Recent *indirect* evidence suggests that *deprotonated* amides and anionic inhibitors bind in a similar manner by competing with solvent hydroxyls for coordination to the active site metal of carbonic anhydrase.[9] In view of the implications of such binding to the mechanism of pyruvamide hydration catalysis and in view of the favorable potential for using pyruvamide to elucidate the mode of binding of amides, we have utilized ^{15}N NMR to characterize the enzyme-pyruvamide *equilibrium* complex. The proton-decoupled ^{15}N NMR spectrum of 99% ^{15}N-enriched pyruvamide[10] shows two resonances at 101.4 and 103.4 ppm[11] (integral ratio of 5:3) that we tentatively assign to the amide resonances of the keto and *gem*-diol forms, respectively.[12] Figure 2A shows the proton-decoupled ^{15}N NMR spectrum of labeled pyruvamide in the presence of 1 equiv of enzyme. Only a single resonance can be seen at 126.7 ppm whose positive NOE (determined in a separate experiment) confirms its assignment to the enzyme-bound pyruvamide.[14] ^{13}C NMR studies on C-2 labeled pyruvamide[15] unambiguously demonstrate that the bound pyruvamide *within the complex* is overwhelmingly in the keto form.

By using the approach pioneered by Kanamori and Roberts,[16a] we examined the *proton-coupled* ^{15}N NMR spectrum of the complex to see whether it is a triplet ($-NH_2$) or doublet ($-NH^-$). Careful examination of the proton-coupled spectrum (Figure 2B) reveals a doublet ($^1J_{N-H}$ = 68 Hz) centered at the decoupled position (126.7 ppm) and an additional resonance about 0.7-0.8 ppm upfield from the doublet center. The amide group is expected to be about 18% deuteriated, since 18% D_2O was used for locking purposes. Independent experiments in which the extent of deuteriation was varied confirmed that the additional component is the resonance of a deuteriated ^{15}N. Very similar ^{15}N isotope shifts *per deuterium* have been reported for ammonia.[17] Although the deuterium-shifted resonance is an unresolved shoulder in Figure 2A, it is clearly resolved at the higher field of 7.05 T. The doublet structure in the proton-coupled spectrum of labeled pyruvamide unambiguously shows that *pyruvamide is bound as the deprotonated amide anion.*[16] Studies on metal ion complexes indicate that this is almost certainly due to substitution of an amide proton by the zinc.[18] Such complexes are normally stabilized with respect to alkaline metal ion hydrolysis by formation of chelate structures.[18] The active site can provide stabilizing interactions, such as hydrogen bonding to the NH and CO of the amide,[19] and the keto group could orient toward the metal to form a five-membered chelate.[20] The unexpectedly small N-H coupling constant we see suggests that the presumably coordinated nitrogen is largely pyramidal in character.[21]

It should be emphasized that *any relation of the dominant pyruvamide binding we see at equilibrium to the catalytically productive binding mode remains to be established.* Should they prove to be the same, our results would have important implications.[22] Since anionic ligands compete with solvent hydroxyls for binding at the active site metal of carbonic anhydrase,[5] our results raise the important question of whether hydration catalysis can be achieved in this enzyme in absence of the zinc-hydroxide mechanism. The striking dissimilarities reported[3,8] in the pH profiles of different carbonyl hydration substrates, along with our present observations, suggest that this enzyme may be capable of a hitherto unrecognized mechanistic diversity in its hydration catalysis.

Acknowledgment. We are especially grateful to Dr. Charles Hignite for the method of synthesis of labeled pyruvamide and to Dr. Angelo Vedani for stimulating discussions. The financial support of the Medical Research Service of the Veterans Administration (to R.G.K.) is gratefully acknowledged. The Varian XL-300 utilized at the University of Kansas (Lawrence) was purchased through the N.I.H. Biomedical Research Support Shared Instrumentation Grant Program.

(9) Rogers, J. I.; Mukherjee, J.; Khalifah, R. G. *Biochemistry* **1987**, *26*, 5672-5679.

(10) Pyruvamide was synthesized by treating acetylbromide with $KC^{15}N$ followed by carrying out a limited hydrolysis of the resulting pyruvonitrile.[15]

(11) Chemical shifts are reported as being downfield from ammonia, by using aqueous $Na^{15}NO_3$ (assumed to be at 376.0 ppm[21]) as an external reference.

(12) The hydration equilibrium constant for pyruvamide has been reported to be 0.75-0.80.[13]

(13) (a) Fischer, G.; Sieber, M.; Schellenberger, A. *Bioorg. Chem.* **1982**, *11*, 478-484. (b) Fischer, G.; Kullertz, G.; Schellenberger, A. *Tetrahedron* **1976**, *32*, 1503-1505.

(14) At 4.7 T, dipolar calculations suggest that an NOE near 0.7 should be obtained for an immobilized pyruvamide on carbonic anhydrase.

(15) Mukherjee, et al., manuscript in preparation.

(16) (a) Kanamori, K.; Roberts, J. D. *Biochemistry* **1983**, *22*, 2658-2664. (b) Blackburn, G. M.; Mann, B. E.; Taylor, B. F.; Worral, A. F. *Eur. J. Biochem.* **1985**, *153*, 553-558.

(17) Litchman, W. M.; Alei, M.; Florin, A. E. *J. Chem. Phys.* **1969**, *50*, 1897.

(18) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385-426.

(19) (a) Vedani, A.; Meyer, E. F. *J. Pharm. Sci.* **1984**, *73*, 352-358. (b) Vedani, A.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 7653-7658.

(20) Bertini, I.; Luchinat, C.; Scozzafava, A. *Bioinorg. Chem.* **1978**, *9*, 93-100.

(21) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience: New York, 1979.

(22) Our results also contribute to understanding the mode of binding of the CO_2 competitive inhibitor imidazole.[23] In view of the similarity in pK_a and coordination potential of deprotonated amides and deprotonated "pyrrole" nitrogens of imidazole,[18] our present findings make the proposed inhibition of carbonic anhydrase by the imidazole anion at high pH[23] much more tenable.

(23) (a) Bertini, I.; Luchinat, C. *Acc. Chem. Res.* **1983**, *16*, 272-279. (b) Khalifah, R. G.; Rogers, J. I.; Mukherjee, J. *Biochemistry*, in press.

$^{11}C/^{14}C$ Kinetic Isotope Effects

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Received June 5, 1987

Kinetic isotope effect (KIE) measurements employing the isotopes of hydrogen as well as many heavy elements have frequently been utilized in the elucidation of organic and enzymatic reaction mechanisms.[1] In this paper we report a method for the determination of $^{11}C/^{14}C$ KIE.[2] The radionuclide ^{11}C is a positron emitter with a half-life of 20.34 min. There are several reasons why the combined use of ^{11}C and ^{14}C may be useful in isotope effect studies. (1) A large mass range of carbon isotopes is used, resulting in a large rate ratio. (2) Both isotopes are radioactive and can be analyzed with high precision. (3) Direct rate measurements can be performed reacting the isotopic species in the same reaction pot, thus eliminating interexperimental errors. There is, of course, also a fundamental interest in this new carbon KIE.

The main obvious drawbacks in using ^{11}C are the restrictions imposed by its short half-life and the need for accelerator facilities. However, the increased use of positron emission tomography (PET) in biomedical research as well as in clinical applications[3] have accelerated the development of rapid labeling synthesis. Today, a large range, including quite complex, ^{11}C labelled molecules, is available.[4] The use of ^{11}C in the study of physio-

(1) See, e.g.: Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980.

(2) (a) See Matsson (Matsson, O. *Abstracts of Uppsala Dissertations from the Faculty of Science*; 1984; 723) for a preliminary report of the method. (b) This work was presented in part at the IVth Conference on the Application of Medical Cyclotrons, Turku, Finland, 1986, the VIIIth IUPAC Conference in Physical Organic Chemistry, Tokyo, Japan, 1986, and the Gordon Conference on Isotopes in Chemistry and Physics, Oxnard, CA, 1986.

(3) (a) *The Metabolism of the Human Brain Studied with Positron Emission Tomography*; Greitz, T., Ingvar, D. H., Widén, L., Eds.; Raven Press: New York, 1985. (b) *Positron Emission Tomography and Autoradiography: Principles and Applications for the Brain and Heart*; Phelps, M., Mazziotta, I., Schelbert, H., Eds.; Raven Press: New York, 1986. (c) *Biomedical Imaging*; Hayaishi, O., Torizuka, K., Eds.; Academic Press: New York, 1986.

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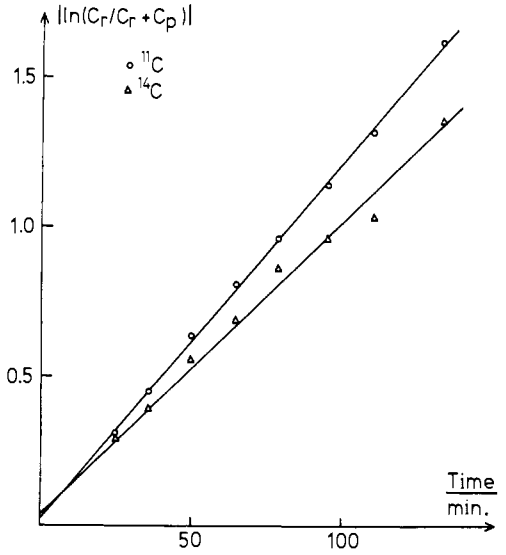

Figure 1. Kinetic plots for ^{11}C and ^{14}C, respectively, in the reaction of labeled methyl iodide with *N,N*-dimethyl-*p*-toluidine in methanol at 30 °C.

logical processes, such as brain metabolism of neurotransmitters, also provides further reason for investigating ^{11}C KIEs, although in most applications the isotope effect in PET studies is presumably negligible. In the present investigation the $^{11}C/^{14}C$ KIE method was applied to the determination of the primary carbon KIE in the methylation of *N,N*-dimethyl-*p*-toluidine with methyl iodide.

$$H_3C\text{-}C_6H_4\text{-}N(CH_3)_2 + {}^*CH_3I \xrightarrow[MeOH]{30\ ^\circ C} H_3C\text{-}C_6H_4\text{-}N^+(CH_3)_2{}^*CH_3I^-$$

* = 11 or 14

In this methodological study the reasons for choosing this reaction were as follows: the availibility of labeled methyl iodide; the fairly large $^{12}C/^{14}C$ KIE reported for this reaction by Buist and Bender;[5] the possibility of running the reaction under pseudo-first-order conditions; and the convenient rate of the reaction at a reasonable temperature. The reaction also proceeds in a mechanistically pure way. ^{11}C was produced as [^{11}C]carbon dioxide, which was used in a two-step synthesis of [^{11}C]methyl iodide.[6] The kinetic experiments were performed in the following way.

Methanolic solutions of the labeled methyl iodides and the amine were mixed.[7] The resulting solution was transferred to eight vials, which were capped and thermostated at 30.0 °C. At 15–20-min intervals, vials were withdrawn, and the reaction was stopped by adding 20 μL of phosphorus acid to the vials. The samples were analyzed by HPLC,[9] with use of a UV detector in series with a β^+-flow detector.[10] Two fractions containing the radioactive reactants and products, respectively, were collected in bottles containing scintillation liquid. The fractions were analyzed for ^{11}C content with a sodium iodide scintillation crystal counter and/or a liquid scintillation counter.[11] The samples were stored in a refrigerator overnight and the ^{14}C radioactivity was then measured in the liquid scintillation counter. The ^{11}C and ^{14}C CPM (counts per minute) values were corrected for decay, dead time, and background radiation. The rate constants were obtained from the kinetic data by plotting $\ln[C_r/(C_r + C_p)]$ versus reaction time, C_r and C_p corresponding to the CPM values of the reactant and product fractions, respectively. Straight lines were then fitted to the data by the method of least squares. The results from three experiments are shown in Table I. The value of $^{11}k/^{14}k$ (1.230 ± 0.036; T = 30.0 °C)[12] is, as expected, higher than the value $^{12}k/^{14}k$ (1.117 ± 0.011, T = 48.5 °C) reported by Buist and Bender.[5] The temperature dependence for carbon KIEs is expected to be normal (smoothly decreasing with increasing temperature) and of small magnitude for S_N2 reactions.[13] The temperature effect is not likely to exceed 1% in the present case. The $^{12}C/^{14}C$ KIE was predicted by Bigeleisen[14] to be a little less than twice that for $^{12}C/^{13}C$. This prediction, which was based on simple theoretical arguments, has later been confirmed in model calculations by Stern and Vogel,[15] who concluded that for r = ln ($^{12}k/^{14}k$)/ln ($^{12}k/^{13}k$), $1.8 \le r \le 2.0$ except for cases where the KIEs are of unusually small magnitude or associated with temperature dependence anomalies. Application of the simple treatment[16] yields a value of approximatively 1.6 for ln ($^{11}k/^{14}k$)/ln ($^{12}k/^{14}k$). By using this number, a value of $^{12}k/^{14}k$ = 1.138 ± 0.02 is obtained from the present $^{11}k/^{14}k$ value. Having the crudeness of the models in mind, we find this to be in fair agreement with the experimentally observed $^{12}k/^{14}k$ value.[5] The precision in the ^{14}C and ^{11}C kinetics is dependent on the magnitude of the CPM values.[17a] The statistical error in ^{11}C CPM values in the experiments ranges between ±0.3 and ±1.1%; and in the ^{14}C CPM values it was less than ±0.2 %. These values can, by careful planning, repeated measurements, and prolonged counting times, be reduced to about ±0.1%. The possible error caused by quenching[17] was investigated and, in the present system, there is no difference in the counting efficiency between the fractions. However, in less favorable cases appropriate quench corrections should be applied. In addition, errors are introduced in the chromatographic sampling and fractionation. The high volatility of methyl iodide is also a potential source of error. For this reason, the gas phase in the vials was kept to a minimum. To decrease

Table I. Rate Parameters for $^{11}C/^{14}C$ KIE Experiments

exp no.	$^{11}k/10^{-4}$ s^{-1}	$^{14}k/10^{-4}$ s^{-1}	$^{11}k/^{14}k$
1	1.592 ± 0.024[a]	1.306 ± 0.020	1.219 ± 0.026[b]
2	1.372 ± 0.028	1.106 ± 0.024	1.241 ± 0.036
3	1.980 ± 0.027	1.608 ± 0.023	1.232 ± 0.024

[a] Standard deviation of the slope, $s = s_{y/x}/(\Sigma(x_i - \bar{x})^2)^{1/2}$, where $s_{y/x}$ is the standard deviation of the dependent variable (experimentally determined), x_i are the quenching times, and $\bar{x}$ is the mean value of the quenching times. [b] $r = {}^{11}k/{}^{14}k\ [({}^{11}s/{}^{11}k)^2 + ({}^{14}s/{}^{14}k)^2]^{1/2}$ where r is the relative uncertainty, ^{11}k and ^{14}k are the slopes, and ^{11}s and ^{14}s are the standard deviations of the slopes.

(4) Fowler, J. S.; Wolf, A. P. In *Positron Emission Tomography and Autoradiography: Principles and Applications for the Brain and Heart*; Phelps, M., Mazziotta, J., Schelbert, H., Eds.; Raven Press: New York, 1986; pp 413–420.
(5) Buist, G. J.; Bender, M. L. *J. Am. Chem. Soc.* **1958**, *80*, 4308.
(6) Långström, B. et al. *J. Nucl. Med.* **1987**, *28*, 1037.
(7) The [^{11}C]methyl iodide was transferred to a cooled vial containing 0.8 mL of absolute methanol (Fisons, HPLC-grade, distilled and kept over 3Å molecular sieves, under nitrogen atmosphere). The radioactivity of this solution was 1–2.5 GBq, and the specific activity was 1–4 GBq μmol^{-1} 10 min before the kinetic experiment was started. A 1-mL [^{14}C]methyl iodide solution in absolute methanol had previously been prepared from [^{14}C]methyl iodide (Amersham, 3.7 MBq, specific activity 2.15 GBq mmol^{-1}) by using a vacuum line. To a 0.9 mL, 1.5 M solution of *N,N*-dimethyl-*p*-toluidine (>99% checked by GLC, purified according to ref 8) in absolute methanol, thermostated at 30.0 °C, were added 700 μL of the [^{11}C]methyl iodide and 200 μL of the [^{14}C]methyl iodide solutions simultaneously.
(8) Meltzer, T. H.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1954**, *76*, 5178.
(9) HP 1084, column: Alltech C-18, mobile phase: 30 mM tetramethylammonium chloride in a mixture of 0.05 M NaH_2PO_4 (aqueous) and methanol (60:40), isocratic flow 2.0 mL min^{-1}, injected vol: 20 μL, UV detector: 230 nm, reference 450 nm.
(10) Långström, B.; Lundquist, H. *Radiochem. Radioanal. Lett.* **1980**, *42*, 40.
(11) LKB 1214 liquid scintillation counter.
(12) The mean value of three experiments ± the standard deviation of the worst case.
(13) (a) Vogel, P. C.; Stern, M. J. *J. Chem. Phys.* **1971**, *54*, 779. (b) Bron, J.; Stothers, J. B. *Can. J. Chem.* **1968**, *46*, 1435. (c) Lynn, K. R.; Yankwich, P. E. *J. Am. Chem. Soc.* **1961**, *83*, 790. (d) Lynn, K. R.; Yankwich, P. E. *J. Am. Chem. Soc.* **1961**, *83*, 3220.
(14) Bigeleisen, J. *J. Phys. Chem.* **1952**, *56*, 823.
(15) Stern, M. J.; Vogel, P. C. *J. Chem. Phys.* **1971**, *55*, 2007.
(16) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980; pp 52–54.
(17) (a) Saunders, W. H., Jr. In *Techniques of Chemistry*; Bernasconi, C. F., Ed.; John Wiley and Sons: New York, 1986; Vol. VI, pp 586–588. (b) Faires, R. A.; Boswell G. G. J. *Radioisotope Laboratory Techniques*; Butterworth & Co: London, 1981; pp 165–172.

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.

(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.

$$ArI{=}CR_2 \longleftrightarrow ArI^{+}{-}\bar{C}R_2 \qquad ArI{=}C{=}CR_2 \longleftrightarrow ArI^{+}{-}\bar{C}{=}CR_2$$
1 **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**.

(1) DFG Postdoctoral Fellow.
(2) For reviews, see: (a) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (b) Varvoglis, A. *Synthesis* **1984**, 709. (c) Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: 1983; Chapter 25, pp 1265-1351. (d) Olah, G. A. *Halonium Ions*; Wiley: New York, 1975. (e) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.
(3) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 154.
(4) Beringer, F. M.; Gindler, E. M. *Iodine Abstr. Rev.* **1956**, 3.
(5) For an excellent review, see: Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Ed.; Wiley: 1983, Chapter 18, pp 774-806.
(6) (a) Moriarty, R. M.; Prakash, I.; Prakash, O.; Freeman, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6082, and references therein. (b) Moriarty, R. M.; Bailey, B. R., III; Prakash, O.; Prakash, I. *Ibid.* **1985**, *107*, 1375.
(7) Numerous X-ray structures of diverse polyvalent iodine species are known,[5,8] but none so far of a vinyliodinane species.

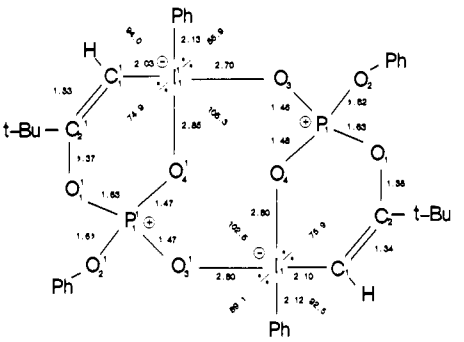


Figure 1. Critical bond length (Å) and geometric features of the 12-I-4 vinyliodonium dimer **6**.

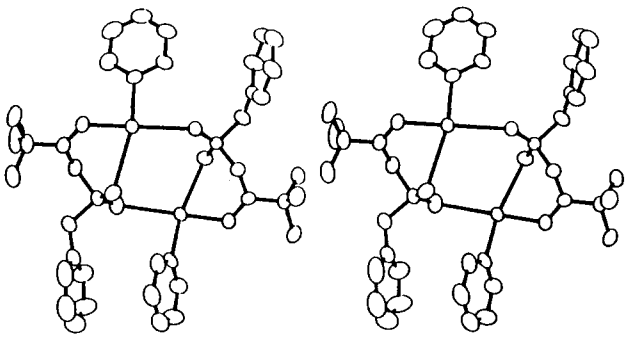
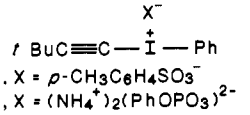
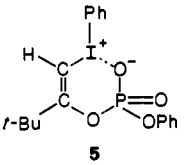


Figure 2. Stereoview of dimer **6**.

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



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-

(8) Batchelor, R. J.; Birdiall, T.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 1415 and references therein. Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1973**, *15*, 1.
(9) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4703. Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. Stang, P. J.; Surber, B. W. *Ibid.* **1985**, *107*, 1452.
(10) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832.
(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=*C*H)], 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, (PO*C*=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.
(13) Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. Martin, J. C. *Science (Washington, D.C.)* **1983**, *221*, 509.

0002-7863/87/1509-7235$01.50/0