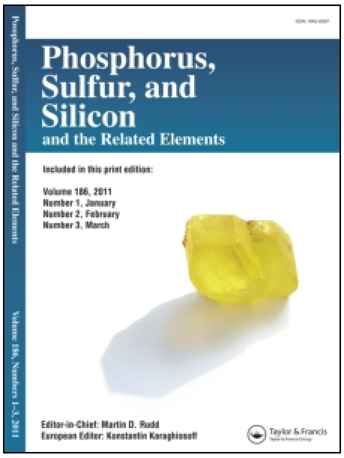

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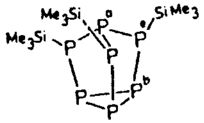
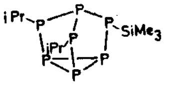
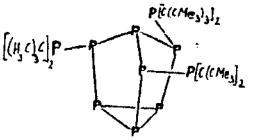
Influence of the Substituents on the Chemical Behaviour of P Rich Silylphosphanes

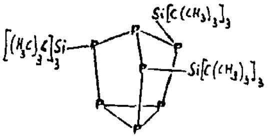
G. Fritz, B. Mayer, E. Layher, I. Kovacs, V. Balema, E. Matern

At first I will cover our investigations on the formation of transition metal complexes with variously substituted heptaphosphanortricyclanes. The formation of transition metal complexes of R_3P_7 (R = Et, iPr) with $Cr(CO)_5THF$ or $Cr(CO)_4NBD$ considerably changes the electronic conditions in the P_7 skeleton. Comparable effects can be expected when using various substituents R. To study these dependencies the behaviour of $(Me_3Si)_3P_7$, $iPr_2(Me_3Si)P_7$, $(tBu_2P)_3P_7$ and $(tBu_3Si)_3P_7$ in reactions with the chromium carbonyls was investigated [1].

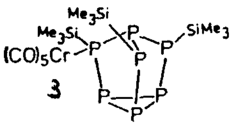








$(Me_3Si)_3P_7$ **1** reacts with one equivalent of $Cr(CO)_5THF$ **2** to give the yellow $(Me_3Si)_3P_7[Cr(CO)_5]$ **3**. The $Cr(CO)_5$ group is attached to a P^e atom. Yellow $(Me_3Si)_3P_7[Cr(CO)_5]_2$ **4** is obtained from reacting **1** with two equivalents of **2**. One $Cr(CO)_5$ group in **4** is coordinated to a P^e atom, the other one to a P^b atom.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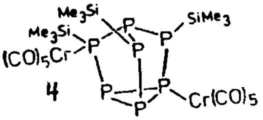
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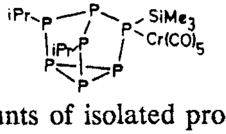
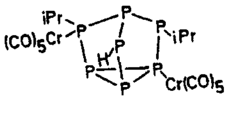
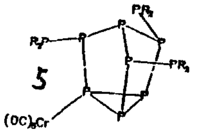
A series of investigations was carried out with $iPr_2(Me_3Si)P_7$ to elucidate the influence of the iPr or Me_3Si substituents, resp., on the selective formation of transition metal complexes. The reaction with $Cr(CO)_5THF$ yields $iPr_2(H)P_7[Cr(CO)_5]$ containing a $iPrPCr(CO)_5$ group together with $iPr_2(Me_3Si)P_7[Cr(CO)_5]$ containing a $Me_3SiPCr(CO)_5$ group.





From the amounts of isolated products it can be concluded that the Me_3SiP^e position is clearly favoured over the sterically less requiring alkylated P groups in the formation of transition metal complexes.

Continuing our investigations of the sterical and electronic influence of the substituents on the determination of the reaction center in the P_7 skeleton during the formation of transition metal carbonyl complexes we synthesized $(tBu_2P)_3P_7$. The reaction of $(t\text{-}Bu_2P)_3P_7$ with $Cr(CO)_5{\cdot}THF$ in a molar ratio of 1:1 yields yellow crystals of $(t\text{-}Bu_2P)_3P_7[Cr(CO)_5]$ **5** having the $Cr(CO)_5$ group coordinated to a P^b atom (basal). With a molar ratio of 1:2 compounds, $(t\text{-}Bu_2P)_3P_7[Cr(CO)_5]_2$ **6**, $(t\text{-}Bu_2P)_3P_7[Cr(CO)_5][Cr(CO)_4]$ **7** and $(t\text{-}Bu_2P)_3P_7[Cr(CO)_4]_2$ **8**, $(tBu_2P)_3P_7[Cr(CO)_4]_3$ **9** were obtained. In **6** (yellow crystals) one $Cr(CO)_5$ group is linked to a P^b atom, the other one to an exocyclic P^{exo} atom. On irradiation **6** by loosing one CO group generates **7** (orange red crystals) with one unchanged $Cr(CO)_5$ group linked to the P^b atom and a five membered chelate-like ring containing an apical P^a atom, two equatorial P^e atoms, one P^{exo} atom and the Cr atom of the carbonyl group. Compound **8** (orange red crystals) contains two and **9** three such five membered rings.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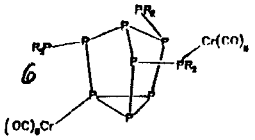
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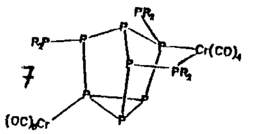
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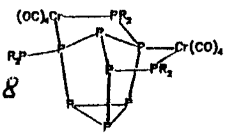
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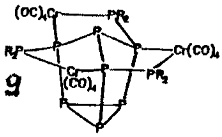
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For a long time we spent many efforts to obtain a P_7-derivative with a skeleton sterically blocked as much as possible. tBu_3P_7 would be a suitable compound but could not be synthesized so far. N. Wiberg reported the formation of $(tBu_3Si)_3P_7$ which was obtained by reacting $(tBu)_2Si{=}Si(tBu)_2$ with white phosphorus and characterized by ^{31}P nmr. Of course we were interested in this compound and in agreement with N. Wiberg we established a preparative access to it and performed an X-ray structure determination. Complexation with $Cr(CO)_5THF$ proceeds very slowly and reacts only with a basal P atom. These investigations show that the substituents of the equatorial P atoms determine the course of the formation of complex products and that in addition to sterical also electronic influences effect the reactions.

As reported previously $[(tBu)_2P]_2PLi$ suspended in toluene does not form a new P-P linkage with 1,2-dibromoethane; however, a solution of $(tBu)_2P\text{-}P{=}P(tBu)_2Br \cdot LiBr$ is obtained, which under Li/Br exchange and rearrangement of the brominated triphosphane gives an ylide according to

$(tBu)_2P\text{-}P(Br)\text{-}P(tBu)_2 \rightarrow (tBu)_2P\text{-}P{=}P(tBu)_2Br$ [2].

The ylide is present as a LiBr adduct. Similarly, $(tBu)_2P\text{-}P{=}PCl(tBu)_2$ is obtained starting from PCl_3 and $LiP(tBu)_2$. The formation of phosphanylidene-phosphorane is not influenced by the choice of the halogene substituent, but the presence of the tBu groups is strongly required. $(tBu)_2P\text{-}P(Li)\text{-}P(SiMe_3)_2$, e.g., yields $(tBu)_2P\text{-}P(Br)\text{-}P(SiMe_3)_2$ with $BrH_2C\text{-}CH_2Br$; however neither this nor $(tBu)_2P\text{-}P(Cl)\text{-}P(SiMe_3)tBu$ do rearrange to a phosphanylidene-phosphorane. Such, partly silylated triphosphanes do not rearrange to ylides because via elimination of Me_3SiCl a stepwise formation of cyclotetraphosphanes determines the course of the reaction. To achieve the rearrangement to an ylide the substituents of the triphosphane must not be suitable for elimination. So for example $(tBu)_2P\text{-}P(Li)\text{-}P(Ph)_2$ with 1,2-dibromoethane gives $(tBu)_2P\text{-}P{=}P(Ph)_2Br$ which even at 20°C over 36 h does not decompose.

Now I which to deal a bit closer with the chemical behaviour of $(tBu)_2P\text{-}P{=}P(Br)tBu_2$. Compounds $(tBu)_2P\text{-}P{=}P(X)tBu_2$ (X = Cl,Br) display a characteristic temperature dependent behaviour. While they decompose at +20°C via the reactive intermediate $(tBu)_2P\text{-}P$ to form the cyclophosphanes $P_3[P(tBu)_2]_3$ and $P_4[P(tBu)_2]_4$, they give crystals of $[(tBu)_2P]_2P\text{-}P[P(tBu)_2]_2$ at -20°C (from a solution in toluene). When stored at -78°C, solid $(tBu)_2P\text{-}P{=}PBr(tBu)_2 \cdot LiBr$ forms some $(tBu)_2P\text{-}P{=}P(H)tBu_2$.

According to ^{31}P nmr spectra ot the solution in toluene taken at -60°C, -20°C and 0°C a rearrangement to a triphosphane according to

$(tBu)_2P\text{-}P{=}P(H)tBu_2 \rightarrow (tBu)_2P\text{-}P(H)\text{-}P(tBu)_2$

is favoured with increasing temperature. However no back reaction could be observed when lowering the temperature again.

Reacting $(tBu)_2P\text{-}P{=}P(Br)tBu_2$ **10** with tBuLi produces $(tBu)_2P\text{-}P{=}PH(tBu)_2$ **11** and $(tBu)_2P\text{-}P(H)\text{-}P(tBu)_2$ **12**. Initially, a transmetallation yields tBuBr and $(tBu)_2P\text{-}P{=}PLi(tBu)_2$ **13**, then LiBr and isobutene are eliminated and **11** is formed which can rearrange to produce **12**. Without the elimination of isobutene, **10** reacts with nBuLi to give **13** which can be trapped with Me_3SiCl as $(tBu)_2P\text{-}P(SiMe_3)\text{-}P(tBu)_2$. The main product in this reaction is however $[(tBu)_2P]_2P\text{-}nBu$. In a similar way $(tBu)_2P\text{-}P{=}P(tBu)_2Br$ reacts with $LiP(SiMe_3)_2$. The main products are the isotetraphosphane $[(tBu)_2P]_2P\text{-}P(SiMe_3)_2$ and $(Me_3Si)_2P\text{-}P(SiMe_3)_2$. The isotetraphosphane results from a substitution at the ylide and the diphosphane is formed after a Li/Br exchange between $(tBu)_2P\text{-}P{=}P(tBu)_2Br$ and $LiP(SiMe_3)_2$ to some intermediate $BrP(SiMe_3)_2$. The product mixture also contains $(tBu)_2P\text{-}P{=}P(H)tBu_2$, $(tBu)_2P\text{-}P(H)\text{-}P(tBu)_2$ and $[(tBu)_2P]_2P\text{-}P[P(tBu)_2]_2$.

When investigating the ability of $(Me_3Si)_2P\text{-}P(SiMe_3)_2$ to form transition metal complexes we could isolate $[(CO)_4Fe](Me_3Si)_2P\text{-}P(SiMe_3)_2$, however no chromium carbonyl complexes could be detected. As $(Me_3Si)_2P\text{-}P(SiMe_3)_2$ itself is readily available from $(Me_3Si)_2PLi$ and 1,2-dibromoethane [3], we intended to synthesize the desired chromium carbonyl complexes similarly starting from $[(CO)_5Cr](Me_3Si)_2PLi$. Surprisingly this attempt resulted in the tetraphosphenide $[Li(DME)_3]_2\{Me_3Si[(CO)_5Cr]_2P\text{-}P{=}P\text{-}P[Cr(CO)_5]_2SiMe_3\}$ which could be fully characterized.

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