

SYNTHESIS OF [μ -1,2-PHENYLENEBISPHOSPHIDO-P,P'] DIIRONHEXACARBONYL COMPLEX AND ITS REACTIVITY

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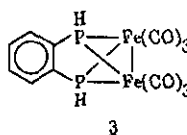
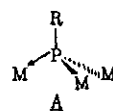
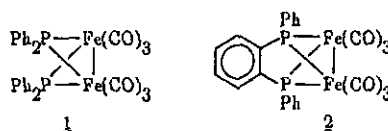
The title compound was prepared from the reaction of *o*-bisphosphinobenzene with nonacarbonyldiiron. The structure was determined by spectroscopic methods. The mechanism of formation of the complex and its reactivity are discussed.

INTRODUCTION

The chemistry of bridging phosphido moieties has been widely investigated. In particular, recent reports have shown that a link between two phosphido groups would give additional stability to bimetallic complexes relative to those that are unlinked^{1,2}, such as 1 vs 2. However, the majority of such phosphido systems have involved secondary phosphines; few complexes with phosphido moieties involved primary phosphines^{3,4}. Furthermore, the primary phosphine moiety potentially could give extra bonding sites to transition metals as in structure A which might play an important role in stabilizing metal clusters. In this paper, we describe the synthesis and chemistry of [μ -1,2-phenylenebisphosphido-P,P'] hexacarbonyldiiron complex with the phosphorus sites being primary phosphines.

EXPERIMENTAL SECTION

Proton and phosphorus-31 magnetic resonance spectra were recorded on a Bruker AM-300WB. Chemical shifts are given in parts per million relative to Me₄Si for ¹H and relative to 85% H₃PO₄ for ³¹P; NMR spectra are in CDCl₃ unless otherwise noted. Chemical shifts upfield of the standard are defined as negative. Infrared spectra were obtained on a JASCO IRA-1. Melting points were determined on a

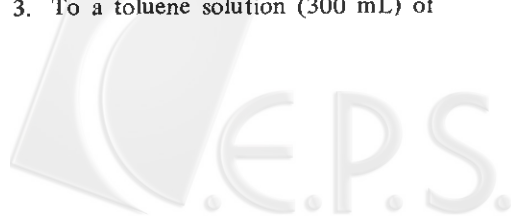


Gallenkamp capillary melting point apparatus, and are uncorrected.

All of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles using nitrogen pressure or by syringe.

Tetrahydrofuran was distilled under nitrogen from the benzophenone ketyl radical. Toluene was purified by distillation over sodium metal under nitrogen. Other solvents and chemicals from commercial sources were used without further purification, except as noted. Bisphosphinobenzene was prepared according to the literature procedure.⁵

[μ -1,2-Phenylenebisphosphido-P,P'] hexacarbonyldiiron 3. To a toluene solution (300 mL) of



bisphosphine (2.28 g, 0.016 mol) was added nonacarbonyldiiron (12.0 g, 0.033 mol) with stirring at room temperature. The resulting solution was then heated to reflux for 24 h. The crude reaction mixture was filtered and the filtrate was concentrated. The residue was chromatographed on alumina with hexane as eluent. A yellow band off column was collected and concentrated to give the desired product as an air-sensitive, golden-yellow solid (0.65 g, yield 10%). mp decomposition upon heating, IR (benzene) 2063, 2023, 1998, 1980 cm^{-1} ; ^1H NMR 7.2 (m, 4H), 3.2 (d, $J_{\text{P-H}} = 325$ Hz); ^{31}P NMR 71.0 ppm. HRMS m/e 419.8324 (calcd. m/e 419.8338, for $\text{C}_{12}\text{H}_6\text{O}_6 \text{P}_2 \text{}^{56}\text{Fe}_2$).

Reaction of 3 with Sodium Naphthalenide, followed by Methyl Iodide Quench. A THF (15 mL) solution of Complex 3 (27.0 mg, 0.065 mmol) was treated with a 0.76 M THF solution of sodium naphthalenide (0.02 mL, 0.15 mmol) at -78°C to give a red solution. This was allowed to warm to room temperature and stirred for 2 h. Excess iodomethane (1.0 mL) was added and the solution stirred at room temperature for 1 h. This solution was concentrated and passed through a silica column using ethyl acetate and hexane (1 : 9) as eluent. This gave a yield of 78% for methylated product as yellow solid.⁶ The ^{31}P NMR spectrum had a singlet at 122.6 ppm; ir (hexane) 2056, 2018, 1987, 1978, 1965 cm^{-1} .

Reaction of 3 with *n*-Butyllithium. A solution of 4.6M *n*-butyllithium in hexane solution was added to a solution of 3 (26.7 mg, 0.0636 mmol) in THF (2 mL) at -78°C . After stirring for 0.5 h, methyl iodide (0.8 mL) was added to this solution. This solution was concentrated and filtered through a silica column to give the desired product (27.3 mg, 96% yield). The spectroscopic properties were identical to the previous case.

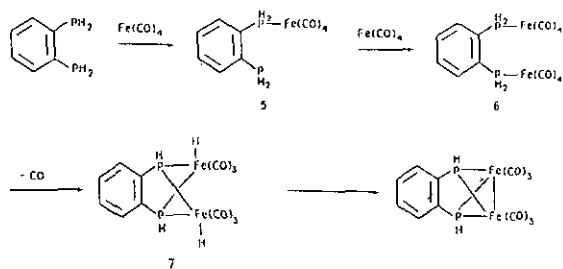
RESULTS AND DISCUSSION

The bis(μ -phosphido)diiron complex 3 was prepared from the reaction of *o*-bisphosphinobenzene with excess nonacarbonyldiiron at refluxing toluene temperature. This complex, an air-sensitive, golden yellow solid was isolated only in 10% yield after chromatography of the reaction mixture on alumina under nitrogen. Attempts to improve the yield by varying the reaction conditions (concentration, solvents, photo-reaction) failed. The ^1H NMR shows, besides the signal due to the aromatic protons, a doublet at 3.2 ppm ($J_{\text{P-H}} = 325$ Hz), which indicates a hydrogen atom on each phosphorus atom. The proton-decoupled ^{31}P NMR spectrum of 3 consists of only a singlet at 71.0 ppm. In mass spectra, the ions m/e 420 (M^+), 392, 364, 336, 308, 280, and 258 were recorded. These ions resulting from subsequent cleavages of carbon monoxide from the molecular ion are characteristic of these types of metal carbonyl compounds. Additionally, the absence of metal hydride absorption in ^1H NMR spectra and bridging carbonyl absorption in infrared spectra are consistent with the assigned structure in which the phosphorus atoms bear one hydrogen atom and each phosphorus atom is coordinated to two $\text{Fe}(\text{CO})_3$ fragments.

The formation of complex 3 was assumed to follow the pathway of scheme 1. Bisphosphine was reacted with one equivalent mole of $\text{Fe}_2(\text{CO})_9$ to give an unisolable species 5 which was assigned by ^{31}P NMR absorption of a pair of doublets at -126.5 ppm and -26.76 ppm and a phosphorus-phosphorus coupling constant of 37 Hz. (The free ligand has ^{31}P shift at 124.3 ppm). Evidently, the $\text{Fe}(\text{CO})_5$ unit generated from $\text{Fe}_2(\text{CO})_9$ did not react with 5 and another one equivalent of $\text{Fe}_2(\text{CO})_9$ was needed to



Scheme 1



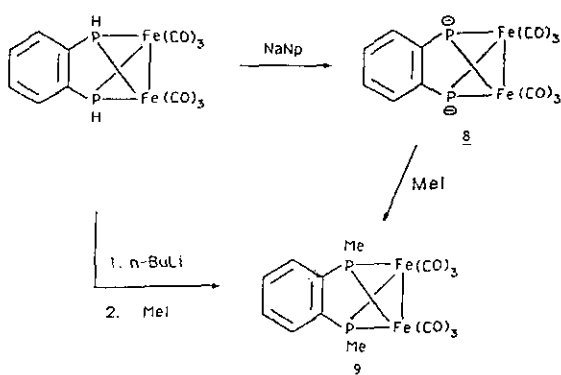
generate the second $\text{Fe}(\text{CO})_4$ fragment which was then coordinated to the second phosphorus site on **5** to give **6** with ^{31}P NMR shift at -31.85 ppm. This resonance disappeared upon heating with the growth of a singlet peak corresponding to **3**. This complex appeared to be formed by the loss of a CO ligand of **6** and insertion to yield **7**, followed by elimination of hydrogen to generate the metal-metal bond. However, the species **7** was not detected during the reaction, presumably it was highly reactive under the reaction conditions.

Treatment of **3** in THF with sodium naphthalenide (NaNp) yielded a red solution of dianion **8** (Scheme 2) without breaking any metal-phosphorus or metal-metal bonds. This result was quite different from that of the phenyl substituted analog which showed a cleavage on the phosphorus-metal bond under similar conditions (eq 1). This dianion, an air-sensitive intermediate, was quenched with methyl iodide to give the methylated product **9**.⁶ Similarly, this dianion could be generated by using a strong base, such as *n*-BuLi, which indicates hydrogens on the phosphorus atoms still retain their acidic character. With the availability of this diiron complex and its reactivity, the opportunity of building heteronuclear metal clusters is currently under investigation.

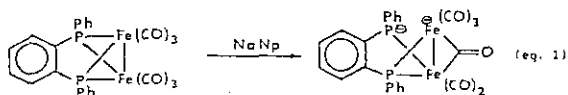
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Scheme 2



Equation 1



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Key word Index

Phosphido complex, ironcarbonyl, bisphosphinobenzene

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