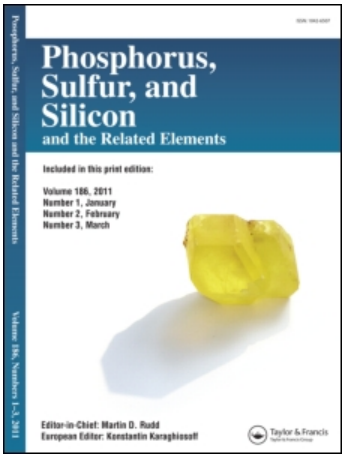

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Linked Bis(μ-Phosphido) and Related Ligands for Metallic Clusters. 2. Reaction of 1,2,3-Triphenyl-1,2,3-Triphosphaindane with Nonacarbonyldiiron

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LINKED BIS(μ-PHOSPHIDO) AND RELATED LIGANDS FOR METALLIC CLUSTERS. 2. REACTION OF 1,2,3-TRIPHENYL-1,2,3-TRIPHOSPHAINDANE WITH NONACARBONYLDIIRON.

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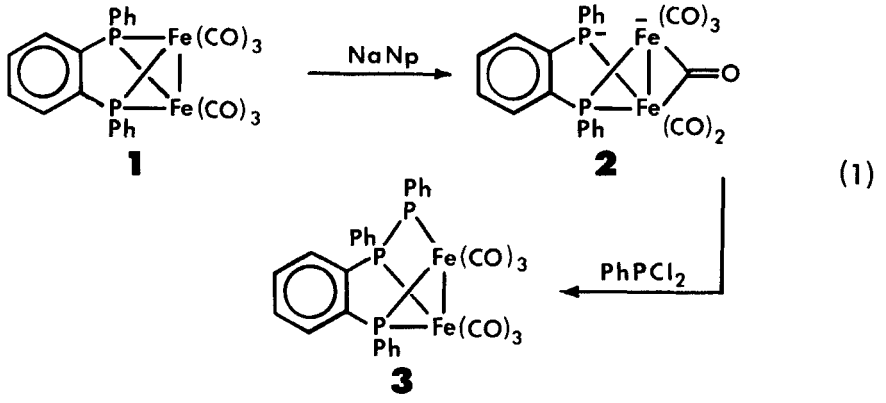
Abstract The reaction of 1,2,3-triphenyl-1,2,3-triphosphaindane with nonacarbonyldiiron in benzene at 80 °C gives rise to a mixture of at least eight components, five of which have been isolated and characterized. Three of these are P_3Fe_3 species, of which two have been unambiguously identified by single crystal x-ray crystallography.

INTRODUCTION

In our recent investigations of the chemistry of the linked, bridged diiron species 1, we observed that the reaction of the dianion 2[1] derived from 1 reacted with phenylphosphonous dichloride to give 3 (equation 1), albeit in low yield.[2] Since 3 contained the elements of 1,2,3-triphenyl-1,2,3-triphosphaindane (4)[3] along with the

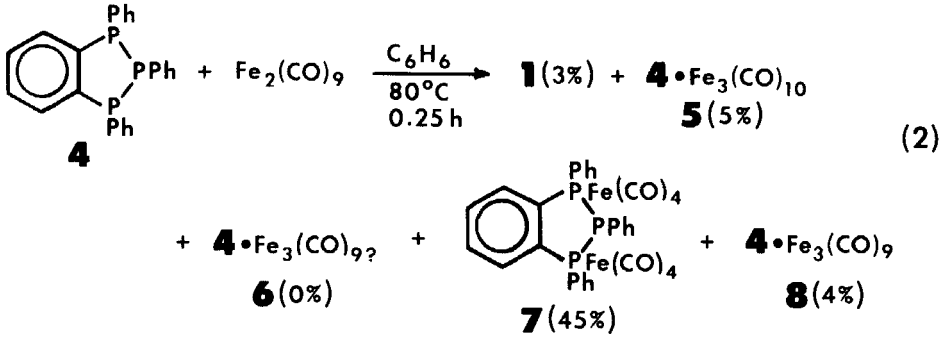


(1)

$Fe_2(CO)_6$ moiety, we investigated the possibility of the formation of 3 directly from 4.

RESULTS AND DISCUSSION

Reaction of 4 with $Fe_2(CO)_9$ was effected by the addition of three equivalents of the iron complex to a hot solution of 4 in benzene. The resulting solution was heated at reflux for 0.25 h, cooled, and analyzed by analytical HPLC, utilizing a 6000 plate microporous silica column and 2% ethyl acetate/hexane as the eluent. The results are presented in equation 2. The major components (1, 5 - 7)



were separated utilizing a Waters Prep 500 LC (SiO_2, 2% EtOAc/hexane). Species 7 was identified by comparison of its ^{31}P NMR spectrum with that of material prepared previously via a different route.[4] Complex 6,[5] which has a HPLC retention volume identical with that of 5, is formed only if the reaction is run for a period of hours, especially in an alkane solvent.

Species 8 was obtained as deep red, regular hexagonal prisms from toluene, and its structure was solved by x-ray crystallography.[6] As can be seen from the ORTEP plot in Figure 1A, the P_3Fe_3 core is a distorted trigonal prism. The iron-iron bond lengths (Fe1-Fe3, 2.71; Fe2-Fe3, 2.86 Å) are somewhat long for μ-phosphido-type systems.[7] There appears to be some distortion of the prism to de-eclipse the carbonyl ligands on Fe2 and Fe3.

Complex 5 was particularly intriguing because in either polar

(CH_2Cl_2, EtOAc) or polarizable (C_6H_6) solvents it transformed to a mixture of 1 and 8 with a half-life at 25 °C of ca. 24 h. The process was retarded by a factor of ca. 20 in hexane or 2% EtOAc/hexane. Species 5 was obtained as regular capped hexagonal prisms from 2% EtOAc/hexane and its structure was determined by x-ray crystallography,[8] and the ORTEP plot is shown in Figure 1B. The structure contains a bis(μ-phosphido)hexacarbonyldiiron moiety similar to 1, as well as a proximal phosphinotetracarbonyl moiety. The latter substructure is trigonal bipyramidal about iron (Fe3) but interestingly, the phosphorus ligand is in the equatorial position rather than the axial position, and appears to be unique in this regard.[9] The ready facility of the 5 → 8 transformation may be understood on the basis of this structure. The loss of CO from Fe3 generates a 16 electron iron atom isolobal with methylene[10] which may insert into the Fe2-P bond to give 8 directly. In fact, given the rate of reaction at room temperature, the process may be an assisted one.

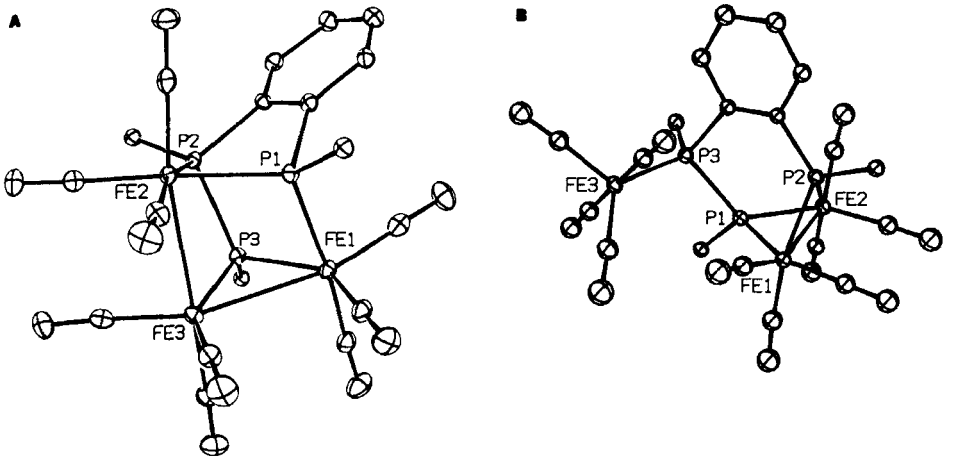


FIGURE 1. A; ORTEP representation of 8. B; ORTEP representation of 5. See equation (2) and relevant text.

ACKNOWLEDGEMENT

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5. Complex 6, ^{31}P NMR: δ 55.6 (1 P), -16.6 (2 P), second order AB_2 spectrum with J_{AB} = 179 Hz. A structure for this material has been proposed,[4] but it is not unique. We will discuss this further in a full paper.
6. Complex 8, ^{31}P NMR: δ 134 (dd, J = 22, 265 Hz), 72 (d, J = 22), 53 (d, J = 265 Hz); monoclinic, $P2_1/c$, Z = 4, at 163 K, a = 15.635 (3), b = 11.856 (2), c = 18.982 (4), β = 112.85 (2), V = 3242.5 Å^3, D_{calc} = 1.679 g/cm^3, R = 0.0450, R_w = 0.0382.
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8. Complex 5, ^{31}P NMR: δ 132 (dd, J = 185, 236), 115 (dd, J = 16, 185), 33 (dd, J = 16, 236); triclinic, $P\bar{1}$, Z = 4, at 163 K, a = 10.499 (1), b = 10.371 (2), c = 34.046 (7), α = 104.55 (1), β = 89.43 (1), γ = 106.20 (1), V = 3438.8, D_{calc} = 1.638 g/cm^3, R = 0.0675, R_w = 0.0546.
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