Figure 2. Detail of adsorption cell 5 (Figure 1) showing preheater coil.

The most obvious results from Table II are (a) the insignificant effect of presure on ΔH_{ads} in the subcritical range, (b) the decrease of ΔH_{ads} in response to increasing temperature at a given pressure, and (c) the significant increase in ΔH_{ads} with increase in pressure above the supercritical threshold at 200 °C. These observations are consistent with the notion that isopropylamine, a strong base, is primarily chemisorbed on the silica gel surface by hydrogen bonds.[14] Increasing the temperature weakens this interaction. The peculiar variations of ΔH_{ads} around the critical point are probably related to complicated changes in the heats of mixing in the fluid phase, such as those reported by Izatt, Christensen, and their co-workers,[9] rather than direct effects on the solid silica.

A crucial component for extending flow calorimetry into the supercritical range is the use of a Setaram-80 heat flow calorimeter which may be operated in the flow mode at temperatures up to 300 K using the sample cell (5) in Figure 1. This was designed for adsorption thermochemistry so that a bed of adsorbent in cell 5 can be placed downstream from the switching valves in the pumps so that either of the fluid streams leaving the piston pumps (A and B) may be directed through the adsorbent bed. An important problem in flow calorimetry (even at ambient conditions) is to balance mass transfer and heat transfer.[15] Unless the stream of fluid containing the adsorbate has been brought to exactly the temperature of the adsorbent (in cell 5) the observed ΔH_{ads} will contain a contribution due to incomplete thermal equilibration of the streams. Figure 2 shows how this problem was solved by forcing the stream through a coil of $^1/_8$ in. (o.d.) × 0.60 in. (i.d.) 316 stainless steel tubing positioned in the preheating chamber of the calorimeter.

In each experiment, about 100–150 mg of silica gel was used. Once the appropriate pressure was obtained, the solvent (isopentane) flow rate was reduced from 75 mL/h to either 7 or 15 mL/h and then the system was thermally equilibrated. Once a steady recorder base line was achieved, the reactive liquid in pump B was pressurized, and, simultaneously, pump A was turned off and pump B was opened to the system at the same flow rate as that of pump A. Heat evolved during the process of interaction of the isopropylamine with the silica gel was monitored by both

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(14) Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979.

(15) It is also important to reduce dead space in cell 5 by the use of a machined metal insert so that mixing of the flow streams is minimized following switching from pure solvent to the solution of base.

(16) "Handbook of Chemistry and Physics", 57th ed.; CRC Press Inc.: Cleveland, 1976–1977.

(17) Kay's approximation has been used to calculate pseudocritical constants for a mixture (Kay, W. B. *Ind. Eng. Chem.* **1936,** *28,* 1014; and Reid R. C.; Sherwood, T. K. "The Properties of Gases and Liquids, Their Estimation and Correlation"; McGraw-Hill: New York, 1958).

(18) P_c(isopropylamine) is an average value from estimates using Riedel's and Lydersen's methods reported in ref 17.

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digital and analog outputs and was presented as an exothermic release of heat up to the point of surface saturation after which the system returned to its original base-line temperature in about 30 min.

New Modes of Ligation for a Phosphorus–Nitrogen Double Bond

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The recent availability of stable compounds with element phosphorus multiple bonds[1] has prompted a surge of interest in the use of these species as ligands. Iminophosphines (RN=PR) have been shown capable of acting as two- or four-electron donors toward transition metals.[2] We report (i) the first example of an iminophosphine behaving as a six-electron donor and (ii) a novel interaction between an RN=PR ligand and a bound carbon monoxide.

In a typical preparation, a mixture of 0.33 g (2.07 mmol) of *t*-BuN=P-*t*-Bu[3] and 1.5 g (4.12 mmol) of Fe$_2$(CO)$_9$ in 25 mL of *n*-hexane was stirred for 20 h at 25 °C. Separation by column chromatography (silica gel, 1:1 toluene/*n*-hexane) afforded two thermochromic solids, **1** (orange, 35% yield) and **2** (red, 60% yield). The EI MS (70 eV) of **1** exhibited a parent peak at *m/e* 439 and a 100% intensity peak at *m/e* 271 assignable to [(*t*-BuNP-*t*-Bu)Fe$_2$(CO)$_6$]$^+$ and [(*t*-BuNP-*t*-Bu)Fe$_2$]$^+$, respectively. Interestingly, the EI-MS of **2** was identical with that of **1** due to the thermal elimination of 2CO. However, the 32.384-MHz ^{31}P{^{1}H} NMR spectra of **1** (s, +81) and **2** (s, +269) were quite different; moreover, in contrast to that of **1**, the IR spectrum of **2** featured a low-energy C–O stretch (1645 cm^{-1}). The structures of both compounds were established by X-ray crystallography.[4]

As shown in Figure 1, the structure of **1** involves a distorted tetrahedral Fe$_2$PN core. The iminophosphine ligand serves as a six-electron donor and adopts a cis conformation (C(11)–P(1)–N–C(7) dihedral angle = 0.3°). By analogy with the isostructural

(1) For reviews, see (a) Fluck, E. *Top. Phosphorus Chem.* **1980,** *10,* 193. (b) Appel, R.; Knoll, F.; Ruppert, I. *Angew Chem., Int. Ed. Engl.* **1981,** *20,* 731. (c) Cowley, A. H. *Polyhedron* **1984,** *3,* 38. (d) Cowley, A. H. *Acc. Chem. Res.* **1984,** *17,* 386.

(2) Pohl, S. *J. Organomet. Chem.* **1977,** *142,* 185, 195. (b) Scherer, O. J.; Konrad, R.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1982,** *115,* 414. (c) Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982,** *21,* 297. (d) Scherer, O. J.; Kerth, J.; Anselmann, R. *Phosphorus Sulfur* **1983,** *18,* 271. (e) Scherer, O. J.; Kerth, J.; Anselmann, R.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 984.

(3) Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 1034. The iminophosphine is in equilibrium with the corresponding [2 + 1] cycloaddition product.

(4) Compound 1: C$_{14}$H$_{18}$Fe$_2$NO$_6$P; M_r = 438.97. Crystal data: monoclinic, $P2_1/n$; a = 8.198 (1) Å, b = 15.331 (2) Å, c = 15.242 (2) Å, β = 93.05 (1)°; V = 1913 (1) Å^3; Z = 4; D(calcd) = 1.524 g cm^{-3}. Compound 2: C$_{16}$H$_{18}$Fe$_2$NO$_8$P; M_r = 494.99. Crystal data: monoclinic, $P2_1/c$; a = 19.839 (10) Å, b = 12.787 (7) Å, c = 26.578 (10) Å, β = 110.49 (3)°; V = 6316 (1) Å^3, Z = 12, D(calcd) = 1.562 g cm^{-3}. Intensity data: Enraf-Nonius CAD-4F diffractometer, ω–2θ scan modes in the range 2.0 ≤ 2θ ≤ 50.0; 3506 and 11 805 unique reflections for **1** and **2**, respectively. The structures of **1** and **2** were solved (Patterson and difference Fourier) and refined (full matrix, least squares) by using 2496 and 6384 data, respectively. Final residuals were **1**, R = 0.0496 and R_w = 0.0564 and, **2**, R = 0.0674 and R_w = 0.0710.
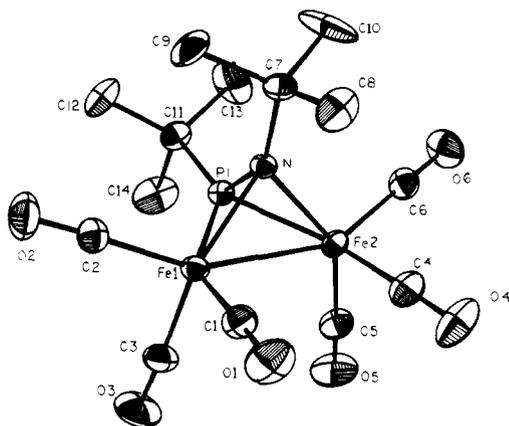
Figure 1. ORTEP view of **1** showing the atom numbering scheme for molecule I. Important parameters: P(1)–N = 1.687 (7), P(1)–Fe(1) = 2.146 (3), P(1)–Fe(2) = 2.147 (3), N–Fe(1) = 2.001 (7), N–Fe(2) = 2.011 (6), Fe(1)–Fe(2) = 2.615 (2) Å; C(11)–P(1)–N = 130.4 (4)°, C(7)–N–P(1) = 139.7 (6)°.
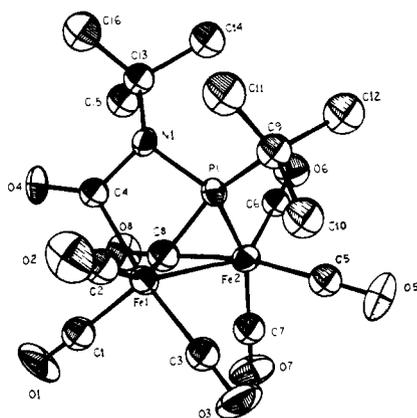
Figure 2. ORTEP view of **2** showing the atom numbering scheme. Important parameters: P(1)–N(1) = 1.729 (10), P(1)–Fe(1) = 2.183 (3), P(1)–Fe(2) = 2.224 (3), Fe(1)–Fe(2) = 2.718 (2), N(1)–C(4) = 1.410 (15), C(4)–Fe(1) = 2.070 (13) Å; Fe(1)–P(1)–Fe(2) = 75.05 (9)°.

diphosphene complex, $(t\text{-}Bu_2P_2)Fe_2(CO)_6$ (**3**),[5] **1** was anticipated to feature a phosphorus–nitrogen double bond. However, the P–N bond length for **1** (1.687 (7) Å) corresponds to a bond order of ~1.0. In this respect, **1** resembles analogous R_2N_2 and S_2 complexes.[6] The reason for the retention of the double bond in **3** is therefore not clear.

Compound **2** possesses a novel bicyclic structure (Figure 2).
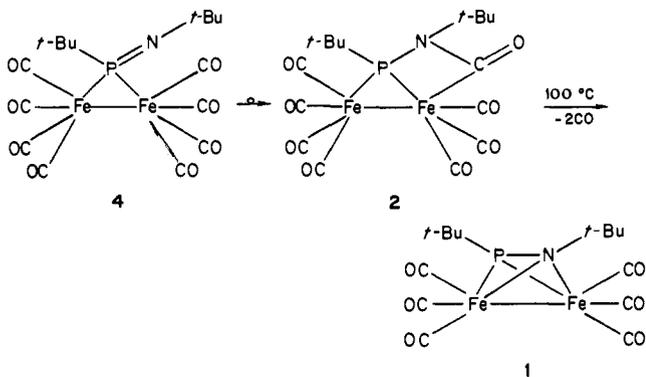
The long P–N bond in **2** (1.718 (2) Å) is consistent with the slight pyramidality at N(1) (sum of angles = 355.2°).[7] Although we

(5) Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.

(6) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103 and references therein.

do not know the origin of **2**, we speculate that it arises from **4** via intramolecular nucleophilic attack of the imino nitrogen on a bound CO. The quantitative conversion of **2** to **1** was established by a thermolysis experiment (100 °C, toluene, 30 min). Further studies of the reactivities of **1** and **2** are in progress.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

(7) For a compilation of P–N single-bond lengths, see, e.g.: Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* **1976**, *4*, 133. Phosphorus–nitrogen double-bond lengths fall in the range 1.50–1.58 Å. See: Reference 2. Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 687. Pohl, S. *Chem. Ber.* **1979**, *112*, 3159.

Benzene Diol Epoxides

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The multistep pathway of metabolic activation of benzene to a species ultimately responsible for the toxic effects ascribed to benzene is not fully understood.[1] Metabolism of benzene proceeds by enzyme-catalyzed oxidation to arene oxide **1** which can undergo
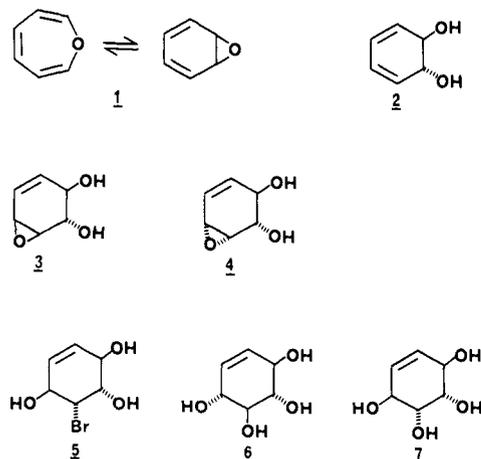
spontaneous isomerization to phenol, enzyme-catalyzed addition

(1) (a) Snyder, R.; Longacre, S. L.; Witmer, C. M.; Docsis, J. J. In "Advances in Experimental Medicine and Biology. Biological Reactive Intermediates—II Chemical Mechanisms and Biological Effects"; Snyder, R., Park, D. V., Kocsis, J. J., Jollow, D. J., Gibson, C. G., Witmer, C. M., Eds; Plenum Press: New York, 1982; Vol. 136A, pp 245–256. (b) Snyder, R. Lee, E. W.; Kocsis, J. J.; Witmer, C. M. *Life Sci.* **1977**, *21*, 1709–1722. (c) Snyder, R.; Andrews, L. S.; Lee, E. W.; Witmer, C. M.; Reilly, M.; Kocsis, J. J. In "Biological Reactive Intermediates. Formation, Toxicity, and Inactivation"; Jollow, D. J., Kocsis, J. J., Snyder, R., Vainio, H., Eds.; Plenum Press: New York, 1977; pp 286–301. (d) Snyder, R.; Kocsis, J. J. *CRC Crit. Rev. Toxicol.* **1975**, *3*, 265–288.