crease with increasing size of the metal cation).

Williams et al.[4b] argue that the regular trends in the solid-state Cp–M–Cp angles must have intramolecular origins, whereas the strongly irregular trends for the thermal average angles in the gas phase are artifacts due to different temperatures of measurement and the large uncertainties in the bending angles. Our results support this reasoning. Indeed, a regular bending potential trend is found (at least at the HF level of theory, where basis set saturation is comparable for all species). For $CaCp_2$ and $YbCp_2$ (and probably $SrCp_2$) small energy contributions provided by intermolecular interactions are likely to be responsible for the observed bent solid-state structures. $BaCp_2$, $SmCp_2$, and $EuCp_2$ may be slightly bent without intermolecular interactions. However, intermolecular forces certainly contribute to the exact angle observed in the solid state.

All MCp_2 species considered are strongly ionic and structurally nonrigid systems. Discussion of the structures of the growing number of floppy organometallics requires detailed information concerning the experimental or theoretical structure determination, i.e., whether a thermal average or equilibrium structure is involved. This should always be stated explicitly. The energy changes along internal coordinates with shallow potential curves are very useful measures of structural nonrigidity. As this information usually is difficult to obtain experimentally, computational studies will be increasingly helpful.

The NAO populations (cf. Table V) and the valence MO energies of the group 2 and lanthanide(II) metallocenes (cf. Table VI) support the correspondance between the electronic structures of the two sets of molecules. The similarities between group 2 (Ca, Sr, and Ba) and lanthanide(II) (Sm(II), Eu(II), Yb(II)) structural organometallic chemistry have been attributed[1,2] to the ionicity of the compounds and comparable ionic radii of the dications. Additionally, our investigations show that in both sets mainly the (n − 1)-d-orbitals are employed for donor–acceptor interactions between ligands and dications. Thus, except for the absence of a 4f-shell (with its spectroscopic and synthetic consequences[2]), the Ca, Sr, and Ba organometallics appear to exhibit very similar electronic structures as their Yb(II), Eu(II), and Sm(II) analogues. As lanthanide(II) organometallics (particularly the Sm(II) compounds) are increasingly important for synthetic purposes,[2] the availability of model systems without f-shell may be a useful option.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk and Convex Computer Corporation. M.K. acknowledges a Kêkulê grant by the Fonds der Chemischen Industrie. M.D. and H.S. are grateful to Professor H.-J. Werner (Bielefeld) and Professor R. Ahlrichs (Karlsruhe) for providing the MOLPRO and TURBOMOLE program systems.

The Thioxophosphane H-P=S and Its Tautomer H-S-P, (Thiohydroxy)phosphinidene, Are Stable in the Gas Phase[†]

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Abstract: Using the technique of neutralization–reionization mass spectrometry (NRMS) we have shown that the elusive thioxophosphane H—P═S and its tautomer H—S—P, (thiohydroxy)phosphinidene, are stable molecules in the gas phase. $H—S—P^{\bullet+}$ radical cations, generated by electron impact ionization of diethylphosphine sulfide, $(C_2H_5)_2HP═S$, are cleanly reduced to H—S—P; whereas $H—P═S^{\bullet-}$ anions, generated in a negative chemical ionization (NCI) experiment with the diethylphosphine sulfide, are readily oxidized to H—P═S. Double collision experiments on the ^{34}S isotopomers of the two tautomeric species were used to confirm the connectivity of the atoms. H—S—P is the first example of a molecule of the composition "XPS" (e.g., X = F, Cl, or Br) in which P does not take the central position.

Introduction

Thioxophosphanes X—P═S belong to the family of low-coordinated phosphorus compounds whose chemistry has received considerable attention.[1] Representative members where X = Cl, Br, and F have been characterized as stable species in the gas phase by IR and PES (photoelectron spectroscopy) spectroscopic techniques.[2] We have recently shown, using the technique of neutralization–reionization mass spectrometry (NRMS),[3] that $CH_3S—P═S$ is a viable species as well.[4] The structural information available from an NR experiment is limited to the connectivity of the atoms, but this versatile technique uses cations or anions which can often uniquely be generated by dissociative electron ionization of suitable precursor molecules. This mass spectrometry based technique was also successfully used to generate two related ternary HPS compounds,[5] viz., the phosphanethiol $H_2P—SH$[6] and the phosphanedithiol $HP(SH)_2$.[7] So far,

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[†] Dedicated to Professor H-Fr Grützmacher on the occasion of his 60th birthday.

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no experimental evidence is available for the existence of the simplest ternary HPS compound, the thioxophosphane **1** (H—P═S) or its tautomer **2**, (thiohydroxy)phosphinidene (H—S—P), two of the last few unknown triatomic molecules of the most important of the nonmetal elements.[8] However, a stable η^2-thioxophosphane–metal complex, $[Os(HPS)(CO)_2(PPh_3)_2]$, has been prepared.[9]

H—P═S **1** H—S—P **2**

On the other hand, state of the art ab initio MO calculations on the HPS[10]/HSP[10a,d] system **1**/**2** and its radical cations $\mathbf{1}^{\bullet+}/\mathbf{2}^{\bullet+}$ indicate that the neutral and ionic isomers lie in deep potential wells with significant barriers toward isomerization.[10a] For the neutral species, the states of lowest energy for the isomers are singlet **1** ($^1A'$) and triplet **2** ($^3A'$). The latter isomer lies 15.3 kcal/mol above the former, and the interconversion barriers **1** ($^1A'$) → **2** ($^1A'$) and **1** ($^3A'$) → **2** ($^3A'$) are predicted to lie high above the singlet **1** ($^1A'$) state (by 41.2 and 51.5 kcal/mol, respectively). For the ions, the stability ordering is reversed with $\mathbf{2}^{\bullet+}$ being 5.2 kcal/mol lower in energy than $\mathbf{1}^{\bullet+}$ with the barrier for interconversion lying 24.5 kcal/mol above $\mathbf{2}^{\bullet+}$.[10a]

These theoretical predictions prompted us to investigate the use of the NRMS technique[3] for the generation of the elusive HPS and HSP neutrals. Having first established the structure of the ion $\mathbf{2}^{\bullet+}$ using collisional activation (CA) mass spectrometry,[11] we were able to show that its reduction in a NRMS experiment indeed leads to the formation of the elusive neutral H—S—P, **2**, as a stable species in the rarefied gas phase. The tautomer H—P═S, **1**, could not be generated as its radical cation, but the anion $\mathbf{1}^{\bullet-}$, which is calculated to be considerably more stable than $\mathbf{2}^{\bullet-}$,[12] is formed in a negative chemical ionization (NCI) experiment,[13] and its subsequent oxidation in a $^-NR^+$ experiment[3f,g] readily yields the desired neutral species **1**. Our experimental findings provide a gratifying confirmation of the theoretical predictions.

Experimental Section

All experiments were carried out with the VG Analytical ZAB-R mass spectrometer, a new three sector BE_1E_2-type instrument whose design is based on the standard, nonextended geometry of the ZAB-2f.[14] The instrument is equipped with three collision gas chambers for NR experiments in the second field free region (ffr) between B and E_1, and it has an additional collision gas chamber in front of E_2 for double collision (MS/MS/MS) experiments in the third ffr. The NR mass spectra were obtained using *N*,*N*-dimethylaniline for neutralization (main beam transmission, $T = 80\%$) and oxygen for reionization ($T = 80\%$); oxygen was also used as the collision gas in the collisional activation (CA) and charge reversal (CR) experiments. The spectra were recorded with a small PC-based data system developed by Mommers Technologies Inc. (Ottawa). The MS/MS/MS spectra shown in Figures 1c, 2a, and 3a represent the accumulation of 20 scans at 30 s per scan. The compound $(C_2H_5)_2HP{=}S$ was synthesized by standard procedures.[15]

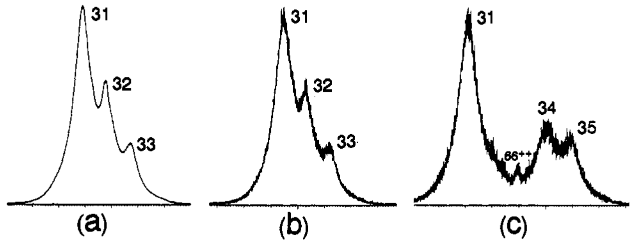

Figure 1. (a) Partial CA mass spectrum of *m/z* 64 $[H^{32}SP]^{\bullet+}$ ions $[\mathbf{2}]^{\bullet+}$ generated in the ion source; (b) and (c) Partial CA mass spectra of the $[H^{32}SP]^{\bullet+}$ ion $[\mathbf{2}]^{\bullet+}$ and its isotopomer $[H^{34}SP]^{\bullet+}$ generated from the collision-induced dissociation reactions $[H_3{}^{32}SP]^{\bullet+} \rightarrow [H^{32}SP]^{\bullet+} + H_2$ and $[H_3{}^{34}SP]^{\bullet+} \rightarrow [H^{34}SP]^{\bullet+} + H_2$.

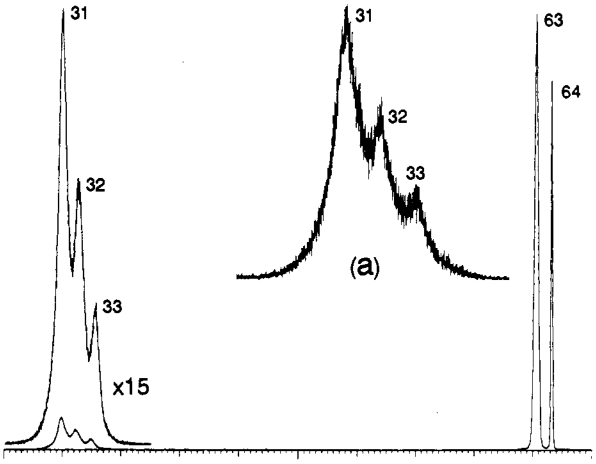

Figure 2. NR mass spectrum of *m/z* 64 $[H^{32}SP]^{\bullet+}$ ions $[\mathbf{2}]^{\bullet+}$; inset a: the partial CA mass spectrum of ions $[\mathbf{2}]^{\bullet+}$ resulting from the NR reaction $[\mathbf{2}]^{\bullet+} \rightarrow [\mathbf{2}] \rightarrow [\mathbf{2}]^{\bullet+}$.

Results and Discussion

H-S-P. Dissociative ionization (70-eV electron impact) of diethylphosphine sulfide, $(C_2H_5)_2HP{=}S$, abundantly yields *m/z* 64 $[H,P,S]^{\bullet+}$ ions via the consecutive loss of two C_2H_4 molecules and a H_2 molecule.[15] Mass selection of *m/z* 64 and subsequent collision-induced dissociation of the fast moving ions with O_2 afforded the collisional activation (CA) mass spectrum. The full spectrum shows an intense peak at *m/z* 63 (PS^+), resulting from the reaction of lowest energy requirement,[16] and a less intense cluster (ca. 10% of *m/z* 63) of structure diagnostic peaks at *m/z* 31 (P^+), *m/z* 32 ($S^{\bullet+}$), and *m/z* 33 (SH^+) shown in Figure 1a. These observations are fully compatible with the exclusive generation of ions of structure $\mathbf{2}^{\bullet+}$.[17] Had the tautomer $H{-}P{=}S^{\bullet+}$, $\mathbf{1}^{\bullet+}$, been (co)generated, then considering the energy requirements for the dissociation reactions,[16] a substantial fraction of the *m/z* 32 ions should have been $PH^{\bullet+}$ ions. This is clearly not the case: Figure 1b and c shows the partial *m/z* 31 – *m/z* 35 CA mass spectra of *m/z* 64 $[H,P,{}^{32}S]^{\bullet+}$ and *m/z* 66 $[H,P,{}^{34}S]^{\bullet+}$ ions generated from the collision-induced H_2 loss of mass selected *m/z* 66 $[H_3P^{32}S]^{\bullet+}$ and *m/z* 68 $[H_3P^{34}S]^{\bullet+}$. It follows from these MS/MS/MS experiments[18] that the $[H,P,{}^{32}S]^{\bullet+}$ ions do not yield *m/z* 32 $PH^{\bullet+}$ but rather *m/z* 32 S^+ ions, and thus they have structure $\mathbf{2}^{\bullet+}$ and not $\mathbf{1}^{\bullet+}$, in accordance with earlier observations that thiophosphorus radical cations favor structures with an SH moiety over those with a PH moiety.[4,6,19] Note that the CA mass

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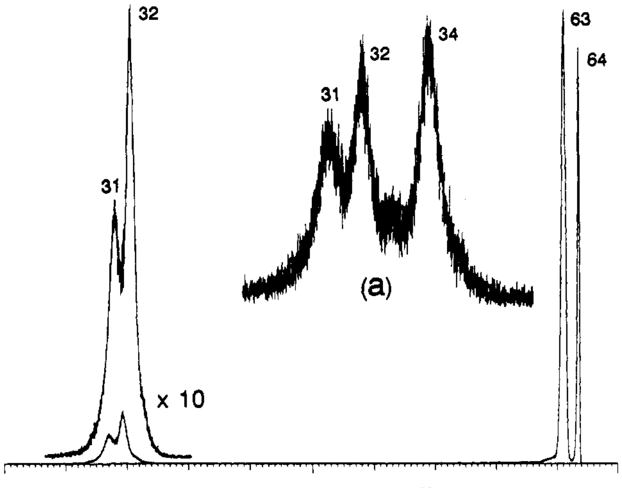

Figure 3. $^{-}$NR^{+} mass spectrum of *m/z* 64 $[HP^{32}S]^{\bullet-}$ ions $[1]^{\bullet-}$; inset a: the partial $^{-}$NR^{+} mass spectrum of *m/z* 66 ions $[HP^{34}S]^{\bullet-}$, $[1]^{\bullet-}$.

spectrum of *source* generated *m/z* 66 $[HP^{34}S]^{\bullet+}$ ions cannot readily be obtained since these ions are predominantly *m/z* 66 $[H_3P^{32}S]^{\bullet+}$ ions and that the poor resolution of the peaks in Figure 1 is due to an intrinsic property of the HPS system, i.e., the large kinetic energy release associated with the formation of the *m/z* 31 P^+ ions.

A neutralization–reionization experiment on $\mathbf{2}^{\bullet+}$ involving neutralization by electron transfer to *N*,*N*-dimethylaniline[20] followed, after ca. 1 μs, by reionization with O_2 yields the NR spectrum of Figure 2 which features an intense recovery signal at *m/z* 64. This, quite likely, reflects the stability of the neutral **2** and may point to relatively favorable Franck–Condon factors in the vertical electron transfer processes $\mathbf{2}^{\bullet+} \rightarrow \mathbf{2} \rightarrow \mathbf{2}^{\bullet+}$, in agreement with the theoretical prediction[10a] that the (bent) geometries of ion and neutral are closely similar. We note further that the intensity distribution of the *m/z* 31–33 peaks in the NR spectrum of $\mathbf{2}^{\bullet+}$ is very close to that of its conventional CA mass spectrum, see Figure 1a and b. Thus there is no indication that **2** has isomerized to a significant extent into the more stable isomer **1**. Conclusive evidence that the recovery signal in the NR spectrum of **2** is indeed that of the reionized stable neutral HSP, **2**, and not its counterpart HPS, **1**, comes from a multistep collision experiment in which the reionized species **2** is selectively transmitted through the second sector (E_1) and then subjected to a CA experiment in the third field free region.[3d,f] The resulting "survivor" CA mass spectrum of interference free reionized **2**, see inset in Figure 2, is very close to its characteristic conventional CA mass spectrum (Figure 1). These observations clearly show that following neutralization of the radical cation $\mathbf{2}^{\bullet+}$ the neutral isomer **2** retains its structural identity and that, in excellent agreement with the theoretical predictions, HSP is a stable species in the rarefied gas phase.

H—P═S. When the diethylphosphine sulfide precursor molecule, $(C_2H_5)_2HP{=}S$, was subjected to a NCI experiment using H_2O as the reagent gas,[13] a mass spectrum was obtained in which the deprotonated molecular ion dominated but which also showed *m/z* 64 $[H,P,S]^{\bullet-}$ ions whose immediate precursor is the *m/z* 93 $[M - C_2H_5]^-$ ion. The *m/z* 64 ions were oxidized by collisions with O_2 and subsequently reionized with O_2, and the resulting $^{-}$NR^{+}[3f,g] spectrum is shown in Figure 3. The spectrum shows an intense "survivor" signal, and it is fully compatible with the proposal that negative ions of structure $HPS^{\bullet-}$, $\mathbf{1}^{\bullet-}$, are oxidized to the stable neutral HPS, **1**. In agreement with this assignment, the *m/z* 31–33 region of this $^{-}$NR^{+} spectrum shows peaks at *m/z* 31 (P^+) and *m/z* 32 ($PH^{\bullet+}/S^{\bullet+}$) but *not* at *m/z* 33 (SH^+). The (very weak) $^{-}$NR^{+} spectrum of the ^{34}S isotopomer *m/z* 66 $[HP^{34}S]^{\bullet-}$ was also obtained and, as expected on the basis of the dissociation energetics of $\mathbf{1}^{\bullet+}$,[16] it shows, see inset in Figure 3, signals at *m/z* 32 ($PH^{\bullet+}$) and *m/z* 34 ($S^{\bullet+}$) of similar abundance. The NR spectra of $\mathbf{1}^{\bullet-}$ and its ^{34}S isotopomer are not significantly different from the corresponding charge reversal[21] (CR) spectra. Thus, contributions to the NR spectra from collisionally ionized *neutral* dissociation products of the neutralized ions which sometimes obscure the interpretation of these spectra are negligible.

In conclusion, we have shown that, because of the inverse relationship between the stability of radical cations $\mathbf{1}^{\bullet+}/\mathbf{2}^{\bullet+}$ and radical anions $\mathbf{1}^{\bullet-}/\mathbf{2}^{\bullet-}$, the thioxophosphane anion $H{-}P{=}S^{\bullet-}$, $\mathbf{1}^{\bullet-}$, and the (thiohydroxy)phosphinidene cation $H{-}S{-}P^{\bullet+}$, $\mathbf{2}^{\bullet+}$, can be generated independently in mass spectrometric experiments. Using the NRMS technique it is shown, in agreement with the prediction made for **1** in ref 10a, that the neutral counterparts of these two ions are stable species. In addition, **2** is the first example of a molecule of the composition "XPS" (X = F, Cl, Br, etc.) in which phosphorus does not take the central position.

Acknowledgment. J.K.T. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) and McMaster University for a grant to purchase the VG Analytical ZAB-R mass spectrometer and for further financial support. Research at the University of Düsseldorf has been supported by the "Fonds der Chemischen Industrie". Thanks are due to Mr. F. Ramelan and Dr. A. A. Mommers for valuable technical assistance.

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