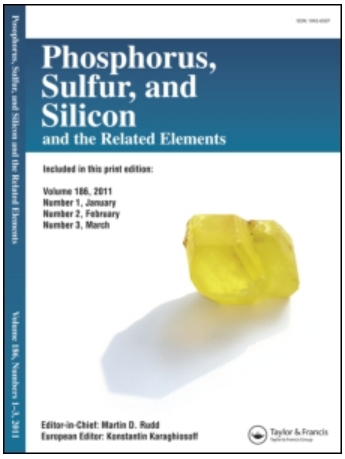

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Alkylation, Oxidation and Decarbonylation of Triferriophosphine $\{CpFe(CO)_2\}_3P$

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ALKYLATION, OXIDATION AND DECARBONYLATION OF TRIFERRIOPHOSPHINE $\{CpFe(CO)_2\}_3P$

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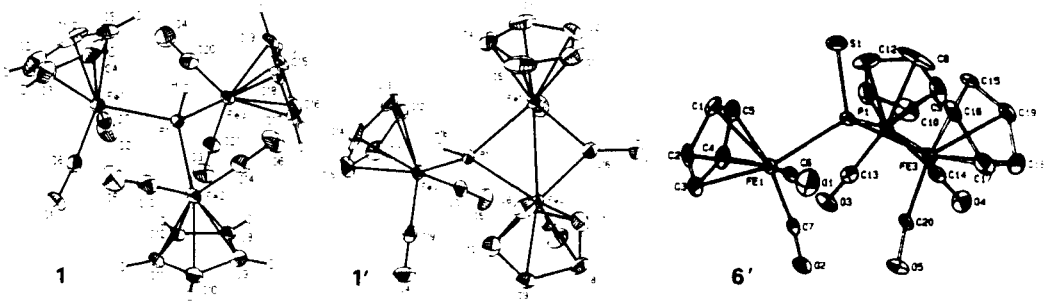
Abstract The syntheses and structures of PH-, PCl-, POR- and PR-triferriophosphonium salts, -phosphines and -chalkogenophosphoranes are discussed.

According to the isolobal analogy we regard the phosphorus atom as a coordination center and the 17-electrons complex fragments like $CpFe(CO)_2$ (= Fp = ferrio substituent) as coordinating ligands.

The reaction of $CpFe(CO)_2X$ (X = Cl, Br) with $P(SiMe_3)_3$ yields the open PH-triferriophosphonium salt $[Fp_3PH]_2FeX_4$ (**1**)[1] which can be decarbonylated to the closed analogue $[\{(\mu\text{-}CO)Fp'_2\}FpPH]_2FeX_4$ (**1'**). In CCl_4 they undergo a hydrogen-halogen exchange reaction giving the PCl-derivatives $[Fp_3PCl]_2FeX_4$ (**2**) which can be decarbonylated to $[\{(\mu\text{-}CO)Fp'_2\}FpPCl]_2FeX_4$ (**2'**). **2** is protolysed by ethanol to the POEt-compound $[Fp_3P(OEt)]_2FeX_4$ (**3**). Both PH-triferriophosphonium salts **1, 1'** are deprotonated by DBU to give the open and closed triferriophosphines Fp_3P (**4**) and $\{(\mu\text{-}CO)Fp'_2\}FpP$ (**4'**). The alkylation reaction is only possible for **4** and affords the open PR-triferriophosphonium salts $[Fp_3PR]Cl$ (**5a-c**)[1]. The directed P-oxidation of **4, 4'** by sulfur or selenium leads to the corresponding chalkogenophosphoranes $Fp_3P{=}E$ (**6**) and $\{(\mu\text{-}CO)Fp'_2\}FpP{=}E$ (**6'**)[1]. Further decarbonylation of **6'** yields the interesting spiro compound $\{(\mu\text{-}CO)Fp'_2\}Fp'P{=}E$ (**7'**) which seems to be the first η^2-P=S complex of a transition metal.



[1] W. Pohl, Thesis, University of Munich, 1995.