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Alkylation, Oxidation and Decarbonylation of Triferriphosphine $\{\text{CpFe}(\text{CO})_2\}_3\text{P}$

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ALKYLATION, OXIDATION AND DECARBONYLATION OF TRIFERRIOPHOSPHINE $\{\text{CpFe}(\text{CO})_2\}_3\text{P}$

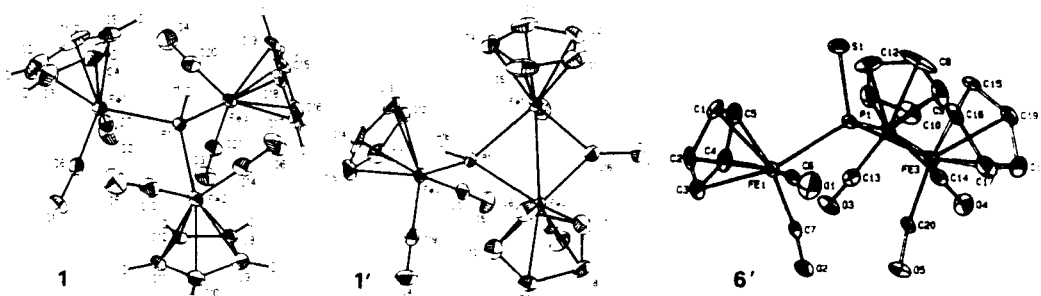
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Abstract The syntheses and structures of PH-, PCl-, POR- and PR-triferriophosphonium salts, -phosphines and -chalkogenophosphoranes are discussed.

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

The reaction of $\text{CpFe}(\text{CO})_2\text{X}$ (X = Cl, Br) with $\text{P}(\text{SiMe}_3)_3$ yields the open PH-triferriophosphonium salt $[\text{Fp}_3\text{PH}]_2\text{FeX}_4$ (**1**)¹⁾ which can be decarbonylated to the closed analogue $[\{(\mu\text{-CO})\text{Fp}'_2\}\text{FpPH}]_2\text{FeX}_4$ (**1'**). In CCl_4 they undergo a hydrogen-halogen exchange reaction giving the PCl-derivatives $[\text{Fp}_3\text{PCl}]_2\text{FeX}_4$ (**2**) which can be decarbonylated to $[\{(\mu\text{-CO})\text{Fp}'_2\}\text{FpPCl}]_2\text{FeX}_4$ (**2'**). **2** is protolysed by ethanol to the POEt-compound $[\text{Fp}_3\text{P}(\text{OEt})]_2\text{FeX}_4$ (**3**). Both PH-triferriophosphonium salts **1**, **1'** are deprotonated by DBU to give the open and closed triferriophosphines Fp_3P (**4**) and $\{(\mu\text{-CO})\text{Fp}'_2\}\text{FpP}$ (**4'**). The alkylation reaction is only possible for **4** and affords the open PR-triferriophosphonium salts $[\text{Fp}_3\text{PR}]\text{Cl}$ (**5a-c**)¹⁾. The directed P-oxidation of **4**, **4'** by sulfur or selenium leads to the corresponding chalkogenophosphoranes $\text{Fp}_3\text{P}=\text{E}$ (**6**) and $\{(\mu\text{-CO})\text{Fp}'_2\}\text{FpP}=\text{E}$ (**6'**)¹⁾. Further decarbonylation of **6'** yields the interesting spiro compound $\{(\mu\text{-CO})\text{Fp}'_2\}\text{Fp}'\text{P}=\text{E}$ (**7'**) which seems to be the first $\eta^2\text{-P}=\text{S}$ complex of a transition metal.



¹⁾ W. Pohl, Thesis, University of Munich, 1995.