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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Generation of a Reactive (i-Pr)<sub>2</sub>NP)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> Intermediate by Extrusion of a Phosphorus-Bridging Carbonyl Group: Matrix Isolation and Chemical Reactivity Studies

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## GENERATION OF A REACTIVE $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ INTERMEDIATE BY EXTRUSION OF A PHOSPHORUS-BRIDGING CARBONYL GROUP: MATRIX ISOLATION AND CHEMICAL REACTIVITY STUDIES

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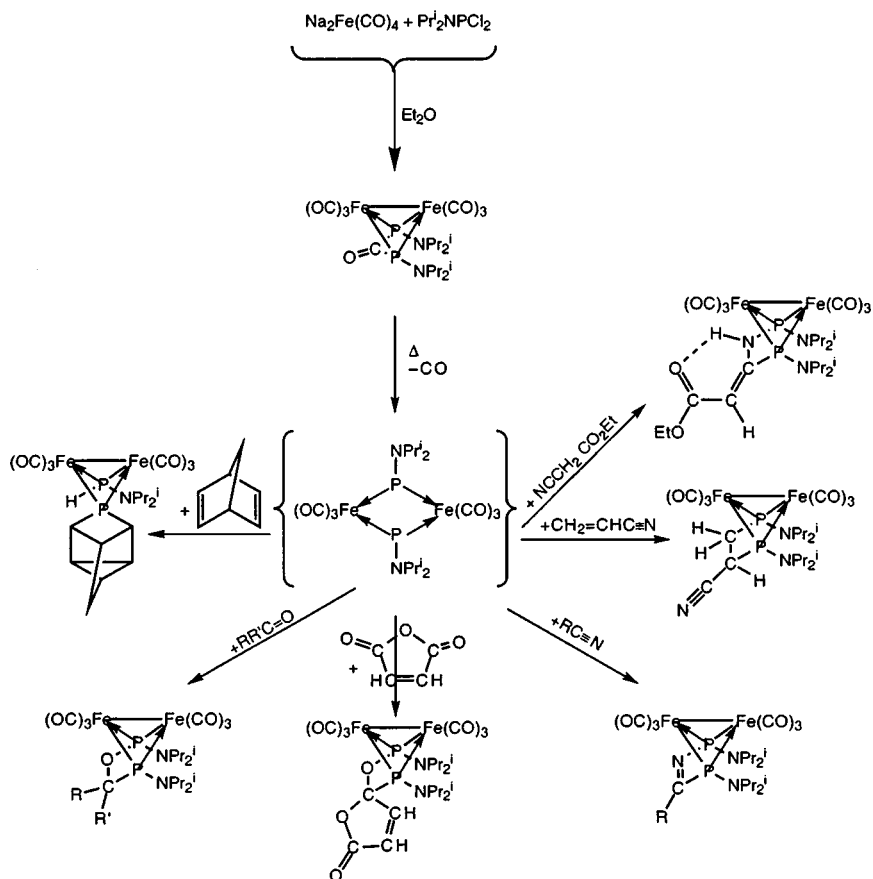
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*A reactive  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  intermediate, which is generated by heating  $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  in boiling toluene, adds to a variety of multiple bonds including the C=O bonds of aldehydes, ketones, maleic anhydride, and phthalic anhydride; the C≡N bonds of saturated nitriles; and the C=C bond of acrylonitrile. Photolysis at <380 nm of  $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  in a Nujol matrix at 90 K also results in extrusion of the phosphorus-bridging CO group to give a pattern of infrared metal  $\nu(\text{CO})$  frequencies suggestive of an intermediate of  $D_{2h}$  symmetry.*

**Keywords:** Iron carbonyls; matrix photochemistry; phosphorus-bridging carbonyls

Heating the phosphorus-bridging carbonyl derivative<sup>1</sup>  $(i\text{-Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  (**I**) with a variety of unsaturated organic molecules at 80–100°C has been shown to result in apparent extrusion of the phosphorus-bridging carbonyl group followed by addition of the resulting  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  unit across a multiple bond of the unsaturated organic compound (Figure 1).<sup>2</sup> The nature of the products in all of these thermal reactions of **I** suggested the intermediacy of a tetrahedrane  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ . In an attempt to isolate such a tetrahedrane, solutions of **I** in inert organic solvents (e.g., toluene) were heated to the reaction temperatures (e.g., 80–100°C) in the absence of a substrate. However, no evidence was obtained for formation of an isolable  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  under such conditions. No tractable intermediates

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**FIGURE 1** Formation and chemical reactivity of  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$  (I) toward unsaturated compounds.

could be isolated at temperatures and reaction times where decomposition of I was first observed. Furthermore, photolysis of I under ambient conditions in an inert solvent failed to provide any evidence of an isolable tetrahedrane  $(i\text{-Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ . A related stable tetrahedrane,  $(t\text{-BuP})_2\text{Fe}_2(\text{CO})_6$ , has been isolated and characterized by Vahrenkamp and coworkers.<sup>3</sup>

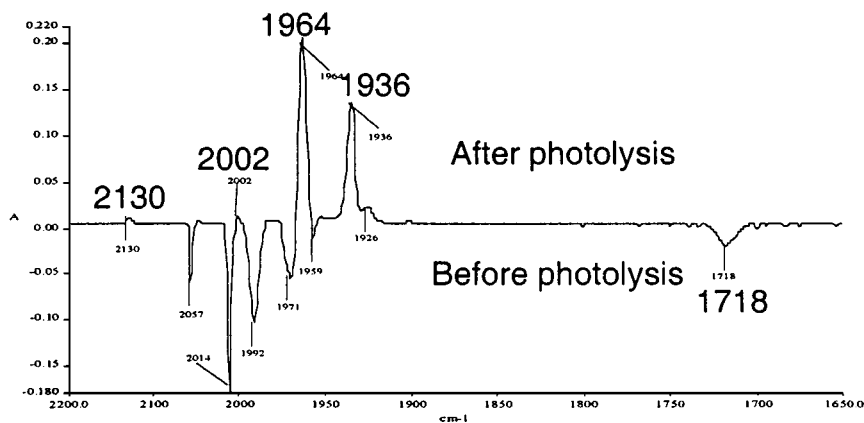
In an attempt to obtain some insight into the mechanisms of the reactions of I, a matrix isolation study was performed involving low-temperature photolysis of I in a Nujol medium using well-established techniques.<sup>4</sup> We present a preliminary report of the unexpected results of these studies.

## RESULTS AND DISCUSSION

The electronic spectrum of **I** consists of a band at 422 nm ( $\epsilon \approx 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a second more intense band at 340 nm ( $\epsilon \approx 10,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). A third strong band is observed with a spectral maximum below the instrument cutoff at 250 nm. By analogy with the very similar electronic spectra of the  $(\text{RS})_2\text{Fe}_2(\text{CO})_6$  derivatives, the lowest energy band is assigned to a  $d \rightarrow \sigma^*$  MLCT transition. The more intense band at 340 nm is tentatively assigned to a  $d \rightarrow \pi^*$  MLCT transition.

Infrared (IR) bands of **I** in Nujol at 90 K in the  $\nu(\text{CO})$  region are found at 2058 (m), 2014 (s), 1992 (m), 1970 (m), 1958 (w), and 1718 (m). The lowest energy band, at  $1718 \text{ cm}^{-1}$ , corresponds to the phosphorus-bridging carbonyl group. Photolysis of **I** ( $\lambda_{\text{irr}} > 330 \text{ nm}$ ) was found to have no detectable effect on the spectrum of the compound. Continued photolysis ( $220 \text{ nm} < \lambda_{\text{irr}} < 420 \text{ nm}$ ) resulted in bleaching of the bands of **I** and appearance of new bands at 2130, 2002 (w), 1964 (s), and 1936 (m)  $\text{cm}^{-1}$  (Figure 2). The band at  $2130 \text{ cm}^{-1}$  is characteristic of a "free" CO in frozen Nujol. The disappearance of bands in the phosphorus-bridging carbonyl region suggests that the CO that is lost upon photolysis arises from extrusion of the phosphorus-bridging CO. Back photolysis at long wavelengths ( $\lambda_{\text{irr}} > 400 \text{ nm}$ ) and annealing of the photolyzed samples resulted in complex new spectra that could not be meaningfully interpreted.

The simple three-band spectrum of the photoproduct requires this product to have high symmetry. Loss of the phosphorus-bridging CO removes the structural constraint holding **I** in a tetrahedrane unit and



**FIGURE 2** Changes in the infrared spectrum of **I** upon photolysis at  $220 \text{ nm} < \lambda_{\text{irr}} < 420 \text{ nm}$ .

may allow the photointermediate to relax into a planar configuration with  $D_{2h}$  symmetry. Vibrational analysis predicts two vibrational bands for this symmetry. The weak band at  $2002\text{ cm}^{-1}$  may arise from a slight bowing of the molecule from planarity owing to the  $i\text{-Pr}_2\text{NP}$  bridging units. The proposed structure of the photointermediate is closely related to the stable compound  $(2,6\text{-}t\text{-Bu}_2\text{-4-MeC}_6\text{H}_2\text{OP})_2\text{Fe}_2(\text{CO})_6$  (**II**) isolated by Power and coworkers.<sup>5</sup>

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