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Polydentate Ligands Containing Phosphorus. 11. Synthesis of Three New Anionic Tripod Ligands, Their Neutral Precursors, and Related Compounds[1]

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The compounds $[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}CH$, where n = 1, 2, or 3, have been synthesized by careful oxidation with H_2O_2 of $[Ph_2P]_n[Ph_2P(S)]_{3-n}CH$, where n = 1, 2, or 3, respectively. The corresponding anions $\{[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}C\}^-$ have been prepared from the neutral precursors by proton abstraction with LiOMe. The lithium and quaternary onium salts of these anions are air-stable, high-melting, crystalline solids. $\{[Ph_2P(O)]_3C\}^-$ has greater hydrolytic stability than the previously reported sulfur analogue, $\{[Ph_2P(S)]_3C\}^-$. The mesomerically stabilized dication, $\{(MePh_2P)_3C\}^{2+}$, has been prepared by reaction of methyl iodide with $[(Ph_2P)_3C]^-$. Several additional new compounds of the type $[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]CH$, where X, Y, and Z are various combinations of O, S, Se, and electron pairs, have also been synthesized. The proton chemical shifts of the methine protons in these compounds are linearly related to the sum of substituent constants for the respective chalcogens, X, Y, and Z.

Introduction

The coordination chemistry of anionic tripod ligands is fairly new. The first anionic tripods,[3] the poly(pyrazolyl)borates, were originally reported by Trofimenko[4] in 1966, but they subsequently have become firmly woven into the fabric of coordination chemistry[3,5] and are still the subject of intense research.[6-8] We have previously shown that tris(diphenylthiophosphinyl)methanide,[1,9] $\{[Ph_2P(S)]_3C\}^-$, $TrisS_3^-$, a mesomerically stabilized ion that is air-stable, functions as an anionic tripod with bonding via the three sulfur atoms.[10-14] This represents only the second type of anionic tripod ligand in the history of coordination chemistry. One advantage of the $TrisXYZ^-$ ligand system,[15] where X, Y, and Z are various combinations of chalcogens, is that the hardness/softness of the ligand can be adjusted so as to accommodate variations in the hardness/softness property of the metal ions. For example, although we have succeeded in preparing and characterizing $TrisS_3^-$ (a soft donor) complexes with Hg(II)[11,12] and Ag(I)[13,14] (typical soft metal acceptors), reactions of $TrisS_3^-$ with some harder metals, e.g., Fe(II), have so far led to intractable products.[16] This is a primary reason for synthesizing $TrisO_3^-$, $TrisO_2S^-$, and $TrisOS_2^-$, which would have a decreasing degree of hardness in the order given. In addition, bidentate and monodentate behavior might also be observed in certain cases, and ambidentate behavior is a possibility for $TrisO_2S^-$ and $TrisOS_2^-$. Further, of the 20 possible HTrisXYZ derivatives, where X, Y, and Z are various combinations of O, S, Se, and a pair of electrons, only eight had been previously reported.[17-19] The inclusion of selenium in these ligands would give an additional NMR probe (^{77}Se, 7.6% abundance, $I = {}^1/_2$) for purposes of characterization and NMR studies.

Results and Discussion

In some previous attempted syntheses of certain HTrisXYZ compounds, facile P–C bond cleavage was observed.[19] For example, the attempted oxidation of HTris with H_2O_2 gave $Ph_2P(O)CH_2P(O)Ph_2$ as the major isolated product (eq 1). The attempted preparation of $HTrisSe_3$ from $HTrisSe_2$ (eq 2) resulted in a similar cleavage product. However, we have now found that

$$(Ph_2P)_3CH + H_2O_2 \text{ (excess)} \xrightarrow{\text{acetone}/H_2O} [Ph_2P(O)]_2CH_2 \quad (1)$$

$$[Ph_2P(Se)]_2[Ph_2P]CH + Se \text{ (red)} \xrightarrow{\text{hot benzene}} [Ph_2P(Se)]_2CH_2 \quad (2)$$

careful oxidation by stoichiometric amounts of H_2O_2 in the cold (ca. 0 °C) will produce $HTrisO_3$, $HTrisO_2S$, and $HTrisOS_2$ in reasonable yields (65–80%) from HTris, HTrisS, and $HTrisS_2$, respectively. Also, $HTrisOSe_2$ and $HTrisO_2Se$ were prepared in the same manner by careful H_2O_2 oxidation of $HTrisSe_2$ and HTrisSe, respectively. These latter products were not isolated in pure form but characterized by their NMR properties.

HTrisOS can be prepared by reaction scheme 3. Further

$$Ph_2P(S)CH_2P(O)Ph_2 \xrightarrow{n\text{-BuLi}} Ph_2P(S)CHLiP(O)Ph_2 \xrightarrow{Ph_2PCl} [Ph_2P(S)][Ph_2P(O)][Ph_2P]CH \quad (3)$$

reaction of HTrisOS wth red selenium produces HTrisOSSe. Also, $HTrisS_2Se$ can be prepared from $HTrisS_2$ by reaction with a twofold excess of red selenium in boiling benzene.

The reaction of HTrisS with excess Se in an attempt to prepare $HTrisSSe_2$ did not give the desired product, nor did it give a cleavage product of the type $Ph_2P(X)CH_2P(Y)Ph_2$, where X and Y are either S or Se. An unusual Se-insertion product $[Ph_2P(S)][Ph_2P(Se)]CHSe[Ph_2P(Se)]$ was obtained instead.[20] The inability to prepare either $HTrisSSe_2$ or $HTrisSe_3$ is probably due to the extra steric requirements of the larger selenium atom compared to sulfur (covalent and van der Waals radii, respectively, are 102 and 180 pm for S and 117 and 190 pm for Se).[21]

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(15) $[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]CH$ is called HTrisXYZ, $[Ph_2P(S)]_2[Ph_2P(O)]CH$ is $HTrisOS_2$, $\{[Ph_2P(O)]_3C\}^-$ is $TrisO_3^-$, $(Ph_2P)_3CH$ is HTris, etc.
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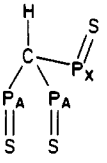
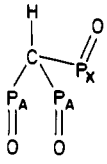
However, these compounds may be stable at lower temperatures if suitable syntheses can be devised. We have previously demonstrated by variable-temperature ^{31}P NMR studies that there is a considerable barrier to rotation about the phosphorus–methine carbon bond in $HTrisS_2$ and $HTrisS_3$, for which the activation energies of the rotation have been estimated at 29 and 49 kJ mol^{-1}, respectively.[22] The ^{31}P NMR spectrum of $HTrisS_3$ is a singlet (41.9 ppm) at room temperature but exhibits an A_2X pattern at −75 °C, with a doublet at 38.6 ppm and triplet at 46.8 ppm.[23] (These values were mistakenly reported in the original paper.) The solid-state molecular structure shows that the stable conformation has two sulfur atoms pointing roughly antiparallel to the C–H (methine) bond with the remaining sulfur parallel to the C–H bond (**1**). Thus the phosphorus of the unique P–S group



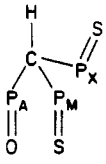
1

δP_A 38.6 (d)
δP_X 46.8 (t)
$^2J(P_A\text{-}P_X)$ = 6.4 Hz
T = −75 °C



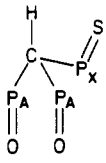
2

δP_A 23.4 (d)
δP_X 35.9 (t)
$J(P_A\text{-}P_X)$ = 4.9 Hz
T = −100 °C



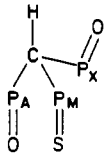
3

δP_A 22.4 (d) $J(P_A\text{-}P_X)$ = 7.3 Hz
δP_M 38.3 (d) $J(P_M\text{-}P_X)$ = 6.3 Hz
δP_X 45.8 ("t") $J(P_A\text{-}P_M)$ = 0 Hz
T = −90 °C



4a

δP_A 23.3 (d)
δP_X 44.8 (t)
$J(P_A\text{-}P_X)$ = 7.3 Hz
T = −80 °C



4b

is noticeably deshielded from the phosphorus atoms in the remaining two P–S groups.

Similar variable-temperature ^{31}P NMR results are observed for $HTrisO_3$ and $HTrisOS_2$, whose energies of activation for rotation about the P–C (methine) bonds are 38.7 and 39.6 kJ mol^{-1}, respectively, as estimated from band-shape analysis of the variable-temperature spectra. The activation energy for rotation increases, as expected, as the chalcogens in HTrisXYZ become larger.

The ^{31}P spectrum of $HTrisO_3$ is a singlet, 25.6 ppm, at room temperature and an A_2X pattern at −100 °C with a doublet at 23.4 ppm and a triplet at 35.9 ppm. By analogy to $HTrisS_3$, the phosphorus of the unique P=O group is considerably deshielded from those of the other two P=O groups and is necessarily assigned by its multiplicity to the P=O aligned nearly parallel to the C–H bond (**2**).

The ^{31}P NMR spectrum of $HTrisOS_2$ is the expected AX_2 pattern at room temperature, but at −90 °C it exhibits an AMX spectrum. Since the two $Ph_2P(S)$ groups are necessarily unique in the stable conformation at −90 °C, the structure shown in **3** has been assigned, with the phosphorus of the P–S group parallel to the C–H group assigned to the most deshielded resonance (45.8 ppm), and the other P–S, antiparallel to the C–H group, is assigned the resonance at 38.3 ppm. Both of these chemical shifts are within 1 ppm of their respective counterparts in the low-temperature stable conformation of $HTrisS_3$. Further, the P=O resonance (22.4 ppm) of $HTrisOS_2$ is similar to its antiparallel counterpart in $HTrisO_3$ (23.4 ppm for P_A in **2**).

The ^{31}P NMR spectrum of $HTrisO_2S$ is the expected A_2X type at room temperature and remains so at −80 °C. This is consistent with structure **4a**, in which the P–S is preferentially parallel to the C–H bond with the two P=O groups antiparallel. When the choice is available, this conformation seems to relieve more steric strain, as in $HTrisOS_2$, than the situation with the P=O parallel and P=S antiparallel. As expected in **4a**, the chemical shift of the presumed parallel P–S group is more highly deshielded (44.8 ppm) than the antiparallel P–S group might be expected to be (38.6 ppm in $HTrisS_3$, P_A in **1**, and 38.3 ppm in $HTrisOS_2$, P_M in **3**). The two antiparallel P=O groups have their ^{31}P resonance at 23.3 ppm, which is comparable to the case of the antiparallel P=O groups of $HTrisO_3$ (23.4 ppm, P_A in **2**) and $HTrisOS_2$ (22.4 ppm, P_A in **3**). At −103 °C the ^{31}P spectrum of $HTrisO_2S$ changes slightly to give new multiplets at 29.9 and 36.5 ppm, which comprises about 10% of the total intensity of the spectrum. It is possible that these arise from a less stable conformation (**4b**) in which the parallel P=O is assigned to the resonance at 29.9 ppm (P_X in **4b**) and the antiparallel P=S to that at 36.5 ppm (P_M in **4b**). The remaining antiparallel P=O may be obscured by the P=O resonance of the major stable conformational isomer, **4a**. No further information is available to confirm these latter assignments, however.

The ^{31}P NMR data at room temperature for the HTrisXYZ compounds, where X, Y, and Z are either O, S, Se, or an electron pair, are given in Table I. The chemical shifts and coupling constants observed are the usual values with the chemical shifts of the phosphine chalcogenides being in the order $\delta(P\text{–}S) > \delta(P\text{–}Se) > \delta(P\text{–}O)$.[24] Also, as noted previously for the bis compounds $Ph_2P(X)CH_2P(Y)Ph_2$, $^2J(P\text{–}P)$ is larger than $^2J(P^V\text{–}P^{III})$, ranging from about 40 to 80 Hz, than for $^2J(P^V\text{–}P^V)$, ranging from 3 to 18 Hz.[24,25] The room-temperature spectrum of $HTrisS_2Se$ is two broad peaks (2:1) rather than the A_2X pattern, indicating that the rotation about the P–C (methine) bonds is intermediate between the fast (A_2X) and slow (A_2X or ABX) rotation limits with respect to an NMR time scale.

The proton data for the methine proton are given in Table II. For this proton, there is a large deshielding in the order $Ph_2P < Ph_2P(O) < Ph_2P(S) < Ph_2P(Se)$, and this effect is additive for the three phosphorus groups attached to the methine carbon in much the same manner as was observed for the methylene protons in the bis compounds $Ph_2P(X)CH_2P(Y)Ph_2$.[24] The effect can be explained in terms of the increasing positive charge on phosphorus and the resulting increasing electronegativity of phosphorus in the order given. This necessarily implies that the canonical form $P^+\text{-}X^-$ is more important for X = Se and S than for X = O or concomitantly that P=X is more important for X = O than for Se and S. For the 16 HTrisXYZ compounds prepared earlier[17–19] and, prepared in this study, the chemical shift of the methine proton can be calculated to be

$$\delta(CH) = 4.16 + \sum_{n=1}^{3}(\text{substituent constants}) \qquad (4)$$

where the substituent constants are 0.25 (O), 0.63 (S), and 0.80 (Se). The equation has a correlation coefficient of 0.989 for the 16 compounds.

Previously, the synthesis of the anion $TrisS_3^-$ has been accomplished by proton abstraction from $HTrisS_3$ with LiOMe in MeOH.[9] The lithium salt, $LiTrisS_3$, is fairly air-stable, melts or decomposes above 360 °C, can be stored in screw-capped vials for several months without change, and hydrolyzes slowly in acetone/water solution. It can also be converted to quaternary onium salts by methathesis. We report here the isolation of $[n\text{-}Bu_4N]TrisS_3$, $[n\text{-}BuPh_3P]TrisS_3$, and $[i\text{-}PrPh_3P]TrisS_3$.

The oxygen-containing analogues $HTrisO_2$, $HTrisO_2S$, and $HTrisOS_2$ also react with LiOMe in MeOH to produce the stable salts $LiTrisO_3$, $LiTrisO_2S$, and $LiTrisOS_2$, respectively. All of these compounds melt above 360 °C. They also can be safely stored for some time in screw-capped vials. $LiTrisO_3$ is hydrolytically more stable than $LiTrisS_3$ and can be recovered un-

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Table I. ^{31}P NMR Data for HTris and Derivatives[a]

compd	δ P	δ P(O)	δ P(S)	δ P(Se)	^2J(P–P), Hz
HTris	−10.4 s				
HTrisS	−13.2 d		46.6 t		62
HTrisSe	−12.4 d				70
$HTrisO_2$	−15.2 t	31.1 d			40
$HTrisS_2$	−10.0 t		43.5 d		49
$HTrisSe_2$	−8.0 t			37.8 d	53
HTrisOS	−11.5 "t"	25.8 dd	43.8 dd		40.8 P–P(O) 41.0 P–O(S) 8.7 P(O)–P(S)
HTrisSSe	−8.7 dd		43.6 dd	37.8 d	57.1 P–P(S) 43.9 P–P(Se) 10.5 P(S)–P(Se)
HTrisO3	24.4 s				
$HTrisS_3$		41.9 s			
$HTrisO_2S$		23.1 d	43.3 t		7.1
$HTrisOS_2$	23.7 t	42.5 d			3.5
$HTrisO_2Se$		24.4 d		35.4 t	9.2
$HTrisS_2Se$[b]			42.0 br	37.1 br	
HTrisOSSe		23.1 dd	40.9 dd	35.8 dd	3.0 P(O)–P(S) 5.0 P(O)–P(Se) 8.5 P(S)–P(Se)
$[n\text{-}Bu_4N]TrisS_3$[c]			44.0 s		
$[n\text{-}BuPh_3P]TrisS_3$[d]			43.9 s		
$[i\text{-}PrPh_3P]TrisS_3$[e]			43.9 s		
$LiTrisS_3$[f]			45.2 s		
$LiTrisS_3$			43.3 s		25.4[g]
$LiTrisO_3$		34.3 s			10 ± 2[g]
$LiTrisO_3$[f]		35.3 s			
$[n\text{-}Bu_4N]TrisO_3$[f]		34.8 s			
$LiTrisO_2S$		39.4 s	39.4 s		
$LiTrisO_2S$[h]		36.6 d	40.7 t		23.5
$LiTrisO_2S$[c,i]		38.4	39.6		17.7
$[n\text{-}Bu_4N]TrisO_2S$[f]		35.6 d	40.9 t		23.0
$LiTrisOS_2$[c]		35.1 t	43.8 d		23.6
$LiTrisOS_2$[f]		34.6 t	44.2 d		23.9

[a] Room-temperature spectra are in $CDCl_3$ unless otherwise noted. Multiple entries for the anions represent different solvents and/or instruments. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad. [b] At room temperature, this spectrum has broad signals with no discernible multiplicity and represents a conformational exchange rate between rapid interconversion (AX_2 spectrum) and slow interconversion (AMX or AX_2). [c] In CH_2Cl_2. [d] n-$BuPh_3P^+$, δ 23.5. [e] i-$PrPh_3P^+$, δ 23.3. [f] $CDCl_3$/MeOH 60/40. [g] Determined from the ^{13}C NMR spectrum. [h] $CDCl_3$/MeOH 80/20. [i] AB_2 spectrum at 24.2 MHz.

changed from an acetone/water (5% water) solution after 3 days. Metathesis of quaternary onium halides with $Li[TrisO_nS_{3-n}]$, where n is 1, 2, or 3, produces salts such as $[Et_4N]TrisO_3$ and $[n\text{-}Bu_4N]TrisO_2S$.

Upon conversion of $HTrisO_nS_{3-n}$ to the corresponding anion $TrisO_nS_{3-n}^-$, the ^{31}P NMR spectra indicate that the P(*O*) groups become considerably less shielded (ca. 10–16 ppm) relative to the neutral parent compound in each case whereas the P(S) groups are deshielded by only 1 or 2 ppm in $TrisS_3^-$ and $TrisOS_2^-$ but a re more shielded by 4 ppm in $TrisO_2S^-$ relative to their neutral conjugate acids. The latter ion is unusual in that the ^{31}P chemical shift of the P(S) and P(O) phosphorus atoms are coincidentally the same in $CHCl_3$ solution. However, the P(O) resonances of the anions $TrisO_nS_{3-n}^-$ show considerable solvent dependence so that addition of progressively larger amounts of MeOH to the $CHCl_3$ solution of $TrisO_2S^-$ causes the P(O) and P(S) resonances to separate so that eventually, with sufficient MeOH present, the expected AX_2 doublet and triplet are observed.

The reaction of HTris with LiOMe in MeOH produces $Tris^-$, which reacts in situ with excess MeI to produce $\{[MePh_2P]_3C\}I_2$, $[TrisMe_3]I_2$, whose cation is an analogue of $[(Me_3P)_3C]^{2+}$ reported earlier by Karsch.[26] $TrisMe_3^{2+}$ was also recently synthesized by an independent route by Schmidbaur et al.[27]

Some ^{13}C NMR data are given in Table III for the central carbon of neutral and ionic derivatives of HTris. Several observations can be made. First, as expected, ^1J(P–C) is significantly larger in the mesomerically stabilized ions $TrisO_3^-$, $TrisS_3^-$, $TrisOS_2^-$, and $TrisMe_3^{2+}$ than in the neutral compounds, reflecting the increased s character in the C hybrid orbital (sp^2) for these ions. Second, the central carbon of the anions is more shielded than the carbon of the respective neutral compound, and the carbon of $TrisMe_3^{2+}$ is the most highly shielded (6.7 ppm) of these compounds. Third, the magnitude of ^1J(P(O)–C) is larger than ^1J(P(S)–C) in each type of compound.

Raman and infrared data for several of the compounds are given in Table IV. It is anticipated that the P–X bond will weaken upon anion formation, i.e., from $HTrisO_nS_{3-n}$ to $TrisO_nS_{3-n}^-$. This is indeed observed for the P–O bond although the exact assignments for $\nu_{P=O}$ are tentative because of a rather complicated situation. The P=O stretching frequency is expected to be in the region 1150–1220 cm^{-1} and is usually a very intense absorption.[28] $HTrisO_3$ has three very intense peaks (1180, 1195, 1210 cm^{-1}) in the P=O region, and it is possible that all three are P=O stretching frequencies. If, for example, the conformation of $HTrisO_3$ is similar to that of solid $HTrisS_3$, then one P=O bond is unique (pointed in the methine C–H direction) whereas the other two P=O's are equivalent (antiparallel to the C–H direction). The former would have a unique P=O stretch whereas the latter, if coupled, could have symmetric and antisymmetric stretches. $HTrisO_3$ also has two very strong absorptions at 1090 and 1110 cm^{-1} of undetermined origin, and the region from 800 to 1000 cm^{-1} is relatively clear. Two important changes occur in the IR spectrum of $Li[TrisO_3]^-$ relative to that of $HTrisO_3$: the peaks at about 1200 cm^{-1} disappear, and new peaks appear at 1125 and 1140 cm^{-1}, which we assign to $\nu_{P=O}$ in $TrisO_3^-$. This decrease

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Table II. ^{1}H NMR Data for HTris and Derivatives

compd	δ(CH)	^2J(P–H), Hz
HTris	4.16 s	
HTrisS	4.81 d	9.6 P(S)–CH
HTrisSe	5.00 d	10.0 P(Se)–CH
$HTrisO_2$	4.81 dt	5.2 d P̈–CH
		12.5 t P(O)–CH
$HTrisS_2$	5.48 dt	2.9 d P̈–CH
		15.7 t P(S)–CH
$HTrisSe_2$	5.98 dt	3.0 d P̈–CH
		16.0 t P(Se)–CH
HTrisOS	5.13 ddd[a]	5.4 P̈–CH
		12.4 P(O)–CH
		19.3 P(S)–CH
HTrisSSe	5.69 ddd	3.0 P̈–CH
		14, 17 P(S)–CH,[b] P(Se)–CH[b]
$HTrisO_3$	4.92 q	14.6
$HTrisS_3$	6.04 q[c]	16.5
$HTrisS_3$	6.04 dt[d]	14.3 t P(S)–CH[e]
		21.0 d P(S)–CH[f]
$HTrisO_2S$	5.21 dt	12.4 t P(O)–CH
		19.2 d P(S)–CH
$HTrisOS_2$	5.62 dt	13.1 d P(O)–CH
		17.1 t P(S)–CH
$HTrisO_2Se$	5.34 dt	11.8 t P(O)–CH
		20.0 d P(Se)–CH
$HTrisOSe_2$	6.17 dt	12.6 d P(O)–CH
		17.8 t P(Se)–CH
$HTrisS_2Se$	6.30 dt	15.7 t P(S)–CH
		18.2 d P(Se)–CH
HTrisOSSe	5.88 ddd[b]	12.6 P(O)–CH
		15.7 P(S)–CH
		19.1 P(Se)–CH

[a] Tentative ^2J(P–H) assignments are based on the observation that J usually varies in the order P̈–CH < P(O)–CH < P(S)–CH < P(Se)–CH in this series of compounds. [b] The P(S)–CH and P(Se)–CH assignments may be made as in footnote *a*, but because of the small difference of about 3 Hz, these assignments are less certain. [c] Room temperature. [d] −75 °C. [e] The P–S group is approximately antiparallel to the C–H bond. [f] The P–S group is approximately parallel to the C–H bond.

Table III. ^{13}C NMR Parameters for Derivatives of HTris

compd	δ(^{13}C)	^1J(P–C), Hz
$HTrisS_3$	52.1 q	22.3
$Li[TrisS_3]$	33.1 q	75.7
$HTrisO_3$	49.6 q	41.2
$Li[TrisO_3]$	42.6 q	83.7
$[TrisMe_3]I_2$	6.7 q	84.0
$HTrisO_2S$	54.0 dt	39.4 (PO)
		22.8 (PS)
$HTrisOS_2$	54.1 dt	40.0 (PO)
		22.6 (PS)
$Li[TrisOS_2]$	38.0 dt	93.8 (PO)
		79.1 (PS)

corresponds to the expected weakening of the P–O bonds. Secondly, a new very intense absorbtion appears at 935 cm^{-1}, which we assign to the P–C(central) stretch. If, as expected, the P–C bond in $TrisO_3^-$ behaves similarly to the P–C bond in $TrisS_3^-$ upon anion formation[1] from their respective $HTrisX_3$ parents, it becomes shorter and stronger upon anion formation. It should be noted that the P=C stretch in some ylides has been assigned values in this region,[28] and $\nu_{P=C}$ in the somewhat analogous $[(Me_3P)_3C]^{2+}$ ion has been assigned at 1060 and 1008 cm^{-1}.[29] Similar changes occur between $HTrisO_2S$ and $TrisO_2S^-$ and between $HTrisOS_2$ and $TrisOS_2^-$ for the P=O stretching region. Table V gives the tentative assignments for $\nu_{P=E}$ and ν_{P-C} for these compounds.

The assignment of the P–S stretching frequency from only the infrared spectra of these compound is very difficult or impossible since its intensity is no greater and often significantly less than other absorptions in the same region of the spectra. Additionally, the assignment of the P–S stretching frequency of simple Z_3PS compounds is not always straightforward, as discussed recently by Durig.[30] The P–S stretching frequency in the Raman spectrum is a very intense absorption and often the most intense absorption in the 400–800-cm^{-1} region of the spectrum. The tentative assignments of $\nu_{P=S}$ are made from the infrared and Raman spectra with greater reliance placed on the latter. The change in $\nu_{P=S}$ upon anion formation is in the range of −18 to −24 cm^{-1}, which is similar to the change observed by Karsch[31] in $[Me_2P(S)]_3CH$ (589, 578, 568 cm^{-1}) and $[Me_4P]^+\{[Me_2P(S)]_3C\}^-$ (568, 557 cm^{-1}).

The coordination chemistry of some of these potential ligands is being actively pursued. It is anticipated, as in the case of $TrisS_3^-$, that these ligands will show a rich and varied coordination chemistry. Results of these studies will be published later.

Experimental Section

Routine phosphorus-31 NMR spectra were recorded with a Bruker WP-200 FT instrument at 80.96 MHz. Carbon-13 and variable-temperature ^{31}P spectra were recorded with a JEOL FX-60 or JEOL FX-90Q spectrometer. Unless otherwise indicated, the NMR solvent was $CDCl_3$. Chemical shifts are positive to the high-frequency (deshielded) side of the reference (85% H_3PO_4, external, or Me_4Si, internal, as appropriate). Raman spectra were obtained on pure solid samples contained in capillary tubes with a Spex 1402 dual monochromator. A coherent 52 argon laser (ca. 200 mW) at 488 Å was used for excitation. The spectral slit width employed was ca. 3 cm^{-1}, and the accuracy of the band positions is ca. ±4 cm^{-1}. Infrared spectra were measured on KBr pellets or as Nujol-mulled samples on a Perkin-Elmer 225 spectrometer. The spectral slit width employed was ca. 2 cm^{-1}, and the calibration checked against a polystyrene film is better than ±2 cm^{-1}.

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

HTris,[17] HTrisS,[18] $HTrisS_2$,[18] $HTrisS_3$,[17,18] HTrisSe,[19] $HTrisSe_2$,[19] and $Ph_2P(O)CH_2P(S)Ph_2$[24] were prepared as described in the literature. LiOMe was prepared by the reaction of Li and MeOH followed by removal of solvent by rotary evaporation and washing of the residue with Et_2O.

Synthesis of $[Ph_2P(O)]_3CH$, $HTrisO_3$. HTris (20.2 g, 35.5 mmol) was suspended in acetone (350 mL) in an Erlenmeyer flask (1 L). The flask was cooled in ice for about 30 min. H_2O_2 (12.2 g of 30% solution), diluted to 100 mL with acetone, was added to the slurry over a period of 1 h and then stirred for another 2 h in the cold and then at room temperature for about 1 h. This mixture was filtered into a dropping funnel and then slowly added to a large pool (4 L) of distilled water with stirring. The white precipitate that formed was collected by filtration and washed several times with distilled water and then finally with pentane. The residue was dried in vacuo at 80 °C to give the pure compound, mp 216 °C, in 81% yield. Anal. Calcd for $C_{37}H_{31}P_3O_3$: C, 72.08; H, 5.07; P, 15.07. Found: C, 72.09; H, 5.07; P, 14.98.

$[Ph_2P(O)]_2[Ph_2P(S)]CH$, $HTrisO_2S$. HTrisS (24.4 g, 40.6 mmol) reacted as described above with 30% H_2O_2 (9.2 g, 81.3 mmol) in the cold. The crude product was dried in vacuo to give pure compound, mp 201 °C, in 78% yield. Anal. Calcd for $C_{37}H_{31}P_3O_2S$: C, 70.25; H, 4.95; P, 14.69. Found: C, 70.11; H, 5.10; P, 14.88.

$[Ph_2P(O)][Ph_2P(S)]_2CH$, $HTrisOS_2$. Pure $HTrisOS_2$ was not obtained in acetone by the direct reaction of $HTrisS_2$ and H_2O_2. Instead, a mixture including oxidation products of the thiophosphinyl group (P=S) was obtained. This is presumably due to the relative insolubility of $HTrisS_2$ in acetone. However, pure $HTrisOS_2$ was isolated when dioxane was used as solvent. $HTrisS_2$ (12.5 g, 19.8 mmol) reacted in dioxane as described above with 30% H_2O_2 (2.24 g, 20 mmol) in the cold. The crude product, after having been dried in vacuo, melted at 215 °C and was formed in 65% yield. Anal. Calcd for $C_{37}H_{31}P_3OS_2$: C, 68.51; H, 4.82; P, 14.32. Found: C, 68.34; H, 5.00; P, 14.58.

$[Ph_2P(O)][Ph_2P(S)][Ph_2P]CH$, HTrisOS. $Ph_2P(O)CH_2P(S)Ph_2$ (10.0 g, 23.1 mmol) was suspended in THF (60 mL). *n*-BuLi (23.1 mmol) was added with a syringe. The orange solution was stirred for about 4 h at room temperature, and then Ph_2PCl (25 mmol) was added slowly from a syringe. The mixture was stirred for about 15 h, and then solvent was removed by rotary evaporation. Addition of EtOH/hexane solution gave a white precipitate. The ^{31}P NMR spectrum indicated the presence of HTrisOS with slight contamination by the starting material, $Ph_2P(O)CH_2P(S)Ph_2$. HTrisOS was identified by its ^{31}P and ^{1}H NMR spectra.

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Table IV. Raman and Infrared Spectra of $[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}CH$ and $\{[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}C\}^-$ Where n = 0, 1, 2, or 3

compd	method	band freq, cm^{-1}
$HTrisS_3$	Raman	404 (8), 449 (4), 486 (6), 509 (14), 574 (100), 617 (34), 643 (10), 682 (45)
	IR	485 (47), 506 (21), 528 (16), 572 (16), 615 (6), 631 (5), 642 (38), 682 (63), 692 (51), 705 (41), 731 (100), 758 (50), 766 (51), 998 (18), 1025 (11), 1090 (57)
$LiTrisS_3$	Raman	381 (17), 445 (7), 469 (46), 490 (9), 511 (10), 550 (100), 591 (22), 612 (45), 660 (31), 693 (9)
	IR	380 (68), 489 (82), 510 (52), 550 (88), 591 (32), 612 (30), 659 (98), 679 (81), 692 (60), 702 (65), 735 (87), 746 (42), 753 (29), 904 (100), 992 (98), 998 (17), 1023 (17), 1063 (32), 1090 (76)
$[n\text{-}Bu_4N]TrisS_3$	Raman	403 (7), 431 (10), 451 (11), 461 (12), 546 (100), 603 (9), 616 (28), 666 (31)
	IR	373 (37), 418 (13), 445 (10), 495 (72), 508 (37), 543 (14), 601 (100), 623 (74), 664 (22), 682 (64), 692 (91), 701 (58), 735 (68), 744 (64), 756 (29), 930 (90), 959 (83), 1026 (9), 1035 (8), 1065 (10), 1085 (51)
$HTrisOS_2$	Raman	548 (7), 581 (12), 593 (14), 613 (28), 641 (13), 659 (8), 697 (11), 997 (100), 1026 (45), 1096 (15), 1157 (7), 1188 (6)
	IR	441 (9), 485 (39), 498 (68), 511 (35), 518 (32), 548 (43), 592 (10), 612 (25), 642 (47), 660 (21), 665 (18), 682 (62), 693 (60), 723 (95), 733 (100), 774 (69), 995 (20), 1028 (15), 1092 (56), 1105 sh (46), 1201 (32)
$LiTrisOS_2$	Raman	536 (18), 574 (55), 605 (10), 617 (45), 656 (11), 706 (14), 1000 (100), 1028 (60), 1097 (26), 1137 (8), 1164 (9)
	IR	404 (38), 432 (38), 498 sh (65), 502 (75), 518 (43), 537 (32), 547 (31), 575 (55), 604 (56), 616 (30), 628 (35), 658 (67), 686 (77), 694 (80), 710 (67), 718 sh (48), 740 (87), 912 (89), 938 (100), 980 (48), 999 (30), 1024 (29), 1065 sh (59), 1076 (69), 1093 (70), 1110 (59), 1118 sh (58)
$HTrisO_2S$	Raman	525 (4), 565 (8), 605 (8), 615 (35), 644 (14), 698 (18), 999 (100), 1027 (42), 1098 (13), 1160 (8), 1189 (7)
	IR	410 (35), 460 (18), 488 (27), 505 (90), 530 (69), 568 (35), 605 (9), 615 (19), 645 (35), 665 (16), 686 (69), 697 (67), 721 (69), 738 (100), 785 (73), 1000 (24), 1028 (16), 1098 (60), 1110 (64), 1160 (20), 1204 (50)
$LiTrisO_2S$	Raman	401 (7), 460 (5), 490 (5), 509 (5), 584 (59), 612 (55), 708 (22), 998 (100), 1025 (68), 1094 (19), 1113 (7), 1146 (23)
	IR	419 (65), 435 (41), 461 (51), 485 (57), 490 (64), 510 (93), 536 (73), 548 (83), 552 (84), 582 (100), 612 (19), 645 (68), 689 (100), 693 (98), 718 (83), 740 (88), 900 (97), 980 (95), 998 (72), 1024 (45), 1060 (77), 1088 (88), 1109 (85), 1121 (83), 1134 (83)
$HTrisO_3$	Raman	530 (17), 576 (10), 615 (82), 649 (26), 703 (48), 739 (4), 793 (4), 847 (4), 922 (5), 998 (100), 1027 (91), 1070 (8), 1101 (37), 1158 (29), 1188 (29)
	IR	410 (58), 452 (24), 508 (100), 530 (85), 558 (20), 575 (48), 615 (21), 648 (46), 689 (94), 692 sh (90), 720 (75), 738 (100), 790 (94), 993 (38), 1025 (33), 1070 sh (56), 1094 (90), 1110 (93), 1183 sh (83), 1198 (89), 1204 sh (86)
$LiTrisO_3$	Raman	615 (39), 695 (5), 715 (18), 840 (5), 919 (6), 999 (100), 1026 (47), 1103 (19), 1155 (30)
	IR	444 (51), 472 (55), 518 (100), 560 (76), 580 (49), 615 (15), 620 (19), 690 (95), 718 (84), 741 (91), 890 (90), 930 (51), 992 (84), 1010 (82), 1028 (63), 1065 (81), 1094 (93), 1100 sh (91), 1110 (91), 1125 sh (92), 1136 (94)

[a] In the approximate range of 400–700 cm^{-1} for $HTrisS_3$ and $TrisS_3^-$ (Raman) and 400–1200 cm^{-1} for the remaining spectra. The numbers in parentheses are the peak heights relative to 100 for the strongest absorption in each spectrum. Abbreviation: sh, shoulder.

Table V. Tentative Assignments for the Principal Stretching Frequencies in $(Ph_3P)_3CH$ Derivatives and Analogues

compd	ν_{PS}, cm^{-1}	ν_{PO}, cm^{-1}	ν_{P_3C}, cm^{-1}
$HTrisS_3$	574		758
$LiTrisS_3$	550		904, 922
$[n\text{-}Bu_4N]TrisS_3$	546		930, 959
$HTrisOS_2$	593	1201	774
$LiTrisOS_2$	574	1118	912, 938, 980 (?)
$HTrisO_2S$	605	1204	785
$LiTrisO_2S$	584	1121, 1134	900, 980
$HTrisO_3$		1183, 1198, 1204	790
$LiTrisO_3$		1125, 1136	890, 930, 1010 (?)
$[Me_2P(S)]_3CH$[a]	568, 578, 589		
$Li\{[Me_2P(S)]_3C\}$[a]	547, 603		
$[Me_4P]\{[Me_2P(S)]_3C\}$[a]	557, 568		

[a] Reference 31.

$[Ph_2P(O)][Ph_2P(S)][Ph_2P(Se)]CH$, HTrisOSSe. HTrisOS (2.0 g, 3.2 mmol) from the previous experiment was suspended in 30 mL of benzene with 0.26 g (3.2 mmol) of red Se. The mixture was heated at reflux for 15 h and then filtered. The filtrate was evaporated to an oil. Addition of CH_2Cl_2/pentane (40/60 by vol) produced a slightly yellowish precipitate. The product HTrisOSSe was identified by its ^{31}P NMR spectrum. The sample contained some minor impurities.

$[Ph_2P(O)][Ph_2P(Se)]_2CH$, $HTrisOSe_2$. $HTrisSe_2$ (10.0 g, 13.8 mmol) was suspended in 300 mL of acetone and cooled in an ice bath. Aqueous 30% H_2O_2 (1.6 g, 14 mmol) in 100 mL of acetone was slowly added to the suspension with stirring. After 2 h the reddish mixture was filtered, and the filtrate was added slowly to a large pool of distilled H_2O. The resulting precipitate was isolated by filtration, washed with water and pentane, and dried in vacuo at 60 °C. The product contained some impurities, but the ^1H NMR spectrum clearly identified the product $HTrisOSe_2$.

$[Ph_2P(O)]_2[Ph_2P(Se)]CH$, $HTrisO_2Se$. The reaction was carried out as above with 11.0 g (17.0 mmol) of HTrisSe and 34 mmol of H_2O_2. The product, $HTrisO_2Se$, was contaminated with some impurities, including $HTrisO_3$, formed by complete oxidation of the phosphine selenide as well as the phosphine groups. The product was identified by its characteristic ^1H and ^{31}P NMR spectra.

$[Ph_2P(S)]_2[Ph_2P(Se)]CH$, $HTrisS_2Se$. To $HTrisS_2$ (1.0 g, 1.6 mmol) suspended in benzene (60 mL) was added red selenium (0.25 g, 3.2 mmol, 100% excess). This mixture was deoxygenated and refluxed for about 30 h. The black slurry was filtered hot, and the solvent was removed via rotary evaporation. The resulting yellow-red oil was dissolved in CH_2Cl_2. Slow addition of hexane gave a finely divided yellowish powder. The product was collected by filtration and washed with pentane. $HTrisS_2Se$ was identified by its ^{31}P and ^1H NMR spectra.

$Li\{[Ph_2P(S)]_3C\}$, $Li^+TrisS_3^-$. LiOMe (0.99 g, 26 mmol) was suspended in methanol (5 mL) in a Schlenk flask (500 mL). A solution of $HTrisS_3$ (11.5 g, 17.3 mmol) in dried deoxygenated CH_2Cl_2 (300 mL) was added slowly from a dropping funnel (ca. 1 h). The resulting yellowish solution was then stirred at room temperature under N_2 for another 4 h. This solution was filtered and concentrated via rotary evaporation. Addition of ether resulted in precipitation of a white powder. Recrystallization from CH_2Cl_2/Et_2O gave pure compound, mp >360 dec, in 72% yield. Anal. Calcd for $C_{37}H_{30}LiP_3S_3$: C, 66.26; H, 4.51; P, 13.85. Found: C, 65.91; H, 4.93; P, 13.89.

$[n\text{-}Bu_4N][TrisS_3]$, $[n\text{-}BuPh_3P][TrisS_3]$, and $[i\text{-}PrPh_3P][TrisS_3]$. $LiTrisS_3$ was prepared as described above but not isolated from solution. $[n\text{-}Bu_4N]I$ (6.4 g) dissolved in 30 mL of CH_2Cl_2 was added slowly, and the solution was stirred for 4 h, filtered, and the filtrate concentrated via rotary evaporation. Addition of Et_2O gave a yellowish crystalline product, mp 212°C, in 78% yield. Anal. Calcd for $C_{53}H_{66}NP_3S_3$: C, 70.24; H, 7.34; P, 10.25. Found: C, 69.68; H, 7.60; P, 10.23.

$[n\text{-}BuPh_3P][TrisS_3]$, mp 210 °C, was prepared similarly in 61% yield from $[n\text{-}BuPh_3P]Br$ and $LiTrisS_3$. Anal. Calcd for $C_{59}H_{54}P_4S_3$: C, 72.08; H, 5.54; P, 12.60. Found: C, 71.70; H, 5.67; P, 12.72.

$[i\text{-}PrPh_3P][TrisS_3]$, mp 213 °C, was prepared similarly in 59% yield from $[i\text{-}PrPh_3P]Br$ and $LiTrisS_3$. Anal. Calcd for $C_{58}H_{52}P_4S_3$: C, 71.88; H, 5.41; P, 12.79. Found: C, 71.50; H, 5.61; P, 12.99.

$Li\{[Ph_2P(O)]_3C\}$, $Li^+TrisO_3^-$. The procedure described for $LiTrisS_3$ was employed for this compound with $HTrisO_3$ (10.0 g, 16.2 mmol) as the starting material. The product, $LiTrisO_3$, mp >360 °C, was recrystallized from $CHCl_3/Et_2O$ to give a yield of 78% (7.9 g). Anal. Calcd for $C_{37}H_{30}LiO_3P_3$: C, 71.39; H, 4.86; P, 14.93. Found: C, 71.06; H, 4.97; P, 14.95. ^{13}C NMR (ppm): CP_3, 42.6 (q, $^1J(P\text{–}C)$ = 83.7 Hz); PhC_1, 137.0 ("d"d, $^1J(P\text{–}C)$ = 114 Hz, $^3J(P\text{–}C)$ = 2.4 Hz); $PhC_{2,6}$, 132.3 (N^{32} = 9.8 Hz); $Ph_{3,5}$, 127.3 (N = 11.7 Hz); PhC_4, 129.5 (s).

[*n*-Bu$_4$N][TrisO$_3$]. Metathesis of LiTrisO$_3$ (19.5 mmol) with [*n*-Bu$_4$N]I (19.5 mmol) in MeOH for 4 h followed by filtration, concentration of the filtrate by rotary evaporation, and addition of hexane produced the product [*n*-Bu$_4$N][TrisO$_3$], mp 300 °C dec, in 50% yield. Anal. Calcd for $C_{55}H_{66}O_3NP_3$: C, 74.19; H, 7.75; P, 10.83. Found: C, 72.99; H, 7.80; P, 10.79.

Li{[Ph$_2$P(O)]$_2$[Ph$_2$P(S)]C}, Li$^+$TrisO$_2$S$^-$. HTrisO$_2$S (16.7 g, 26.9 mmol) reacted as described above with LiOMe. Addition of Et$_2$O gave the desired product, mp >360 °C, in 82% yield. Anal. Calcd for $C_{37}H_{30}LiO_2P_3S$: C, 69.59; H, 4.74; P, 14.55. Found: C, 68.91; H, 4.99; P, 14.48.

[*n*-Bu$_4$N][TrisO$_2$S]. Metathesis of LiTrisO$_2$S and [*n*-Bu$_4$N]I in MeOH gave the product, mp 335 °C, in 51% yield. Anal. Calcd for $C_{53}H_{66}NO_2P_3S$: C, 72.83; H, 7.61; P, 10.63. Found: C, 72.59; H, 7.81; P, 10.61.

Li{[Ph$_2$P(O)][Ph$_2$P(S)]$_2$C}, Li$^+$TrisOS$_2^-$. HTrisOS$_2$ (9.42 g, 14.5 mmol) and LiOMe (0.82 g, 22 mmol) reacted as described above. Addition of Et$_2$O gave the desired product, mp >360 °C, in 73% yield. Anal. Calcd for $C_{37}H_{30}LiOP_3S_2$: C, 67.89; H, 4.62; P, 14.20. Found: C, 67.39; H, 4.91; P, 14.23.

[(MePh$_2$P)$_3$C]I$_2$, TrisMe$_3^{2+}$I$^-_2$. HTris (2.23 g, 3.94 mmole was dissolved in 100 mL of CH_2Cl_2, and the mixture was slowly added under N_2 to a suspension of LiOMe (0.224 g, 50% excess) in 3 mL of MeOH. All solvents were thoroughly deoxygenated. After the mixture was stirred for 2 h at room temperature, MeI (4 mL, 5-fold excess) was added. The reaction vessel was tightly closed, and the mixture was stirred for about 20 h. The mixture was filtered to remove excess LiOMe, and the filtrate was concentrated via rotary evaporation to a yellowish oil. Addition of CH_2Cl_2/hexane produced colorless crystals, mp 298 °C dec, in 66% yield. ^{31}P NMR (ppm): 19.3 (s (lit.[27] 19.9), ^2J(P-P) = 22 ± 0.5 Hz (from ^{13}C AXX'$_2$ spin system)). ^{1}H NMR (ppm): CH_3, 2.76 ("filled in" doublet, N = 12.5 Hz (lit.[27] 2.62, N = 19.2 Hz)). ^{13}C NMR (ppm): CP_3, 6.7 (q, ^1J(P-C) = 84 Hz (lit.[27] 10.8 q, J = 82 Hz))); PCH_3, 17.8 (^1J(P-C) = 60.6 Hz); PhC_1, 123.5 (^1J(P-C) = 88.7 Hz, ^3J(P-C) = 2.6 Hz); $PhC_{2,6}$, 133.6 (^2J(P-C) = 10.8 Hz); $PhC_{3,5}$, 130.4 ($3J$(P-C) = 12.7 Hz); PhC_4, 134.1.

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Registry No. HTrisO$_3$, 89915-89-9; HTrisO$_2$S, 89915-88-8; HTrisOS$_2$, 89915-87-7; HTrisOS, 102615-37-2; HTrisOSSe, 102615-38-3; HTrisO$_2$Se, 102615-39-4; HTrisS$_2$Se, 102615-40-7; Li$^+$TrisS$_3^-$, 102615-41-8; [*n*-Bu$_4$N][TrisS$_3$], 84507-40-4; [*n*-BuPh$_3$P][TrisS$_3$], 102615-42-9; [*i*-PrPh$_3$P][TrisS$_3$], 102615-43-0; Li$^+$TrisO$_3^-$, 102615-44-1; [*n*-Bu$_4$N][TrisO$_3$], 102615-45-2; Li$^+$TrisO$_2$S$^-$, 102615-46-3; [*n*-Bu$_4$N][TrisO$_2$S], 102615-47-4; Li$^+$TrisOS$_2^-$, 102615-48-5; [TrisMe$_3$]$^{2+}$I$^-_2$, 88811-59-0; HTris, 28926-65-0; HTrisS, 75425-86-4; HTrisS$_2$, 75425-87-5; Ph$_2$P(O)CH$_2$P(S)Ph$_2$, 73395-68-3; Ph$_2$PCl, 1079-66-9; HTrisSe$_2$, 76241-55-9; HTrisSe, 76241-54-8; HTrisS$_3$, 28926-66-1; [*n*-BuPh$_3$P]Br, 1779-51-7; [*i*-PrPh$_3$P]Br, 1530-33-2; HTrisSSe, 76241-56-0; HTrisO$_2$, 28981-32-0; HTrisOSe$_2$, 102615-49-6.

(32) $N = (^nJ + {}^{n+2}J)$, where n = 2 for the ortho carbons and n = 3 for the meta carbons of the phenyl group: Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 141.

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A Chronoamperometric and Cyclic Voltammetric Study of the Sequential Two-Electron-Transfer Process Induced in Binuclear Copper(II) 1,3,5-Triketonates by Simple Cations. Effect of Cation Variation and Ligand Substitution on the Transfer of Two Electrons at Very Similar Potentials

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Simple cations of the alkali and alkaline-earth metals have been shown to induce the reversible, sequential transfer of two electrons at nearly the same potential in bis(1,3,5-triketonato)dicopper(II) complexes and their diamine Schiff bases. They also cause a positive shift in redox potentials of 300–400 mV. These effects are interpreted as being due to the complexation of the cations to the electron pairs of the terminally coordinated oxygens in the reduced species, $[Cu^{II}Cu^{I}L_2]^-$ and $[Cu^{I}Cu^{I}L_2]^{2-}$. This is supported by the fact that no cation effect is observed when a terminal ketonate oxygen is replaced by an imine nitrogen from $C_2H_5NH_2$, for example. Presence of the amine group precludes electron-pair donation to the added cation. The potential shift is highly correlated to the size/charge ratio of the cations such that $Ba^{2+} > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. This is also consistent with a complexation phenomenon.

Introduction

In previous papers[1] we reported the observation that, in the absence of alkali-metal cations, bis(1,3,5-triketonato)dicopper(II) complexes undergo the reversible transfer of one electron at about −0.9 V vs. SCE, with no further reduction before about −1.8 V. Addition of Na^+ or Li^+ to the electrochemical cell results in two significant changes in the electrochemistry of these binuclear Cu(II) molecules. First, the electron transfer is switched from simple one-electron transfer to the sequential, reversible transfer of two electrons at very nearly the same potential, i.e. $E_1 - E_2 \cong 30$ mV. Second, the reduction potential is shifted to more positive values by about 300–400 mV and the shift is a function of the cation, with $Li^+ > Na^+$. These effects are consistent with some type of complexation/association of the added cation with the reduced complex. The present study was undertaken to investigate the nature of this interaction.

Experimental Section

Compounds. The bis(1,3,5-triketonato)dicopper(II) complexes used in this study have been prepared and characterized previously.[2]

Cu$_2$(PAAea)$_2$. The ligand was prepared by adding 1.5 mL (8.3 mmol) of 2,2-dimethyl-3,5,7-octanetrione[3] (H_2PAA) and one drop of concentrated H_2SO_4 to 100 mL of refluxing methanol. Ethylamine (9.6 mmol) was added and the solution refluxed for 0.33 h. Slow evaporation of the solvent yielded a yellow oil, which was used without further purification. The oil was dissolved in 10 mL of methanol and added dropwise to a refluxing solution of 1.66 g (8.3 mmol) of $Cu_2C_2H_3O_2 \cdot H_2O$ in 100 mL of methanol. Upon addition of 2.0 mL (14.0 mmol) of triethylamine, a

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