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(14) The rates were measured by monitoring the integrals of the two methyl absorptions over a period of 20 min. Separate ^1H NMR measurements on a sample of **1** partially deuterated in the syn position in Me_2SO-d_6 in the absence of base showed that, in this solvent, the half-life for inversion is 2 h. Thus, under the conditions of integral measurements, the effect of a "lateral shift" would be small (and would only cause a slight diminution in selectivity). The assignment of absorptions to *syn*- and *anti*-methyl protons was made previously[13] by three independent methods.
(15) The ^{13}C NMR spectra clearly indicated the stereochemistry of the alkylation products. The syn and anti α carbons of ketimines exhibit a 10–11-ppm difference in shieldings with the syn carbon appearing at higher field, as has been observed for oximes, oxime ethers, hydrazones, and nitrosamines.[16] Axial substituents were clearly identifiable by the γ-shielding effect. Confirmatory proof that the syn carbon was at higher field was obtained as follows. A sample of **1** was selectively deuterated in the syn position in Me_2SO-d_6–*tert*-butyl alcohol-*O*-*d*, as indicated by the ^1H NMR NMR and then immediately examined by ^{13}C NMR. The high-field methyl signal (δ 18.7) was no longer visible above the noise, while the lower field methyl absorption (δ 29.4) remained a singlet.
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Structure and Triboluminescence of Polymorphs of $(Ph_3P)_2C$

Sir:

Hexaphenylcarbodiphosphorane[1] ($(Ph_3P)_2C$) has attracted recent interest because of its triboluminescent properties,[2,3] its structure-bonding relationships,[4,5] and its organometallic chemistry.[6] During our spectroscopic studies of its triboluminescence (TL), we found that triboluminescent crystals lose their TL upon standing. Further investigation revealed that single crystals of the non-TL polymorph could be obtained from solution by slow crystallization. The crystal structure of the non-TL phase, its differences from the previously reported[4] phase, and its implication to the triboluminescence mechanism are reported here.

Nontriboluminescent, moisture sensitive, yellow diamond-shaped crystals of ~0.20 by 0.16 mm were cleaved from needles grown by slow cooling of a diglyme solution in an insulated container. X-ray diffraction data collected at −160 °C under a stream of cold, dry nitrogen indicated the orthorhombic space group $P2_12_12_1$; a = 11.184 (4), b = 12.956 (4), c = 19.410 (5) Å; V = 2812.5 Å^3; Z = 4; d_{calcd} = 1.267 g/cm^3. Data were collected on a Syntex $P\bar{1}$ automated diffractometer with monochromatic Mo Kα radiation up to a 2θ maximum of 47°; 1776 reflections of $I > 3\sigma$ were used in the solution and refinement of the structure (R_{final} = 0.041). No correction for crystal absorption was made (μ = 1.38 cm^{-1}). In addition to the low temperature structure determination, diffraction data were collected at room temperature and refined to a final R factor of 0.059. Crystal decomposition was observed in this case with a decrease in standard reflection intensities of ~30%. However, the crystal and molecular structures were essentially the same as those observed at low temperature.[7]

The previously reported phase of hexaphenylcarbodiphosphorane contains two different molecular forms in a monoclinic $C2$ unit cell (β = 95.1°).[4] Bond length and bond angle differences between the molecular structures of the nontriboluminescent molecule reported here (crystal A, Figure 1) and the two molecules of the previous structure (Bl and Bll) are shown in Table I. Torsion angles, defined as C–P–P–C, range from 25.0 to 27.5° in the nontriboluminescent structure compared with the previously reported[4] range of 5.5 to 8.3°.

Table I. Hexaphenylcarbodiphosphorane: Molecular Data

molecule	P=C=P angle, deg	distance, Å		
		C=P	P···P	P—C(Ph)
$(Ph_3P)_2C$ (A)[a]	134.4	1.610	2.968	1.853
$(Ph_3P)_2C$ (A)[b]	131.7 (3)	1.635 (5)	2.984	1.831
$(Ph_3P)_2C$ (Bl)	130.1 (6)	1.633 (4)	2.961	1.837
$(Ph_3P)_2C$ (Bll)	143.8 (6)	1.629 (3)	3.097	1.832
$(Ph_3P)_2CH^+$	128.2 (3)	1.702 (5)	3.063	1.808

[a] Room temperature. [b] Low temperature.

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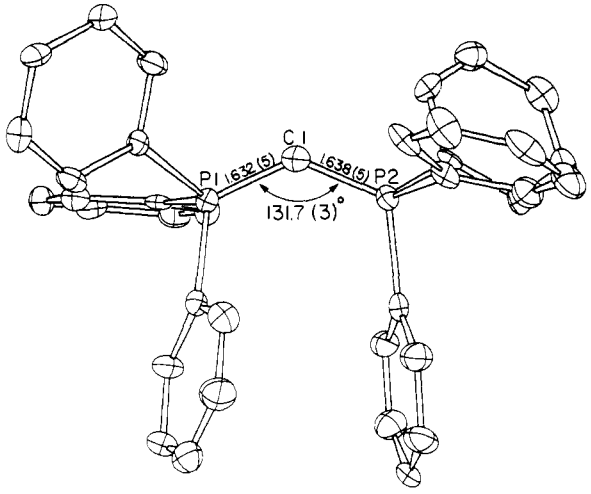

Figure 1. Molecular structure of the nontriboluminescent form of $(Ph_3P)_2C$.

Systems containing adjacent double bonds on a central carbon (e.g., C=C=C, C=C=N, or N=C=N) are expected to be linear by conventional bonding schemes. Studies on crystals of molecules containing these units have shown that the bond angle about the central carbon can deviate from linearity by at most only 10° owing to lattice forces.[8-11] When a phosphorus atom is included in the chian, adjacent double bond angles as small as 130° have been observed.[4] In salts of the isoelectronic $(Ph_3P)_2N^+$ cation, P-N-P bond angles range from 134.6 to 180° as the anion is changed.[12-18] Both linear and bent forms of this cation can exist in the same unit cell.[19]

Microcrystals of triboluminescent hexaphenylcarbodiphosphorane obtained by more rapid cooling of a diglyme solution in an insulated flask exhibit different spectroscopic properties from crystal A. The photoluminescence of microcrystals of B consists of a broad band centered at 530 nm, while that of crystal form A is centered at 575 nm. When the microcrystals of B are left standing for a long period of time at room temperature, the luminescence shifts to 575 nm with no chemical decomposition of the crystals and the triboluminescence disappears as they convert slowly to crystal form A. In addition to the luminescence differences, Raman spectra of powdered samples of the triboluminescent phase include two peaks of roughly equal intensity at 661 and 652 cm^{-1}, while the nontriboluminescent sample shows only one vibration at 661 cm^{-1}. These bands are tentatively assigned to the P-C-P symmetric stretches of the molecules with bond angles of 130 and 144°, respectively, in the TL-active phase and the molecule with the 132° angle in the TL-inactive phase.

The different molecular geometries and crystal structures of the TL-active and -inactive phases illustrate the sensitivity of the P-C-P bond angle to packing forces. The difference in the packing forces, calculated using the model of Williams,[20] is only on the order of 1 kcal/mol. More importantly, the polymorphs illustrate the sensitivity of TL to structure. The piezoelectric properties of the crystal are a significant difference between the two polymorphs and perhaps are pertinent to the TL mechanism.[3] The TL-active phase belongs to a polar space group, while the TL-inactive phase is nonpolar and can exhibit piezoelectric charging only under torsion.

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Monomeric Molybdenum(V) Oxo Complexes with Tetradentate Aminoethanethiols

Sir:

Much of the current understanding of molybdenum enzymes is based on electron spin resonance (ESR) investigations of Mo(V) signals arising during turnover of the enzymes.[1] These studies strongly suggest one (or more) of the ligands of the Mo(V) binding site in xanthine oxidase, aldehyde oxidase, sulfite oxidase, and nitrate reductase is the sulfur of a cysteine side chain.[1-3] As pointed out by Bray,[2] there is, however, a lack of ESR data from well-characterized monomeric Mo(V) complexes which could be used, by comparison, to obtain structural information concerning the enzymatic Mo(V) centers. Moreover, there are no ESR data for complexes of known structures bonded to thiol ligands within a saturated framework.[4] A number of solution ESR spectra of such complexes have been reported, but these are generally for a small amount of monomer of unknown structure in equilibrium with an ESR inactive dimer.[4-6]

We report the preparation, ESR, visible and IR spectra, and electrochemical parameters of two monomeric Mo(V) ovo complexes with tetradentate aminoethanethiols. These appear to be the first such Mo(V) complexes to be described and their properties are of considerable interest with respect to the possible structure of enzymatic Mo(V) centers (in addition to cysteine sulfur, an NH ligand has been proposed as a likely group present at the Mo binding site of xanthine oxidase[1,2,4]).

The complexes have the formula MoOClL, where L = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine (L_1)[7] and *N,N'*-bis(2-methyl-2-mercaptopropyl)ethylenediamine (L_2).[8] The complexes were obtained by refluxing, under nitrogen, a dilute (0.010 M) equal molar mixture of the ligand

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