disappearance of the red selenium. The standard procedure for the synthesis of $(C_6H_5)_3PSe$ from $(C_6H_5)_3P$ and KSeCN in acetonitrile[18] works also for dppmSe although significant amounts (perhaps 20%) of dppm$Se_2$ are also produced. This impurity necessitates considerable purification procedures in order to isolate dppmSe from the mixture. It was also found that the reaction sequence (1) and (2),[8,9,15–17] which is convenient for the synthesis of dppmO and dppmS, does not work well for the selenide, in which case very little dppmSe is produced, but unidentified side products of selenium with horrible odors are produced. Because of the well-known

$$Ph_3PX + CH_3Li \rightarrow Ph_2P(X)CH_2Li + PhH \qquad (1)$$

$$Ph_2P(X)CH_2Li + Ph_2PCl \rightarrow Ph_2P(X)CH_2PPh_2 \qquad (2)$$

$$X = O, S$$

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[1] (a) Reported at the International Conference on Phosphorus Chemistry, Halle, DDR, Sept 1979. (b) Taken in part from the Ph.D. Dissertation of E. D. Walton, University of Maryland, 1979.

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toxicity of volatile organoselenium compounds,[19] this reaction sequence was not pursued further for the selenide case.

Oxide derivatives such as dppmOX where X is S or Se can be conveniently synthesized by the gentle $H_2O_2$ oxidation of dppmS and dppmSe, respectively. Vigorous or extended heating or excess $H_2O_2$ results in further oxidation of the dppmXO compounds to dppm$O_2$. In addition, the same compounds can be synthesized from dppmO by addition of S or Se. Likewise, dppmSSe can be produced from dppmS via addition of Se or from dppmSe by reaction with S. The methyl- and benzylphosphonium salts are synthesized by simple quaternization of dppmX compounds, where X is O, S, or Se, with the corresponding organic bromide or methyl iodide. We have found no evidence for reaction at sulfur or selenium in this reaction, although the reaction of methyl halide with tertiary phosphine sulfides is well established.[20]

The proton NMR data for the dppmXY compounds are given in Table I. The chemical shifts of the bridging methylene protons display an important trend which can be used to infer bonding properties of the adjacent chalcogeno–phosphoryl bonds. The methylene proton chemical shifts increase in the order $Ph_2P– < Ph_2P(O)– < Ph_2P(S)– < Ph_2P(Se)– < Ph_2PR^+–$. Furthermore, the effect of the two phosphorus moieties attached to the methylene group is additive. For example, if the charge on phosphorus in dppm is assumed to be zero and that on each $Ph_2P^+Me–$ group in dppmMe and dppm$Me_2$ is assumed to be 1+, then the average chemical shift in the methylene protons caused by the addition of one positive charge on phosphorus can be estimated by averaging the chemical shift differences in the five pairs of compounds: $\delta$ in dppmMe – $\delta$ in dppm (1.34); $\delta$ in dppmOMe – $\delta$ in dppmO (1.69); $\delta$ in dppmSMe – $\delta$ in dppmS (2.00); $\delta$ in dppmSeMe – $\delta$ in dppmSe (1.81); $\delta$ in dppm$Me_2$ – $\delta$ in dppmMe (1.43). The average of these five chemical shifts differences is 1.65 ppm, indicating an approximate effect of 1.65 ppm/positive charge. Although the standard deviation of this small set of five numbers is quite large (±0.27 ppm), it is still considered better to average the five values rather than use only one arbitrarily. In a consistent manner, the chemical shifts in the five oxidized pairs average 0.48 ppm: $\delta$ dppmO – $\delta$ dppm (0.22); $\delta$ dppmMeO – $\delta$ dppmMe (0.63); $\delta$ dppm$O_2$ – $\delta$ dppmO (0.56); $\delta$ dppmSO – $\delta$ dppmS (0.53); $\delta$ dppmSeO – $\delta$ dppmSe (0.45). Since the average effect of adding an oxygen causes a 0.48 ppm chemical shift, this corresponds to the oxygen causing a charge on phosphorus of (0.48 ppm/1.65 ppm)/charge or 0.29+. Similar calculations give a 0.47+ charge on phosphorus for the diphenylthiophosphoryl group and a 0.52+ charge on phosphorus in the diphenylselenophosphoryl group. The correlation coefficient between the sum of the charges on the two phosphorus atoms (Table II) and the chemical shift of the methylene proton for all 15 dppmXY compounds, including those in which X and/or Y are electron pairs is 0.98. The equation for the line is $\delta_{CH_2}$ (ppm) = $1.57\sum q_i + 2.65$, where $q_i$ is the charge generated on each phosphorus atom. The average deviation of the chemical shift for a particular compound calculated by using the charges in Table II according to this equation is ±0.10 ppm. It should be noted that the methylene chemical shift between dppm and dppmX for each series is considerably less than the chemical shift between dppmY and dppmXY; i.e., the effect on the methylene shift is less when adding an oxygen to dppm than when adding an oxygen to dppmX, dppmSe, dppmO, or dppmMe. It appears that the remaining electron pair in dppmX can buffer or ameliorate the effect of the first positive charge which develops on one phosphorus in the compound, but when the second phosphorus is oxidized or quaternized, no electron pair remains and the effect of the positive charges developed on both phosphorus atoms is more drastically felt by the intervening methylene protons. As might be expected, a correlation between the sums of the charges on phosphorus and the methylene proton chemical shifts is better when only the dppmXY compounds without lone pairs are included. Inherent in the above correlation between charge and chemical shift is the assumption that the chemical shifts are essentially determined by diamagnetic shielding (inductive) considerations in much the same way as the original electronegativity scale of Allred and Rochow[21] was proposed for the group 4 elements from the proton chemical shifts of the $(CH_3)_4M$ compounds, where M = C, Si, Cr, Sn, or Pb. That concept was attacked, however, because of the possible anisotropic effects of the heavy (and different) atoms in those compounds.[22] That objection would not apply here because in each case the identical atoms, i.e., two phosphorus atoms, are attached to the methylene group.

The conclusion is therefore that the charge developed on the diphenylphosphino group in dppmXY compounds increases in the order $Ph_2P–(0.0) < Ph_2P(O)–$ (0.29+) $< Ph_2(S)–$ (0.47+) $< Ph_2P(Se)–$ (0.52+) $< Ph_2PMe–$ (1.0+). Since this is not in the expected order on the basis of the electronegativity of the chalcogens, these data furnish additional corroborative evidence that contribution of the double-bonded canonical form a for the chalcogeno–phosphoryl bond is more important in the case of oxygen[23] than in the case of sulfur and selenium, for which the dipolar form b is of greater importance.

a b

The effect of phenyl replacement by methyl in the dppmXY compounds also has a large effect on the chemical shifts of the methylene protons, although in the mixed methyl–phenyl ligands it is not possible to include these compounds in the earlier correlations. The methylene proton chemical shift between dppm ($\delta$ 2.78) and the analogous $Ph_2PCH_2PMe_2$ ($\delta$ 2.12) is 0.66 ppm, between dppmS ($\delta$ 3.32) and $Ph_2P(S)CH_2PMe_2$ ($\delta$ 2.64) is 0.68 ppm, between dppmSO ($\delta$ 3.85) and $Ph_2P(S)CH_2P(O)Me_2$ ($\delta$ 3.04) is 0.81 ppm, between dppm$S_2$ ($\delta$ 3.98) and $Ph_2P(S)CH_2P(S)Me_2$ ($\delta$ 3.45) is 0.53 ppm, between dppmSSe ($\delta$ 4.12) and $Ph_2P(S)CH_2P(Se)Me_2$ ($\delta$ 3.60) is 0.52 ppm, and between dppmSMe ($\delta$ 5.32) and $Ph_2P(S)CH_2PMe_3^+$ ($\delta$ 4.69) is 0.63 ppm. On average the compounds with the two methyl groups instead of two phenyl groups have the $CH_2$ chemical shifts 0.64 ppm to higher field. This is expected from the lower electronegativity of methyl compared to phenyl. In a similar comparison the methylene proton chemical shift in $Ph_3PCH_2PPh_3^{2+}$ is 6.75 ppm[24] compared to 5.55 ppm in dppm$Me_2^{2+}$. The explanation for this dramatic influence of phosphinophenyl compared to phosphinomethyl on the bridging methylene protons is not clear. Perhaps a favored conformation would result in a ring current effect for the aromatic compounds.

Phosphorus-31 NMR data are given in Table III. Except for dppm$Se_2$, which is discussed below, the dppm$X_2$ compounds are simple singlets. The dppmXY compounds exhibit the expected doublet of doublet signals. The assignments of the peaks are generally straightforward since the tertiary phos-

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**Table I.** $^1$H NMR Data for $(C_6H_5)_2P(X)CH_2P(Y)(C_6H_5)_2$ Derivatives and Similar Compounds[a]

| compd | $\delta_{CH_2}$ | $^2J_{P(:)CH}$ | $^2J_{P(O)CH}$ | $^2J_{P(S)CH}$ | $^2J_{P(Se)CH}$ | $^2J_{P(Me^+)CH}$ | $\delta_{C_6H_5}$ | $\delta_{CH_3}$ | $^2J_{PCH_3}$ |
|---|---|---|---|---|---|---|---|---|---|
| dppm | 2.78 t | 1.2 | | | | | | | |
| dppmO | 3.06 d | <0.5 | 12.5 | | | | 7.0–7.9 m | | |
| dppmS | 3.32 dd | 1.0 | | 12.8 | | | 7.0–8.0 m | | |
| dppmSe | 3.44 dd | 2.0 | | | 12.7 | | 6.9–7.9 m | | |
| [dppmMe]I | 4.12 d | <0.5 | | | | 14.1 | 7.1–8.2 m | 2.78 d | 14.0 |
| $dppmO_2$ | 3.62 t | | 15.0 | | | | 7.1–8.1 m | | |
| $dppmS_2$ | 3.98 t | | | 13.5 | | | 7.1–8.0 m | | |
| $dppmSe_2$ | 4.28 t | | | | 13.0 | | 7.1–8.1 m | | |
| $[dppmMe_2]Br_2$ | 5.55 t | | | | | 15.5 | 7.5–8.4 m | 2.56 d | 14.0 |
| dppmOS | 3.85 dd | | 14.2 | 12.5 | | | 7.1–8.2 m | | |
| dppmOSe | 3.89 dd | | 14.3 | | 12.1 | | 7.2–7.9 m | | |
| dppmSSe | 4.12 t | | | 13.0 | 13.0 | | 7.1–8.1 m | | |
| [dppmOMe]Br | 4.75 dd | | 12.0 | | | 17.0 | 7.2–8.0 m | 2.82 d | 14.6 |
| [dppmSMe]Br | 5.32 dd | | | 12.6 | | 15.6 | 7.1–8.4 m | 2.96 d | 13.9 |
| [dppmSeMe]Br | 5.25 dd | | | | 11.6 | 14.3 | 7.4–8.2 | 2.10 d | 14.0 |
| $[dppmPh_2]I_2$[b] | 6.75 t | | | | | 16.0 | 7.3–8.2 m | | |
| $[dppmSe]Cr(CO)_4$ | 3.80 dd | 7.5 | | | 11.0 | | 7.2–7.7 m | | |
| $[dppmSeMo(CO)_4$ | 3.76 dd | 9.0 | | | 11.5 | | 6.9–7.4 m | | |
| $[dppmSe]W(CO)_4$ | 3.60 dd | 9.0 | | | 12.0 | | 7.1–8.0 m | | |
| $[dppmS]Cr(CO)_4$[c] | 3.63 dd | 7.8 | | 10.0 | | | 7.1–7.8 m | | |
| $[dppmS]Mo(CO)_4$[c] | 3.62 dd | 7.5 | | 10.0 | | | 7.1–7.8 m | | |
| $[dppmS]W(CO)_4$[c] | 3.70 dd | 7.6 | | 10.5 | | | 7.1–7.7 m | | |
| $Ph_2P(S)CH_2PMe_2$[c] | 2.64 d | <0.5 | | 13.0 | | | 7.3–8.1 m | 1.08 d | 3.8 |
| $Ph_2P(S)CH_2P(S)Me_2$[c] | 3.45 dd | | | *d* | | | 7.4–8.2 m | 1.87 d | 13.5 |
| $Ph_2P(S)CH_2P(Se)Me_2$ | 3.47 dd | | | 12.5 | 14.3 | | 7.2–8.0 m | 1.98 d | 13.5 |
| $Ph_2P(Se)CH_2P(S)Me_2$ | 3.49 dd | | | 14.5 | 12.5 | | 7.2–8.0 m | 1.82 d | 13.3 |
| $[Ph_2P(S)CH_2PMe_3]Br$[c] | 4.69 dd | | | 12.9 | | 16.4 | 7.5–8.4 m | 2.10 d | 14.1 |

[a] Chemcial shifts in ppm from $Me_4Si$; coupling constants in Hz. [b] Reference 23. [c] Reference 9. [d] On the basis of the magnitudes of $^2J_{Ph_2P(S)CH_2}$ and $^2J_{Me_2P(S)CH_2}$ in similar compounds, these are assigned the values of 12.5 and 15.0 Hz, respectively.

**Table II.** Some Parameters in $Ph_2P(X)CH_2P(Y)Ph_2$ and the Sum of the Estimated Charges on Phosphorus

| X | Y | $\delta_{CH_2}$ | $\Sigma q_i\,(+)$ | $J_{PSe}$, Hz | $\nu_{PSe}$, $cm^{-1}$ |
|---|---|---|---|---|---|
| ep[a] | ep | 2.78 | 0 | | |
| ep | O | 3.06 | 0.29 | | |
| ep | S | 3.32 | 0.47 | | |
| ep | Se | 3.44 | 0.52 | 730.0 | 528 |
| O | O | 3.62 | 0.58 | | |
| O | S | 3.85 | 0.76 | | |
| O | Se | 3.89 | 0.81 | 739.2 | 525 |
| S | S | 3.98 | 0.94 | | |
| S | Se | 4.12 | 0.99 | 746.5 | 535 |
| ep | $Me^+$ | 4.12 | 1.00 | | |
| Se | Se | 4.28 | 1.04 | 751.7 | 531 |
| O | $Me^+$ | 4.75 | 1.29 | | |
| Se | $Me^+$ | 5.25 | 1.52 | 754.0 | 539 |
| S | $Me^+$ | 5.32 | 1.47 | | |
| $Me^+$ | $Me^+$ | 5.55 | 2.00 | | |
| Se | $Bz^+$ | | | 751.9 | 538 |

[a] Electron pair.

**Table III.** $^{31}P$ NMR Data for $Ph_2P(X)CH_2P(Y)Ph_2$ Compounds[a]

| X | Y | $\delta_{P(ep)}$ | $\delta_{P(O)}$ | $\delta_{P(S)}$ | $\delta_{P(Se)}$ | $\delta_{PR^+}$ | $J_{PP}$, Hz |
|---|---|---|---|---|---|---|---|
| ep[b] | ep | −23.0 | | | | | . . . |
| ep | O | −28.4 | 27.7 | | | | 50.0 |
| ep | S | −28.0 | | 40.1 | | | 76.0 |
| ep | Se | −27.2 | | | 30.7 | | 85.1 |
| ep | $Me^+$ | −26.5 | | | | 22.9 | 61.0 |
| O | O | | 24.2 | | | | . . . |
| O | S | | 23.1 | 35.6 | | | 15.6 |
| O | Se | | 23.0[c] | | 24.7[c] | | 18.0 |
| O | $Me^+$ | | 24.6 | | | 20.8 | 12.0 |
| S | S | | | 34.6 | | | . . . |
| S | Se | | | 34.9 | 24.4 | | 14.6 |
| S | $Me^+$ | | | 33.7 | | 21.2 | 9.0 |
| Se | Se | | | | 24.4 | | 15.8[e] |
| Se | $Me^+$ | | | | 21.9[c] | 21.0[c] | 6.7 |
| $Me^+$ | $Me^+$ | | | | | 20.0 | . . . |
| Se[d] | $Bz^+$ | | | | 23.4 | 23.4 | 8.6[e] |

[a] Chemical shifts in ppm (positive if deshielded from 85% $H_3PO_4$). [b] Electron pair. [c] Assignment unequivocal since the $^{77}Se$ satellites uniquely determine the phosphine selenide δ. [d] $J_{PSe}$ is 752 Hz. [e] Obtained from $^{77}Se$ satellites.

phines have a resonance upfield and the chemical shifts downfield are in the order $PMe^+ < P(O) < P(Se) < P(S)$. In cases where the chemical shift is small, as, for example, in dppmOSe (23.0 and 24.7 ppm) and dppmSeMe (21.9 and 21.0 ppm), the assignments can be made unequivocally because the phosphine selenide exhibits selenium-77 satellites. Phosphorus–phosphorus couplings are large for dppmX (50 to 85 Hz) and small for dppmXY (6.7 to 18 Hz), where X and Y are other than an electron pair. These are in the range previously observed for unsymmetrical bis-phosphorus ligands.[9] The $dppmSe_2$ gives an unusual spectrum in that 14.0% of the molecules contain an atom of $^{77}Se$. This 14% of the compound results in an AA′X spectrum in which each observable half of the selenium satellites is a doublet, from which $J_{PP}$ can be determined, even though the phosphorus atoms are chemically equivalent.[6] Another unusual case is the spectrum of [dppmSeBz]Br in which the chemical shifts of the selenophosphoryl–phosphorus and the phosphonium–phosphorus are coincidentally the same, resulting in a single main peak. However, the selenium satellites are a doublet of doublets, from which $J_{PP}$ can be determined.

Selenium satellites are observed in each of the dppmSeX compounds. As X generates a greater positive charge on the one phosphorus atom (i.e., electron pair < O < S < Se < $Me^+$), $J_{PSe}$ on the geminal phosphorus atom increases. This is expected since $J_{PSe}$ increases in $Z_3PSe$ compounds as the electronegativity of Z increases.[25] The correlation coefficient between $J_{PSe}$ and the charge calculated on the geminal phosphorus atoms by the earlier calculations is 0.91. The correlation of phosphorus–selenium stretching frequencies as determined by laser Raman techniques, with $J_{PSe}$, $\delta_{CH_2}$, or estimated charge on the geminal phosphorus in dppmSeX compounds is not good probably because of the small range of values (13 $cm^{-1}$) compared to the precision of measurement (±1 $cm^{-1}$). As expected, however, the quaternary salts (X = $Me^+$ and $benzyl^+$) do have the largest PSe stretching frequencies and dppmSeS and $dppmSe_2$ have intermediate frequencies. For dppmSe and dppmSeO the frequencies are lowest but inverted from what is expected.

The two new compounds $Ph_2P(S)CH_2P(Se)Me_2$ and $Ph_2P(Se)CH_2P(S)Me_2$ have phosphorus–selenium coupling constants (699 and 747 Hz, respectively) consistent with the expected values for dimethylselenophosphoryl and diphenylselenophosphoryl compounds.[25] Other data for these compounds are given in the Experimental Section.

Carbon-13 NMR data for the compounds are given in Table IV. Of principal interest is the methylene carbon which is generally a triplet for $dppmX_2$ and a doublet of doublets for dppmXY or dppmX. The magnitude of $^1J_{PC}$ for the bridging methylene carbon increases in the order $^1J_{P(:)C} < {}^1J_{P(Se)C} < {}^1J_{P(S)C} < {}^1J_{P(O)C}$. This is in agreement with previous observations.[26] Also the magnitude of $^1J_{P(X)C}$ is larger in dppmX than in the corresponding dppmXY. For example, $^1J_{P(O)C}$ is 62.0 Hz in dppmO but is 58.6, 59.4, and 55.9 Hz in $dppmO_2$, dppmOS, and dppmOSe, respectively. The explanation for these trends is not immediately obvious.

The reaction of dppmSe with $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ in diethylene glycol dimethyl ether (diglyme) and methylcyclohexane (5:1 by volume) for several hours at 130 °C produced the expected chelated tetracarbonyls in about 50% yield. As previously observed with the analogous dppmS complexes,[9] the molybdenum compound is the least stable in solution, turning black after some minutes. This hampered NMR measurements so the $J_{PSe}$ was not obtained for $(dppmSe)Mo(CO)_4$. As has been found with five-membered chelated rings including a phosphine donor, the coordination shift (Table V) of the phosphine is quite large,[27,28] viz., 96.3, 69.0, and 54.7 ppm, respectively, in the Cr, Mo, and W complexes, which corresponds to a chelate ring effect of about 35 ppm, in agreement with previous work[28–30] involving a variety of phosphorus donors. The corresponding coordination shifts of the phosphine selenides are 8.7, 7.6, and 11.1 ppm, respectively, in the Cr, Mo, and W complexes, which compares with 25.5, 24.4, and 29.9 ppm in similar phosphine–phosphine oxide complexes, and 17.4, 15.1, and 19.5 ppm in the analogous dppmS complexes for Cr, Mo, and W, respectively. In each case the coordination shift of the chalcogenyl phosphorus is least for the Mo compound. It should be emphasized that the coordination of the chalcogen atom in phosphine chalcogenides within a five-membered chelate ring does not result in the extraordinarily large chelate ring effect for the chalcogenyl phosphorus vis-à-vis that of a phosphorus directly bound to the metal. Several monodentate complexes of the type $R_3PXM(CO)_5$ where X is S or Se and M is Cr, Mo, or W have

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**Table IV.** $^{13}C$ NMR Data for $Ph_2P(X)CH_2P(Y)Ph_2$ Compounds[a]

| X | Y | $\delta$-$CH_2$- | $J_{P(:)C}$ | $J_{P(O)C}$ | $J_{P(S)C}$ | $J_{P(Se)}$ | $\delta_{C_6H_5}$[b] |
|---|---|---|---|---|---|---|---|
| ep[c] | ep | 28.2 t | 22.2 | | | | 129–139 |
| ep | O | 29.7 dd | 32.7 | 62.0 | | | 127–138 |
| ep | S | 34.4 dd | 31.7 | | 54.7 | | 127–138 |
| ep | Se | 30.4 dd | 31.6 | | | 47.7 | 127–138 |
| O | O | 34.5 t | | 58.6 | | | 127–135 |
| O | S | 36.0 dd | | 58.4 | 44.9 | | 127–135 |
| O | Se | 37.9 dd | | 55.9 | | 37.4 | 128–135 |
| S | S | 38.9 t | | | 45.1 | | 128–135 |
| S | Se | 38.2 dd | | | 44.0 | 38.2 | 128–135 |
| Se | Se | 38.2 t | | | | 36.4 | 128–133 |
| $Cr(CO)_4$ | Se | 37.0 dd[d] | | | | | 125–136 |

[a] Chemical shifts are in ppm downfield from $Me_4Si$. *J*s are in Hz. [b] The individual resonances in the phenyl region have not been assigned. [c] Electron pair. [d] $^1J_{PC} = 60.8$ and 5.3 Hz. $\delta_{CO}$(axial) = 218.7 d ($^2J_{PCrC} = 13$ Hz), $\delta_{CO}$(equatorial) = 227.3 d ($^2J_{PCrC} = 11.9$ Hz), and $\delta_{CO}$(equatorial) = 227.7 d ($^2J_{PCrC} = 12.8$ Hz). If the trans PCrC coupling is smaller than the cis PCrC coupling as has been observed previously, then the latter resonance (227.7 ppm) would be due to the CO trans to Se and the 227.3 ppm resonance would be due to the CO trans to P.

**Table V.** $^{31}P$ NMR Data for $[Ph_2P(X)CH_2PPh_2]M(CO)_4$, X = S or Se and M = Cr, Mo, or W[a]

| X | M | $\delta_{P(X)}$ | $\Delta_{P(X)}$[b] | $\delta_P$ | $\Delta_P$[b] | $J_{PP}$, Hz |
|---|---|---|---|---|---|---|
| Se | ep[c] | 30.7 | . . . | −27.2 | . . . | 85.1 |
| Se[d] | Cr | 39.4 | 8.7 | 69.1 | 96.3 | 91.4 |
| Se | Mo | 38.3[e] | 7.6[e] | 41.8[e] | 69.0[e] | 85.5 |
| Se[f] | W | 41.8 | 11.1 | 27.5 | 54.7 | 83.7 |
| S[g] | ep[c] | 40.1 | . . . | −28.0 | . . . | 76 |
| S[g] | Cr | 57.5 | 17.4 | 63.9 | 91.9 | 83 |
| S[g] | Mo | 55.5 | 15.1 | 37.9 | 65.9 | 78 |
| S[g,h] | W | 59.6 | 19.5 | 25.2 | 53.2 | 76 |

[a] $\delta$ in ppm is positive if deshielded from 85% $H_3PO_4$. [b] Coordination shift = $\delta$(complex) − $\delta$(free ligand). [c] Free ligand. [d] $J_{PSe} = 645$ Hz. [e] The spectrum is an AB pair. The assignments are based on what appears to be Se satellites symmetrically disposed about the upfield resonance. However, the assignments are not absolutely certain. [f] $J_{PSe} = 627$ Hz; $J_{PW} = 236$ Hz. [g] Reference 9. [h] $J_{PW} = 240$ Hz.

been reported,[31,32] but they are not especially stable and $^{31}P$ NMR data have not yet been reported on these compounds; therefore there is no standard reference point for determining a chelate ring effect in our present type of compound. However, the coordination shifts of $^{31}P$ in complexes of simple $R_3PS$ and $R_3PSe$ complexes of mercury(II) halides[33] are rather small in magnitude (0–10 ppm) as might be expected since the phosphorus in the free ligand is already "coordinated" to the chalcogen. The chelate ring effect on the chemical shift of phosphorus atoms not directly attached to the metal would be worth further investigation.

The $^1H$ spectra of the (dppmSe)$M(CO)_4$ and the (dppmS)$M(CO)_4$ complexes indicate the chemical shift range of the methylene protons as 3.6 to 3.8 ppm. One would expect that the coordination to a metal through the chalcogen of a tertiary phosphine chalcogenide would increase the positive charge on that phosphorus by enhancing the importance of canonical form b, and also the coordination of a tertiary phosphine to a metal would increase the positive charge on the coordinated (quasi-quaternized) phosphorus. Both of these effects should lead to a large (deshielded) chemical shift of the methylene protons by increasing the electronegativities of the two adjacent phosphorus atoms, but the actual chemical shifts are in the range corresponding to a low positive charge on the geminal phosphorus atoms. This can be conviently rationalized by $\pi$ back-bonding from the metal to the phosphorus and the chalcogen. The phosphorus–selenium coupling constant decreases by about 100 ± 10 Hz upon chelation in (dppmSe)$Cr(CO)_4$, (dppmSe)$W(CO)_4$, and (dppmSe)$HgBr_2$ compared to a decrease of 130 ± 10 Hz in the monodentate ligand complexes of $(n\text{-}Bu_3PSe)_2MX_2$, where M is Cd or Hg and X is Cl, Br, or I. The (dppmSe)$HgX_2$ compounds are quite insoluble in common organic solvents. This prevented the usual collection of NMR data for these adducts. However, the $^{31}P$ NMR spectrum of (dppmSe)$HgBr_2$ was obtained on a saturated solution in dichloroacetonitrile by collecting data for 12 h (11070 transients).

In conclusion we have (a) synthesized the complete series of fifteen $Ph_2P(X)CH_2P(Y)Ph_2$ compounds, where X and Y are an electron pair, O, S, Se, or $Me^+$, and in addition several new compounds related to the ones above, e.g., $Ph_2P(S)CH_2P(Se)Me_2$, $Ph_2P(Se)CH_2P(S)Me_2$, and $[Ph_2P(Se)CH_2P(CH_2Ph)Ph_2]Br$, (b) presented the $^{31}P$, $^{13}C$, and $^1H$ NMR data for most of these compounds, (c) shown that there is a good correlation between the chemical shift of the methylene group in the dppmXY compounds and the sum of the positive charge on the phosphorus atoms, which indicate that oxygen is a better $\pi$ back-bonder to phosphorus than sulfur or selenium in the chalcogeno–phosphoryl bond, (d) demonstrated that dppmSe forms complexes readily in which it is a bidentate ligand (Se and P donor atoms) with the group 6 metal carbonyls and with mercury(II) halides, which are analogous to the previously reported dppmS complexes,[9] and (e) established a reasonable correlation between the magnitude of $J_{PSe}$ and the positive charge (electronegativity) residing on the geminal phosphorus atom in $Ph_2P(Se)CH_2P(X)Ph_2$.

## Experimental Section

Phosphorus-31 NMR spectra were obtained with a Varian XL-100 Fourier transform spectrometer equipped with a Nicolet Multi-Observe Nuclei Accessory (MONA) unit operating at 40.5 MHz by using broad-band proton decoupling. Samples were generally contained in spinning 10-mm tubes with a mixture of $CH_2Cl_2$–$CDCl_3$ (1:1 or 2:1) as the solvent system, with a 1-mm capillary tube containing 85% $H_3PO_4$ as reference concentrically inserted in the larger tube. The $CH_2Cl_2$ was used to enhance solubility, and the $CDCl_3$ was used for the internal $^2H$ lock.

Carbon-13 NMR spectra were obtained with the same instrument operating at 25.1 MHz with tetramethylsilane ($Me_4Si$) as reference. Proton data were obtained on the same instrument operating at 100 MHz as well as at 60 MHz with a Varian A-60A or Varian EM-360 spectrometer with $Me_4Si$ as the reference. All chemical shifts are reported as positive if deshielded from the reference.

Raman spectra were obtained on solid samples in melting point capillary tubes with a Spex double monochromator (Model 1401) equipped with an EMI 9658 photomultiplier tube and associated photon-counting unit. The monochromatic light source was a Coherent Radiation Laboratory Model 52 argon ion laser (488 nm).

Microanalyses were furnished by Dr. Franz Kasler, University of Maryland.

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The compounds dppm, dppmS, dppmO, $dppmO_2$, [dppmOMe]Br, [dppmSMe]Br, and $[dppmMe_2]Br_2$ either were prepared by literature methods[9-15] or were authentic samples prepared earlier in these laboratories.[34,35] Because of the toxic nature of selenium compounds,[19] proper precautions should be observed.

**$Ph_2PCH_2P(Se)PPh_2$, dppmSe.** Red Se (1.9 g, 24 mmol) and dppm (9.7 g, 25 mmol) were heated at reflux under $N_2$ in 100 mL of deoxygenated toluene for 2 h, after which the solution was cooled and the solvent removed by rotary evaporation at 10 mmHg. Addition of MeOH to the residue caused the formation of white crystals which were recrystallized from $CH_2Cl_2$–hexane. The product, mp 110–111 °C, weighed 8.9 g (77%). Anal. Calcd for $C_{25}H_{22}P_2Se$: C, 64.80; H, 4.79. Found: C, 64.40; H, 4.79.

**$Ph_2P(Se)CH_2P(Se)Ph_2$, $dppmSe_2$.** Red Se (4.0 g, 51 mmol) and dppm (9.7 g, 25 mmol) were heated at reflux in 100 mL of deoxygenated toluene under $N_2$ overnight. The cooled solution was filtered through diatomaceous earth to remove excess Se. The filtrate was evaporated by using a rotary evaporator and addition of EtOH to the resulting oil caused crystallization. The yield of product, mp 182–184 °C (lit.[36] 183 °C), was 10.4 g (82%).

**$Ph_2P(Se)CH_2P(S)Ph_2$, dppmSSe.** This product can be prepared by the reaction of dppmS with Se as described above or from dppmSe by the analogous reaction with elemental S. For example, dppmS (4.2 g, 10 mmol) with Se (0.79 g, 10 mmol) in toluene produced, after recrystallization of the crude product from EtOH, 4.3 g (87%) of white crystals, mp 202 °C dec. Anal. Calcd for $C_{25}H_{22}P_2SSe$: C, 60.61; H, 4.48. Found: C, 61.59; H, 4.55.

**$Ph_2P(O)CH_2P(Se)Ph_2$, dppmOSe.** An aqueous solution of 30% $H_2O_2$ (2 mmol) in 10 mL of acetone was added dropwise to 0.93 g (2 mmol) of dppmSe in 40 mL of acetone at room temperature. After the solution was stirred for 1 h, the acetone was removed via rotary evaporation leaving a white solid, mp 200 °C dec, weighing 0.6 g (65%), after washing with MeOH. Anal. Calcd for $C_{25}H_{22}P_2OSe$: C, 62.64; H, 4.63. Found: C, 61.98; H, 4.53.

**$Ph_2P(O)CH_2P(S)Ph_2$, dppmOS.** This compound was prepared by the reaction of dppmS and $H_2O_2$ for 2 h as described above. The yield of dppmOS, mp 212–214 °C (lit.[36] 209 °C and lit.[15] 209–213 °C), was 62%.

**$Ph_2P(S)CH_2P(S)Ph_2$, $dppmS_2$.** The compound was prepared from dppmS by the addition of S in refluxing $C_6H_6$ for 0.5 h. The yield of white crystals, mp 178–180 °C (lit.[10] 183–185 °C), was 70%.

**$Ph_2P(O)CH_2P(O)Ph_2$, $dppmO_2$.** dppm was oxidized with $H_2O_2$ in aqueous acetone to give $dppmO_2$, mp 178–179 °C (lit.[12] 181–182 °C), in 90% yield.

**$[Ph_2P(Se)CH_2PPh_2Me]I$, [dppmSeMe]I.** dppmSe (4.6 g, 10 mmol) was heated at reflux with 1.4 g (10 mmol) of MeI in deoxygenated toluene (25 mL) for 3 h under $N_2$. Crystals were formed by cooling to –5 °C. The product, mp 219 °C, weighed 4.5 g (76%). Anal. Calcd for $C_{26}H_{25}P_2ISe$: C, 51.59; H, 4.16. Found: C, 51.61; H, 4.16.

**$Ph_2P(Se)CH_2PPh_2(CH_2Ph)]Br$, [dppmSeBz]Br.** This compound was prepared as described for the dppmMe salt except that $PhCH_2Br$ was used to react with dppmSe. The product, mp 268 °C, was produced in 88% yield (4.2 g). Anal. Calcd for $C_{32}H_{29}BrP_2Se$: C, 60.59; H, 4.61. Found: C, 60.72; H, 4.45.

**$[Ph_2PCH_2PPh_2Me]I$, [dppmMe]I.** MeI (0.7 g, 5 mmol) and 1.9 g (5 mmol) of dppm were heated at reflux in 20 mL of $C_6H_6$ under $N_2$ for 4 h. The white crystals which formed were collected by filtration, washed quickly with cold EtOH and $Et_2O$, and dried. The yield of the monoquaternized iodide, mp 178–180 °C, was 1.8 g (69%). Anal. Calcd for $C_{26}H_{25}IP_2$: C, 59.33; H, 4.79. Found: C, 59.61; H, 4.81.

**$Ph_2P(S)CH_2P(Se)Me_2$ and $Ph_2P(Se)CH_2P(S)Me_2$.** These two isomeric compounds were prepared from $Ph_2P(S)CH_2PMe_2$[9] and $Ph_2PCH_2P(S)Me_2$,[9] respectively, by the reaction with KSeCN in $CH_3CN$.[18] The progress of the reactions was monitored by thin-layer chromatography (TLC), and as anticipated the more reactive $Me_2P$– group was completely selenated in about 20 min whereas the $Ph_2P$– group required about 2 h under the same conditions. $Ph_2P(S)CH_2PMe_2$ (1.0 g, 3.4 mmol) and 0.48 g (3.4 mmol) of KSeCN were stirred magnetically in 50 mL of $CH_3CN$ under $N_2$. After completion of the reaction in about 20 min (as determined by the absence of starting material by TLC), addition of water caused precipitation of the product. The precipitate was dissolved in $C_6H_6$ and combined with $C_6H_6$ extracts of the aqueous layer. Removal of the solvent yielded 1.04 g (2.8 mmol, 82%) of $Ph_2P(S)CH_2P(Se)Me_2$, mp 154–155 °C, after recrystallization from $C_6H_6$–hexane. The $^{31}P$ NMR data are as follows: $\delta_{P(S)}$ 32.9, $\delta_{P(Se)}$ 14.6 ($J_{PP} = 23.1$ Hz, $J_{PSe} = 698.7$ Hz). Anal. Calcd for $C_{15}H_{18}P_2SSe$: C, 48.53; H, 4.89. Found: C, 48.78; H, 5.05.

$Ph_2P(Se)CH_2P(S)Me_2$ was prepared in the same fashion from $Ph_2PCH_2P(S)Me_2$ and KSeCN but the reaction required more than 2 h for completion. The product, mp 155–156 °C, was produced in 78% yield. The $^{31}P$ NMR data are as follows: $\delta_{P(S)}$ 36.4, $\delta_{P(Se)}$ 21.6 ($J_{PP} = 16.0$ Hz, $J_{PSe} = 747.3$ Hz). The $^{13}C$ data are as follows: $\delta_{CH_3}$ 23.2 d ($^1J_{P(S)CH_3} = 56.5$ Hz), $\delta_{CH_2}$ 38.9 dd [$^1J_{P(Se)CH_2} = 32.3$ Hz, $^1J_{P(S)CH_2} = 40.4$ Hz (these two coupling constants are tentatively assigned because of similarities to the values given in Table IV; however, they could possibly have the reverse assignments)], $\delta_{C(1)\ Ph}$, 132.2 d ($^1J_{P(Se)C} = 74.4$ Hz), $\delta_{C(2,6)Ph}$ 132.6 d ($^2J_{P(Se)C} = 13.2$ Hz), $\delta_{C(3,5)Ph}$ 129.5 d ($^3J_{P(Se)C} = 12.5$ Hz), $\delta_{C(4)Ph}$ 131.9 s. Anal. Calcd for $C_{15}H_{18}P_2SSe$: C, 48.53; H, 4.89. Found: C, 48.80; H, 5.15.

**$[Ph_2P(Se)CH_2PPh_2]M(CO)_4$, M = Cr, Mo or W.** dppmSe (1.38 g, 3.0 mmol) and $Cr(CO)_6$ (0.66 g, 3 mm) were dissolved in 20 mL of diglyme and 4 mL of methylcyclohexane and heated under $N_2$ in an oil bath at 130–135 °C for 4 h. The solvent was removed with a rotary evaporator at 60 °C and 5 mmHg, which also causes sublimation of any excess $Cr(CO)_6$. The yellow crystalline residue, mp 124 °C dec, was washed with cold MeOH and $Et_2O$. The yield was 0.80 g (48%). Anal. Calcd for $C_{29}H_{22}O_4CrP_4Se$: C, 55.52; H, 3.53. Found: C, 54.60; H, 3.47. The $(dppmSe)Mo(CO)_4$ complex, mp 129 °C dec, was prepared analogously in 45% yield. Solutions of the yellow compound are less stable than the Cr and W compounds and turn dark after a few minutes in air. Anal. Calcd for $C_{29}H_{22}O_4MoP_2Se$: C, 51.88; H, 3.30. Found: C, 52.10; H, 3.27. The W analogue, mp 142 °C dec, is greenish yellow and was isolated in 48% yield by the above procedure. Anal. Calcd for $C_{29}H_{22}O_4P_2SeW$: C, 45.88; H, 2.92. Found: C, 46.37; H, 2.91.

**$[Ph_2P(Se)CH_2PPh_2]HgX_2$, X = Cl, Br, I.** A saturated solution of $HgCl_2$ (0.27 g, 1.0 mmol) in MeOH was added dropwise with stirring to a solution of 0.46 g (1.0 mmol) of dppmSe in 300 mL of MeOH. The white precipitate was collected, washed with $Et_2O$ and hexane, and dried under vacuum. The yield of product, mp 271 °C dec, was 0.65 g (89%). Anal. Calcd for $C_{25}H_{22}Cl_2HgP_2Se$: C, 40.87; H, 3.02. Found: C, 40.74; H, 3.17. The analogous $(dppmSe)HgBr_2$ compound, mp 261 °C dec, was prepared in the same manner in 87% yield. Anal. Calcd for $C_{25}H_{22}Br_2HgP_2Se$: C, 36.46; H, 2.69. Found: C, 36.51; H, 2.76. The analogous $(dppmSe)HgI_2$ complex, mp 240 °C dec, was formed in 90% yield. Anal. Calcd for $C_{25}H_{22}HgI_2P_2Se$: C, 32.72; H, 2.42. Found: C, 32.63; H, 2.36. These $(dppmSe)HgX_2$ complexes have quite low solubility in common organic solvents.

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**Registry No.** dppmSe, 23176-19-4; $dppmSe_2$, 16675-12-0; dppmSSe, 73395-66-1; dppmOSe, 73395-67-2; dppmOS, 73395-68-3; $dppmS_2$, 14633-92-2; $dppmO_2$, 2071-21-8; [dppmSeMe]I, 73395-69-4; [dppmSeBz]Br, 73395-70-7; [dppmMe]I, 28981-33-1; $Ph_2P(S)CH_2P(Se)Me_2$, 73395-71-8; $Ph_2P(Se)CH_2P(S)Me_2$, 73395-72-9; $[dppmSe]Cr(CO)_4$, 73395-81-0; $[dppmSe]W(CO)_4$, 73395-82-1; $[dppmSe]Mo(CO)_4$, 73395-83-2; $[dppmSe]HgCl_2$, 73395-84-3; $[dppmSe]HgI_2$, 73395-85-4; $[dppmSe]HgBr_2$, 73395-86-5; $[dppmMe_2]Br_2$, 60798-29-0; [dppmOMe]Br, 73395-73-0; [dppmSMe]Br, 62264-60-2; [dppmSeMe]Br, 73395-74-1; dppm, 2071-20-7; dppmS, 54006-28-9; $Ph_2P(S)CH_2PMe_2$, 23176-51-4; $Ph_2PCH_2P(S)Me_2$, 57241-93-7; $Cr(CO)_6$, 13007-92-6; $PhCH_2$, 100-39-0; MeI, 74-88-4; dppmO, 23176-18-3.

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