Studies on the further use of intermediate **6** and **8** in synthesis as well as application of the β-metal ketone strategy to other naked (or ligand free) metal cations are in progress.

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Supplementary Material Available: Spectral data of products listed in Table I (7 pages). Ordering information is given on any current masthead page.

(Iminomethylidene)phosphines ($RP{=}C{=}NR$)

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There has been much recent interest in compounds incorporating $P{=}C$[2,3] and $P{=}P$[4] double bonds. Furthermore, the stable (2,2-dimethylpropylidyne)phosphine, $(CH_3)_3CC{\equiv}P$, featuring a PC triple bond has been prepared.[5] However, previous attempts to isolate cumulenes possessing a two-coordinate phosphorus atom, $RP{=}C{=}X$, have failed,[2,3,6] except in a single case, the preparation of the stable and sterically protected $(CH_3)_3CP{=}C{=}NC(CH_3)_3$.[7] We now wish to report a general method of preparation of unstable (iminomethylidene)phosphines (monophosphorus analogues of carbodiimides), their direct observation by IR and mass spectrometry, and their initial chemical reactions.

The required starting materials, (iminomethyl)phosphines **1**, exist in equilibrium with carbamoylphosphines $[(CH_3)_3SiP(R)\text{-}CON(Ph)Si(CH_3)_3]$ and smaller amounts of alkylidenephosphines $RP{=}C(OSi(CH_3)_3)N(Ph)Si(CH_3)_3$.[8] In analogy with the reaction used in the preparation of $(CH_3)_3CC{\equiv}P$,[5] the compounds **1** could be expected to eliminate hexamethyldisiloxane and thus give rise to the desired (iminomethylidene)phosphines, $RP{=}C{=}NPh$ (Scheme I).

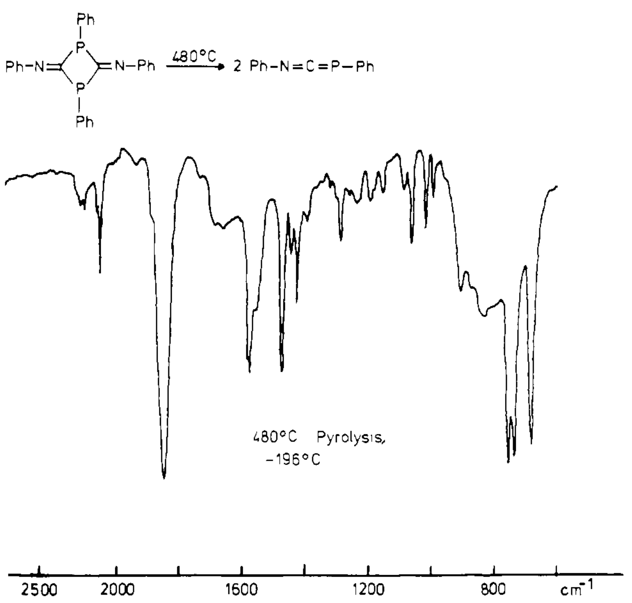
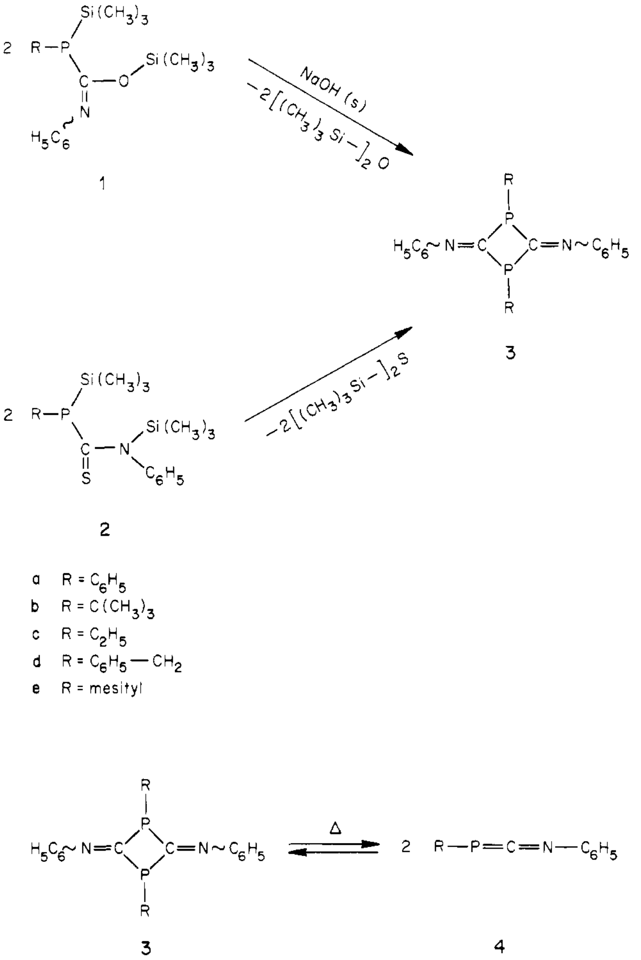


Figure 1. IR spectrum (−196 °C) of the product of pyrolysis of **3a** at 480 °C.

Scheme I



In the event, the treatment of **1** with a catalytic amount of solid NaOH led only to the isolation of the dimers **3**.[9] **3b** and **3e** were also obtained by spontaneous decomposition of the adducts **2b** and

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[9] (a) Satisfactory elemental analyses (C, H, N, P) were obtained for these compounds. (b) X-ray crystallographic determinations of **3c** and **3d** confirm the structure assignments. The two exocyclic phosphorus ligands are trans oriented. Full crystallographic data will be published: Becker, G.; Härer, J.; Riffel, H.; Uhl, G.; Wessely, H.-J., in preparation.

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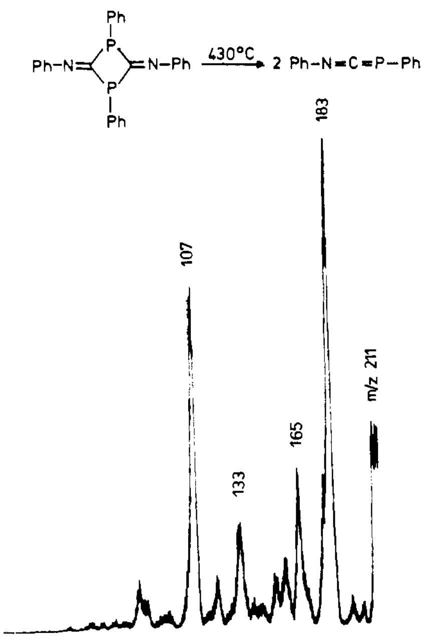

Figure 2. CID mass spectrum of *m/z* 211 from the pyrolysis of **3a** at 430 °C.

2e, the latter formed by the addition of phenyl isothiocyanate to the alkyl- or aryl(trimethylsilyl)phosphine.[10]

If the diphosphetanes **3** are, in fact, dimers of (iminomethylidene)phosphines, the monomers might be regenerated via a cycloreversion under suitable reaction conditions. This, indeed, is readily achieved by flash vacuum pyrolysis of **3**. Product formation was monitored by low-temperature IR spectroscopy, and a pyrolysis unit has also been attached to the ion source of a reversed-geometry Varian MAT 311A mass spectrometer[11] equipped with a collision chamber for obtaining CID (collisionally induced dissociation) spectra of initial pyrolysis products.

2,4-Bis(phenylimino)-1,3-diphenyl-1,3-diphosphetane (**3a**) (mp 139 °C) was vaporized at 139-145 °C (10^{-5} torr). When the pyrolysis temperature was increased to 400 °C, an IR band at 1853 cm^{-1} appeared in the pyrolyzate condensed at −196 °C. The maximum intensity of this band was observed at a pyrolysis temperature at 480 °C (Figure 1). On warming the pyrolyzate to −55 °C, the intensity of the 1853-cm^{-1} band started decreasing; at the same time, a band at 1560 cm^{-1} due to the starting material **3a** started increasing. This process was complete at −30 °C, and after warming to room temperature **3a** was recovered in better than 90% yield.[12]

These observations indicate that **3a** dissociates into two molecules of the (iminomethylidene)phosphine **4a** on gas-phase pyrolysis. The monomeric **4a** reverts to **3a** above −55 °C in the solid state. The strong band at 1853 cm^{-1} in the IR of **4a** is assigned to the asymmetric stretching vibration of the P=C=N moiety. For comparison, carbodiimides (RN=C=NR) absorb near 2100 cm^{-1}.

The analogous pyrolysis of **3b** (mp 220 °C) at 480 °C (sublimation temperature 110 °C, increasing to 200 °C in 35 min) gave rise to a strong IR band at 1839 cm^{-1} ascribed to **4b**. This material started redimerizing to **3b** at −25 °C, a process that was complete at 0 °C. Comparable results were obtained with the precursors **3c-e**.

The IR assignments were corroborated by using the mass spectrometry reactor. With increasing pyrolysis temperature, the $M^{+\cdot}$ peak due to **3a** decreased, while that of **4a** increased. The CID mass spectrum of **4a** obtained at 430 °C is shown in Figure 2. The base peak at *m/z* 183 may be ascribed to the dibenzophospholyl cation, $C_{12}H_8P^+$, which is typical of diphenylated phosphorus compounds.[13] In the pyrolysis of **3b** the parent peak of the precursor (*m/z* 382) disappeared at 490 °C, while that of **4b** (*m/z* 191) reached maximum intensity. Here, the spectrum is dominated by a loss of isobutene to give *m/z* 135, formally corresponding to $PhN{=}C{=}PH^{+\cdot}$ or $PhNH\text{-}C{\equiv}P^{+\cdot}$.

We are continuing the studies of (iminomethylidene)phosphines, in particular cycloaddition reactions and attempts to obtain other phosphorus-containing cumulenes, e.g., RP=C=O.

Registry No. 1a, 24103-42-2; **1b**, 87218-80-2; **1c**, 87729-47-3; **1d**, 87729-48-4; **1e**, 87729-49-5; **2b**, 87729-50-8; **2e**, 87729-51-9; **3a**, 87729-52-0; **3b**, 87218-81-3; **3c**, 87729-53-1; **3d**, 87729-54-2; **3e**, 87729-55-3; **4a**, 87729-56-4; **4b**, 87218-77-7; **4c**, 87729-57-5; **4d**, 87729-58-6; **4e**, 87729-59-7.

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(12) The band at 2120 cm^{-1} in Figure 1 is due to phenyl isocyanide, formed in a competing thermal fragmentation of **3a**. This material evaporates during warm-up and thus does not contaminate the final product. A yield of ca. 10% of phenyl isocyanide was obtained by distilling it into a cold trap and subsequently identifying it by comparison with an authentic sample.

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Enzyme System Generation of Singlet ($^1\Delta_g$) Molecular Oxygen Observed Directly by 1.0-1.8-μm Luminescence Spectroscopy

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Since the discovery of the chemical generation of singlet oxygen,[1,2] numerous attempts have been made to demonstrate the generation of singlet oxygen in biological systems. Using our ultrasensitive 1.2-μm region spectrometer, we now report the observation of a strong singlet Δ oxygen luminescence emission in the IR (Figure 1) produced in the decomposition of hydrogen peroxide by the enzymes *lactoperoxidase*, *catalase*, and *chloroperoxidase*. Preliminary reports on kinetic studies of lactoperoxidase-generated singlet oxygen[3] and a spectroscopic study of chloroperoxidase-generated singlet oxygen[4] have been given recently.

The *lactoperoxidase* system consists of a 0.01 μM/mL solution of lactoperoxidase (from milk, lyophilized; Sigma) in 0.01 M acetate buffer at pH + pD of 4.5 and 0.80 M KBr as a cofactor (Mallinckrodt, Analytical Reagent) at room temperature. The solvent is a 1:1 ratio of H_2O and D_2O. The experimental conditions are chosen to optimize singlet molecular oxygen emission; see the chemical scavenger studies of singlet molecular oxygen by Piatt et al.[5] and by Rosen and Klebanoff.[6] The enzyme and the hydrogen peroxide solutions are mixed in a 1:1 ratio under argon pressure into an optical cell with an overflow.

The luminescence emission spectrum of the lactoperoxidase/H_2O_2 consists of a single emission band (Figure 1A) with a peak at 1.28 μm (1280 nm), and a full bandwidth at half-maximum of 251 cm^{-1}. There is also the suggestion of a broad underlying band which will not be discussed further here. Other singlet molecular oxygen luminescence sources have been characterized

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