evaporation of methyl iodide, the vials were kept cold after the reaction was stopped. Inaccuracies introduced as a result of application of an inappropriate kinetic model, e.g., deviations from pseudo-first-order conditions[18] and the existence of side reactions, are negligible. The radiochromatograms showed three peaks, corresponding to methyl iodide, the quaternary ammonium salt, and about 1% of methanol. The [^{11}C]methanol was formed as the only detectable byproduct in the synthesis of [^{11}C]methyl iodide; the amount of methanol remained constant during the kinetic run.

In forthcoming papers we will report on the use of this ^{11}C/^{14}C method in the determination of a secondary KIE and an application in the study of enzymatic isotope effects.

Acknowledgment. We thank Dr. Petter Malmborg for the radionuclide production and Professor Göran Bergson for discussions. This project is financially supported by the Swedish Natural Science Research Council (through Grants K-KU-2446 to G. Bergson and K-KU-3446 to B. Långström).

Registry No. p-$MeC_6H_4NMe_2$, 99-97-8; ^{11}C, 14333-33-6; ^{14}C, 14762-75-5.

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[18] The reaction solution was 0.75 M in substrate and ca. 0.19 mM in methyl iodide, causing a decrease in substrate concentration of 0.025% for complete reaction.

Crystal Structure of a Novel Tricoordinate Vinyliodinane Species and Evidence for an Alkylidenecarbene–Iodonium Ylide

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Received August 6, 1987

Polycoordinate (hypervalent) iodine chemistry is experiencing a renaissance.[2] Thousands of stable inorganic as well as organic polycoordinate iodine compounds have been prepared since Willgerodt[3] first reported $PhICl_2$ in 1886. The large majority of organic polyvalent iodines are diaryl compounds with much less information[2,4] on alkyl, alkynyl, and vinyliodine species with no available structural data on vinyl systems at all. Moreover, although numerous carbene–iodonium ylides, **1**, are known,[5,6] to our knowledge the homologous alkylidenecarbene–iodonium ylides, **2**, are to date unknown.

$$\underset{\mathbf{1}}{ArI{=}CR_2 \longleftrightarrow Ar\overset{+}{I}{-}\overset{-}{C}R_2} \qquad \underset{\mathbf{2}}{ArI{=}C{=}CR_2 \longleftrightarrow Ar\overset{+}{I}{-}\overset{-}{C}{=}CR_2}$$

Hence, we wish to report the first[7] X-ray structure of a novel vinyliodinane compound and present evidence for an alkylidenecarbene–iodonium ylide, **2**.

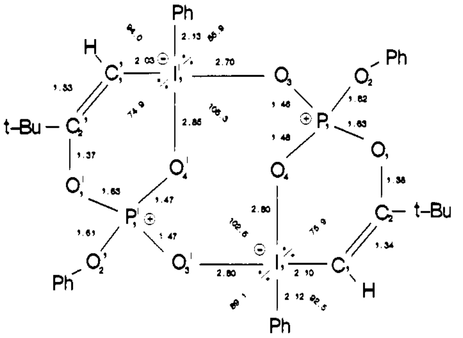


Figure 1. Critical bond length (Å) and geometric features of the 12-I-4 vinyliodonium dimer **6**.

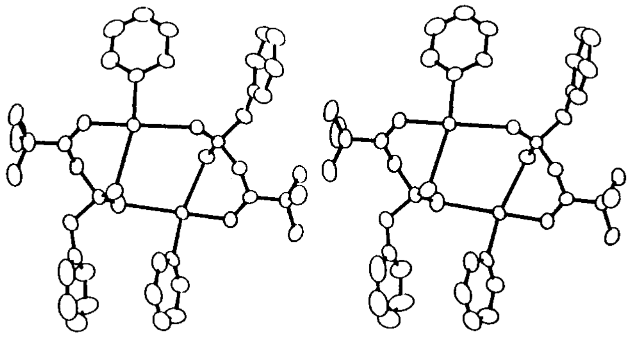
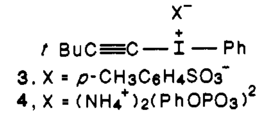


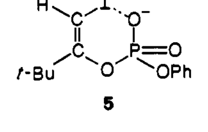
Figure 2. Stereoview of dimer **6**.

Reaction of phenyl(*tert*-butylethynyl)iodonium tosylate,[9] **3**, with $PhOPO_3^{2-}(NH_4^+)_2$ in ethanol at room temperature, in an attempt to prepare the corresponding phosphate salt **4** and thence the alkynylphosphate ester,[10] gave instead a 61% yield of crystalline, zwitterionic species **5** whose spectral properties[11] in solution are



$$t\text{-}BuC{\equiv}C{-}\overset{\overset{X^-}{+}}{I}{-}Ph$$

3, X = p-$CH_3C_6H_4SO_3^-$
4, X = $(NH_4^+)_2(PhOPO_3)^{2-}$



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consistent with the proposed structure. Recrystallization from ether/CH_2Cl_2 at −20 °C and X-ray structure determination indicated a head-to-tail dimeric species **6** in the solid state.[12] The salient features of **6** are summarized in Figure 1. A 3D view of **6** is shown in Figure 2. As seen from the data, **6** represents a 12-I-4 (8-P-4) polycoordinate iodine species in the Martin–Arduengo formalism.[13] Coordination around each iodine is pseu-

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[1] DFG Postdoctoral Fellow.

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[7] Numerous X-ray structures of diverse polyvalent iodine species are known,[5,8] but none so far of a vinyliodinane species.

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[11] Mp 156–156.5 °C; IR (KBr) 3100–3040, 2980–2840, 1590 (C=C), 1270–1200 (P=O), 1075, 900, 795 (C=CH) cm^{-1}; ^{1}H ($CDCl_3$, TMS) δ 1.19 (s, 9, *t*-Bu), 5.91 (d, $^4J_{PH}$ = 2.3 Hz, 1, C=CH), 6.89–7.75 ppm (m, 10, Ar); ^{31}P($CDCl_3$, 85% H_3PO_4) δ −7.85 ppm; ^{13}C ($CDCl_3$) δ 28.3 ($C(CH_3)_3$), 40.0 [d, $^3J_{CP}$ = 2.6 Hz, $C(CH_3)_3$], 82.2 [dd, $^1J_{CH}$ = 194.8 Hz, $^3J_{CP}$ = 4.9 Hz (C=CH)], 116.6, 131.0, 131.1, 134.6 (IC_6H_5), 119.9, 123.1, 129.1, 152.6 (PC_6H_5), 170.3 [d, $^2J_{CP}$ = 11.0 Hz, (POC=C)]; MS (FAB), 459 (100 M + 1), 383 (3), 302(5), 251 (10), 175 (28).

[12] Crystal data for **6**: $(C_{18}H_{20}O_4PI)_2$, triclinic, $P\bar{1}$, a = 1153.5 (7) pm, b = 1232.7 (6) pm, c = 1446.1 (7) pm, α = 87.33 (4), β = 111.68 (4) γ = 91.69 (5), Z = 2, D_{calcd} = 1.59 g/cm^3; crystal size: 0.35 × 0.33 × 0.25 mm; with 5126 reflections [$I > 3\sigma(I)$]. The structure was solved with direct methods (MULTAN 82) and standard Fourier techniques. Final R factors: R = 0.0429 and R_w = 0.0574.

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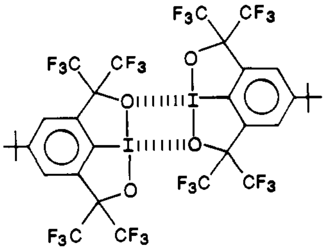
do-octahedral ($AX_2Y_2E_2$) with the four ligands essentially square planar and the two lone pairs anti with respect to each other. Coordination around each phosphorus is tetrahedral (distorted) with two long P–O bond[14] lengths of around 1.62 Å each and two shorter ones of about 1.47 Å each. The remaining structural features (i.e., olefin, *t*-Bu, Ph, etc.) are unexceptional. These novel structural features around the iodines and phosphorus are due to the dimeric nature and consequent secondary bonding interactions[8] in the solid state of the molecule. In particular, both the intra- and intermolecular I–O bond distances are of the same order of magnitude (2.70–2.85 Å)[15] but significantly less than the sum of the van der Waals radii (3.5 Å) of I–O.[16] Such secondary bonding interactions are well precedented in polycoordinate iodine chemistry.[8,15] A similar interaction was reported by Martin and coworkers[17] in the 10-I-3 iodinane **7** with an I---O intermolecular bond length of about 3.0 Å. It is interesting to speculate if the considerably shorter I---O distances in **6** vs **7** are due to the different nucleophilicities of the oxygens involved and the electrophilicities of the respective iodine centers as well as the similarity of the trans substituents in **6**.



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Treatment of **5** in $CDCl_3$ with $NaOD/D_2O$ results in *complete* exchange of the vinylic proton as evidenced by the infrared shift of the C=CH group (from 3080 to 2300 cm^{-1} for the stretching mode and 795 to 564 cm^{-1} for the out-of-plane vibration) and the complete disappearance of the 5.91 ppm vinylic proton signal in the NMR. The deuteriated isomer of **5** is recovered quantitatively. This represents prima facie evidence[18] for the intermediacy of an alkylidenecarbene–iodonium ylide (**2**) with a finite lifetime.

In summary, we report the X-ray structure of a vinyliodinane species with 12-I-4 structural features and present evidence for an alkylidenecarbene–iodonium ylide (**2**). Attempts to isolate a stable ylide **2** as well as further work in this area are underway.

Acknowledgment. This work was supported by the NCI of the NIH (Grant RO1CA16903-11).

Supplementary Material Available: A complete description of the X-ray structure of **6** and tables of positional and thermal parameters (14 pages). Ordering information is given on any current masthead page.

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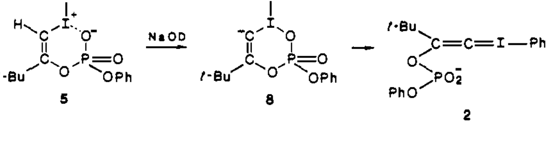
[18] A referee pointed out that a structure such as **8** can account for the results of the base exchange and cannot be ruled out on the basis of our evidence. This is correct, but **8** may be looked upon as a cyclic, closed version of the postulated ylide. Calculations and experiments are under way to distinguish between **8** and **2**.



Nature of the Tin–Tin Double Bond As Studied by Solid-State and Solution Nuclear Magnetic Resonance

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Received May 18, 1987

During the past 10 years interest in multiple bonding between heavier elements of the main group has rapidly increased as more and more examples have been synthesized and characterized.[1] One of the most interesting of these species is the dimer, **1**, of bis[bis(trimethylsilyl)methyl]tin, **2**, the first compound[2] known to formally contain a Sn=Sn double bond. Despite much work[3-5] relatively little is known about the nature of the Sn=Sn bond in **1** or its thermochromic behavior. In this paper we report NMR results that are consistent with the Sn=Sn bond in **1** being a very weak dative interaction and demonstrate that the monomer and dimer exist in equilibrium in solution.

Compound **1** was prepared[4] by standard Schlenk line techniques, and the authenticity of the sample was confirmed by X-ray crystallography.[5] Figure 1A depicts the room temperature ^{119}Sn CPMAS spectrum of **1**, giving an isotropic shift of 692 ppm downfield from tetramethyltin which moves upfield to 613 ppm at 77 K. This spectrum and all subsequent solid-state spectra were collected by using a variable-temperature CPMAS probe head that spins short sealed 5-mm NMR tubes.[6] Such sample cells were necessary due to the extreme sensitivity of **1** to air and moisture. Analysis of the spinning sideband intensities[7] gives the principal values of the chemical shielding tensor as $\sigma_{11} = 1600$, $\sigma_{22} = 400$, and $\sigma_{33} = 100 \pm 20$ ppm. This anisotropy is an order of magnitude larger than those observed for several tin(IV) compounds.[8] Satellites are observed on each line in the CPMAS spectrum due to the 1340 ± 10 Hz scalar coupling to ^{117}Sn. Satellites from coupling to both ^{119}Sn and ^{117}Sn are also clearly observed in single-crystal CP spectra, where the splittings are the sum of the anisotropic direct and indirect (*J*) dipolar couplings.[9] The latter are quite anisotropic as the splittings at some orientations are over 4 times as large as can be accounted for by direct dipolar coupling alone.[10] The ^{13}C CPMAS spectrum at room temperature displays a single line for the methine carbon with satellites due to coupling with both ^{119}Sn and ^{117}Sn. Beginning at ~220 K this resonance splits into three lines which continue to shift smoothly apart down to ~100 K (Figure 2B). This behavior is most easily explained by a conformational equilibrium in the solid that is slowed upon cooling.

Attempts to observe ^{119}Sn spectra in solution at room temperature failed but two signals were observed at 165 K in either ether or toluene at 740 and 725 ppm (Figure 1B). Upon warming, these resonances broaden and shift to lower field, finally disappearing into the base line at ~225 K. Assignment of these peaks on the basis of the ^{119}Sn shifts alone is not possible as no rationale has yet emerged for the interpretation of tin(II) ^{119}Sn shifts even though they span over 4000 ppm.[11] While the shifts are close

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