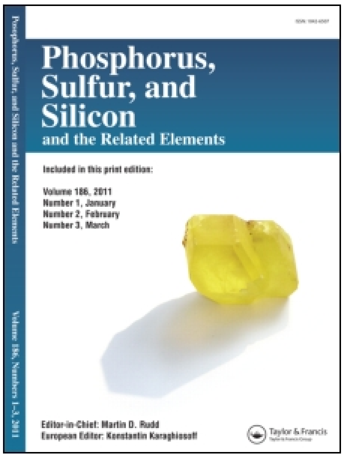

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Polycyclic Polyphosphorus Hydrocarbons

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POLYCYCLIC POLYPHOSPHORUS HYDROCARBONS

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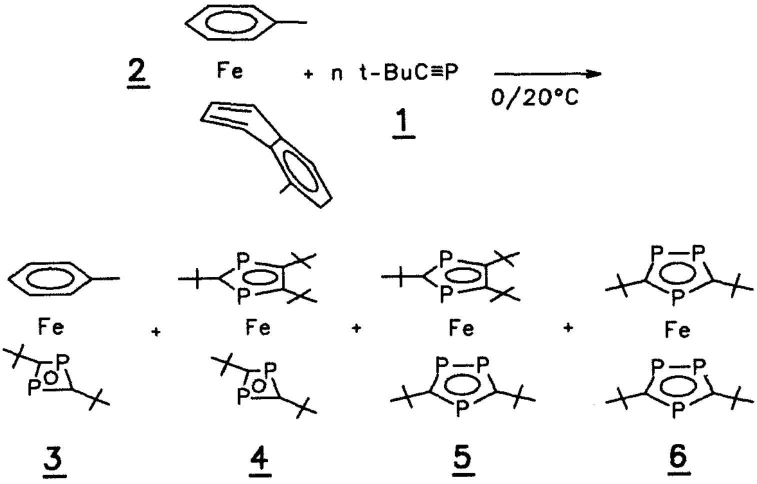
Abstract Highly reactive arene iron complexes are capable of transforming tert.-butylphosphaacetylene into several coordinated organophosphorus compounds by cyclic addition reactions below or at room temperature. Free cage-structured polyphosphorus hydrocarbons are formed from the same educts by increasing the temperature or by low-temperature reduction of the phosphaalkyne.

INTRODUCTION

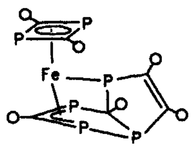
Metal vapor reactions give good access to a number of useful arene iron complexes[1], which exhibit interesting properties like low-temperature reactivity towards unsaturated organic compounds. Therefore it seemed to be reasonable to assume interesting reactions between these complexes and tert.-butylphosphaacetylene[2] 1, especially in the light of first reports about successful cyclic addition reactions of 1 in the coordination sphere of some transition metal complexes, which have been revued in the meantime[3]. Our first aim was the synthesis of (arene)(diphosphete)iron(0) complexes, which should be closely related to the isoelectronic (arene)(cyclobutadiene)iron(0) complexes[4]. These isomers of ferrocene are extremely stable in comparison with other (arene)(diene)iron(0) species.

RESULTS

If we mix (η^4-1-methylnaphthalene)(η^6-toluene)iron(0)[5] 2 ($T_{dec.} \approx 0°C$) with 1 at -20°C in the ratio 1:2, we observe the formation of the desired diphosphete complex 3 in reasonable yield (48%), when the mixture is allowed to reach room temperature within two hours. The sandwich complexes 4 and 5 are formed as side products in small amounts as well, bearing diand triphospholyl ligands[6], which can only be formed in this reaction, if some molecules of 1 are split into its components P and C-R. This seemed to be a rather unlikely reaction at room temperature, however, if we increase the ratio of the educts 1 to 2 to five, the pentaphosphaferrocene derivative 5 becomes a main product (30%) besides 37% 3, 2% 6 and traces of 4. Hence this is a useful preparative route for the synthesis of 3 and 5.



By increasing the ratio 1 to 2 up to 20 we can disfavour the formation of the sandwich complexes and get more complex products[1,7]. The two complexes 7 and 8 are remarkably stable paramagnetic 16-VE species and contain six (7) and seven (8) units of 1 respectively, whereas diamagnetic 18-VE 9 has one P-atom more than C-R-fragments and picked up an extra hydrogen atom. All three contain a diphosphete iron unit in combination with a bicyclic tetramer of 1 (7), a partly opened pentamer cage (8) or a cage, which is best described as a pentaprismane-like structure (9). The amounts of 8 and 9 formed this way are always low, but 7 can be made in 24% yield from bis(ethylene)(toluene)iron(0)[1] and 1 1:11.



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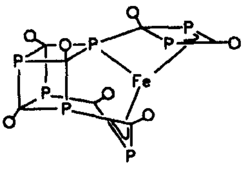

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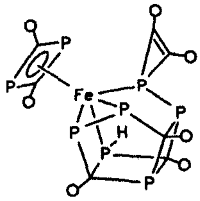


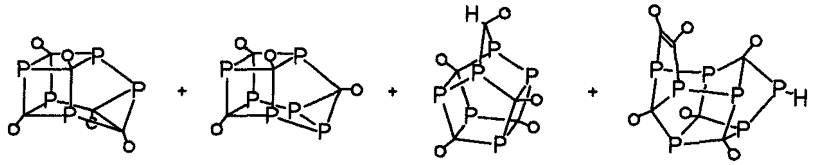
—o = t-Bu

7

8

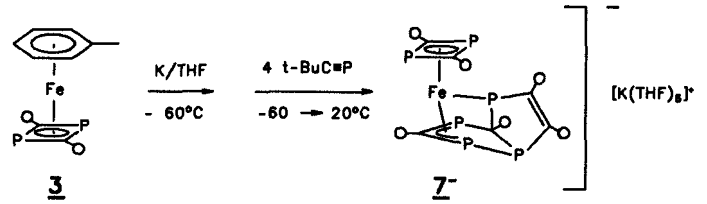
9

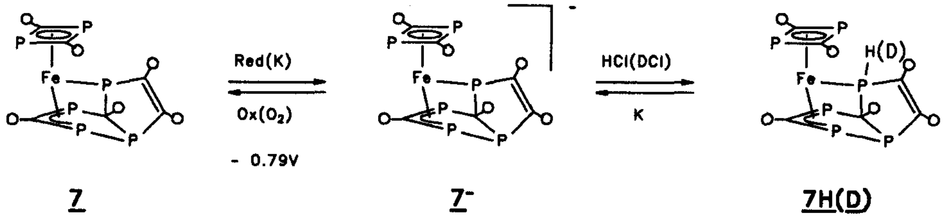
Aiming for metal-free cages, we warmed up the reaction mixtures of 1 and 2 to 100°C for an hour after reacting the educts overnight at room temperature. Repeated MPLC gives several fractions, from which 10 to 13 could be isolated^{1,7}. Only 10 is a telomer of 1, but 11 to 13 are composed from more phosphorus atoms than C-R-fragments and the odd number of vertices in 12 and 13 is compensated by an additional hydrogen.
The yields of the cages are poor, but we found better access to 10 recently (vide infra).



10 11 12 13

Aspecially 3, 5, and 7 can be made from 2 and 1 in several grams in a short time, which qualifies them as potential educts in further syntheses. Reactivity studies can utilize the redox properties of the compounds, and in the case of 3 we can reduce it at -60°C at a K-mirror in THF, add 4 equivalents 1 thereafter and get up to 90% 7^-K^+ after warming up to room temperature. However, this elegant synthesis of 7^- is hampered by the awkward fact, that it works only sometimes and produces in most cases no product at all. The reason for this is not yet clear, but reduction of 1 itself plays an important role. The complex anion in $7^-[K(THF)_6]^+$ is isostructural to the neu-





tral 7 and both are connected by a reversible electron transfer reaction. In addition we can protonate or deuterate 7^{-} with acids yielding **7H** or **7D** respectively. 7^{-}, **7H**, and **7D** are radicals with closely related ESR-spectra.
As the reduction of 1 plays a significant role in the reaction with 3^{-}, we reacted 1 at a K-mirror under ESR-control, this way getting clear evidence for a rapid aggregation of 1^{-} and 1 even at low temperatures. By reproducing this experiment on a preparative scale and quenching reduction by oxidation with air, we can isolate up to 30% 10. Again this route is plagued by changing yields, but 5% is always found in minimum.

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