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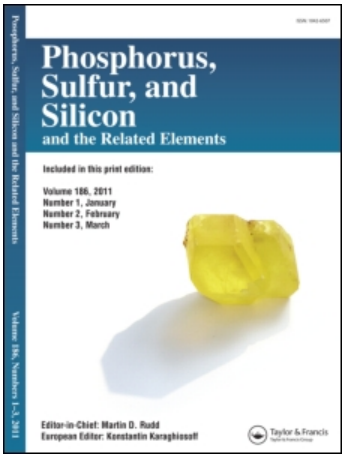

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$[HFe(CO)_4]^-$ A Versatile Reagent toward Dichlorophosphines, Phosphenium Salts, Phospha-alkenes and Diphosphenes

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$HFe(CO)_4^-$ A VERSATILE REAGENT TOWARD DICHLOROPHOSPHINES, PHOSPHENIUM SALTS, PHOSPHAALKENES AND DIPHOSPHENES

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Abstract A new entry to non classical phosphorus complexes is reported.

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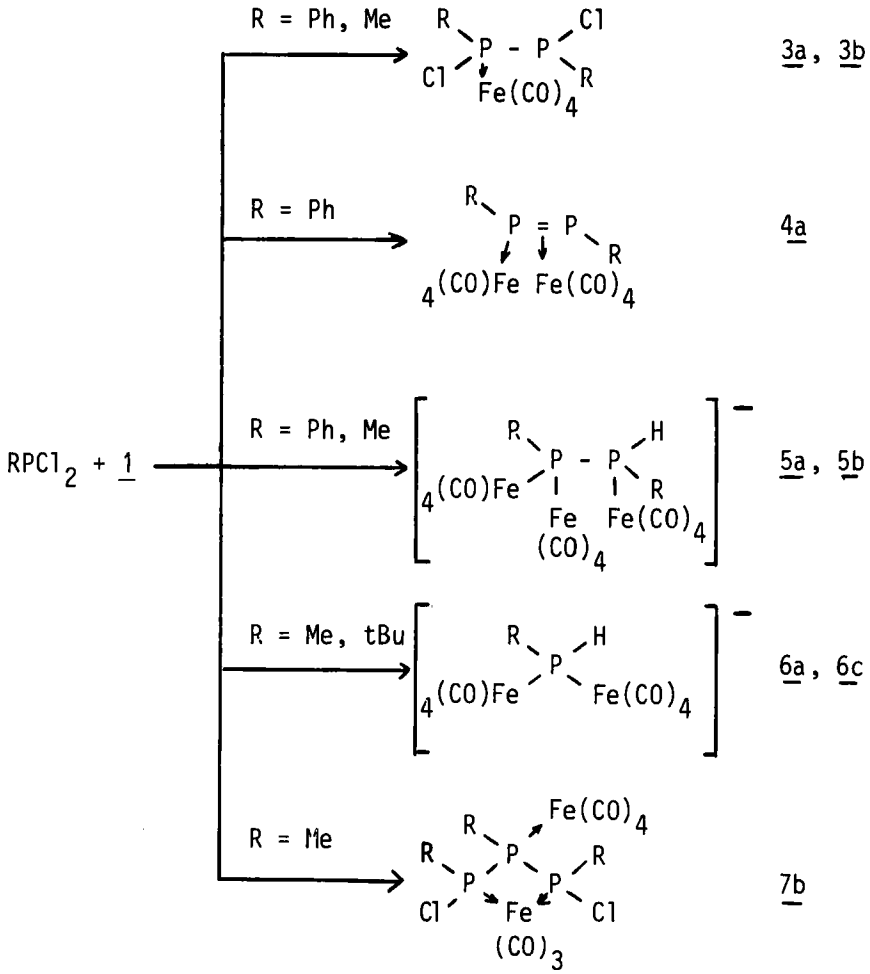
The focus of the present work is to explore the reactivity of dichlorophosphines and neutral or cationic dicoordinated phosphorus compounds towards an anionic iron hydrido carbonyl metalate $[HFe(CO)_4]^-[PPh_4]^+$ 1. Various reactions were observed : complexation of the phosphorus lone pair, HCl elimination, hydride transfer , phosphorus nitrogen bond cleavage, 1.1 or 1.2 addition.

a) The reactivity of dichlorophosphines $RPCl_2$ strongly depends on the nature of the phosphorus substituent and of experimental conditions. In all cases stable secondary halophosphine complexes $RP(H)ClFe(CO)_4$ 2a-d are obtained (R = Ph, Me, t-Bu, $N(iPr)_2$). [1] Moreover treatment of phenyldichlorophosphine with 1 leads to the formation of a 1-2 dihalogenodiphosphane complex $(CO)_4FeP_2Cl_2Ph_2$ 3a, a side-on end-on diphosphene complex $(Fe(CO)_4\ \mu Fe(CO)_4\ (PPh_2))$ 4a and a trimetallic anionic diphosphane species $(PPh_4)((CO)_4Fe)_3P_2Ph_2H$ 5a. Besides the obtention of the diphosphane complex $(CO)_4FeP_2Cl_2Me_2$ 3b and of the anionic diphosphane $(PPh_4)((CO)_4Fe)_3P_2Me_2H$ 5b, the reaction of methyldichlorophosphine with 1 affords an anionic phosphido complex $(Ph_4P)((CO)_4Fe)_2PHMe$ 6b and the dihalogeno triphosphorus iron four-membered ring 7b. On the other hand addition of terbutyldichlorophosphine to two equiva-

lents of 1 gives only the anionic phosphido complex $(Ph_4P)((CO)_4Fe)_2PHtBu$ 6c. The behavior of bis (diisopropylamino)dichlorophosphine toward 1 is entirely different. The transient generation of phosphinidene complexes X-P=$Fe(CO)_4$ 8d-f (X = $N(iPr)_2$, Cl, H) is postulated in order to explain the formation of spectroscopically characterized anionic phosphido complexes $(Ph_4P)((CO)_4Fe)_2PHX$ 9d-f. Addition of methanol to the mixture 9d-f allows the synthesis of an other new anionic phosphido species $(Ph_4P)((CO)_4Fe)_2PHOMe$ 9g. The structure of 9g has been determined by X-ray diffraction.



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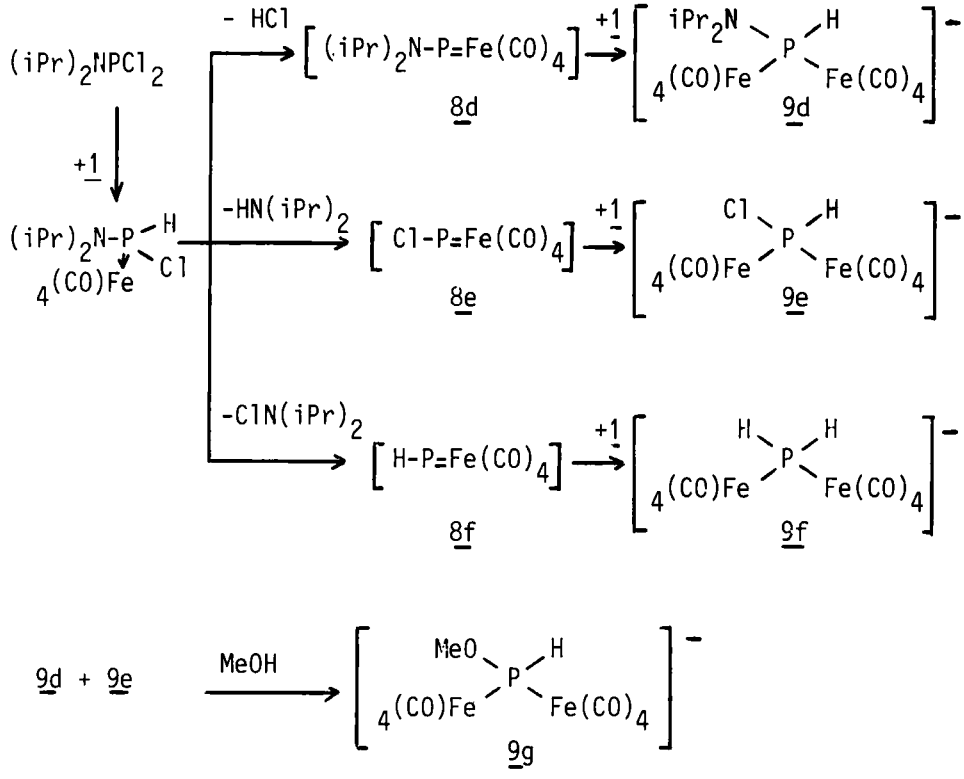
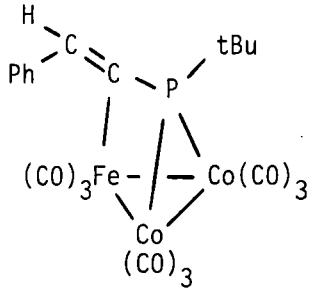


b) The first cluster-stabilized phospha-allene μ_3-η^2 tBuP(C=CHC_6H_5) $FeCo_2(CO)_9$, 10 has been obtained by the following sequence of reactions i) synthesis of P(tBu) (C≡C-Ph)$HFe(CO)_4$ 11, by the reaction of 1 with P(tBu) (C≡C-Ph)Cl, ii) complexation of the CC triple bond by reaction with $Co_2(CO)_8$ leading to P(tBu) (C≡CPh)$HFeCo_2(CO)_{10}$ 12 and refluxing 12 in n hexane. The structure of 10 has been determined by X-ray diffraction.



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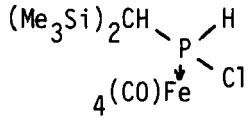
c) No reaction occurs when 1 is added to the phospha-alkene $Ph\text{-}P{=}C(H)NMe_2$ or the diphosphene Ar-P=P-Ar (Ar = ). On the other hand two competitive reactions are observed when the phospha-alkene $Cl\text{-}P{=}C(SiMe_3)_2$ is treated with 1 : elimination of Ph_4PCl and formation of the complex $_4(CO)Fe(H)P{=}C(SiMe_3)_2$ 13 or release of HCl with the transient generation of the anionic dicoordinated phosphorus derivative $[_4(CO)Fe\text{-}P{=}C(SiMe_3)_2][Ph_4P]^+$ 14. The hydrogen chloride thus formed reacts with 13 affording the complex 15 (1.2 addition)



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d) An 1.1 addition of hydride 1 to phosphenium salts leads to the formation of various other halogenophosphine complexes.

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REFERENCES

1 The facile synthesis of these new complexes is in marked contrast to the few reactions previously described in the literature [2].

2 Marinetti, A. ; Mathey, F. Organometallics 1, 1488 (1982) ; Marinetti, A. ; Mathey, F. Phosphorus and Sulfur, 19, 311 (1984); Vahrenkamp, H. Phil. Trans. R. Soc. London A 308, 17 (1982) ; Muller, M. ; Vahrenkamp, H. Chem. Ber. 116, 2322, (1983) ; King, R.B. ; Fu, W.K. J. Organomet. Chem. C33, 272 (1984).