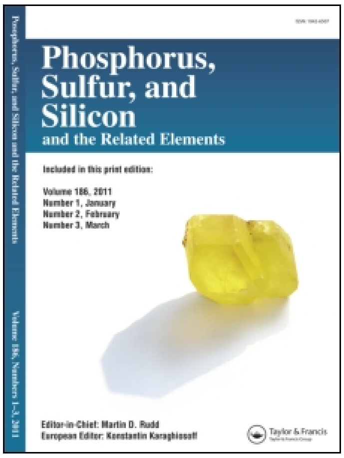

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η^6-PHOSPHININE- AND η^6-1,3-DIPHOSPHININE IRON COMPLEXES

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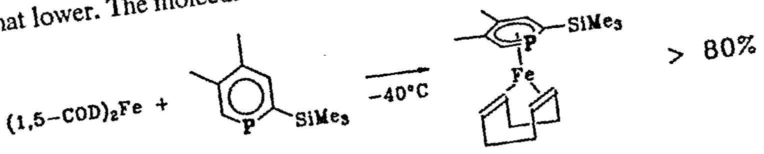
Abstract Efficient synthetic routes are described, leading to novel η^6-phosphinine- (1) and η^6-1,3-diphosphinine (4, 5) iron(0) complexes. 1 is a catalyst for pyridine formation by a [2+2+2]-cyclic addition reaction of nitriles and alkynes and 4 is a useful source of unsaturated free four and six membered organophosphorus rings.

INTRODUCTION

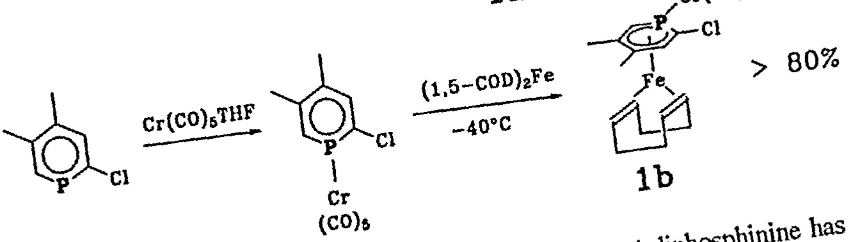
14 valence electron fragment generating complexes are known for their catalytic potential. Prominent examples are (cyclopentadienyl)CoL_2 species, which are catalysts for the formation of substituted pyridine derivatives, [1] whereas recent work on Cp_2ML_n complexes (M = Ti, Zr, Hf; n = 1,2) lead to a real revolution on Ziegler-Natta type catalytic processes. [2] Arene iron complexes are isoelectronic to CpCo species. They exhibit the same principal reaction pattern, but significant milder reaction conditions are observed. This includes catalysis, however, turnover numbers are smaller normally. [3] To solve this problem, P-atoms as part of co-ordinated aromatic rings seem to be appropriate. In principal reactions of phosphaalkynes in the co-ordination sphere of transition metals lead to unsaturated organophosphorus ring ligands, but mainly four and five membered rings are formed. [4] This is true for reactive Fe(0) complexes as well. In contrast to alkynes, the cyclotrimerization is avoided, and two five membered rings are formed from five phosphaalkynes. [5] Only very recently, first proof has been found for a triphosphinine formed in the vicinity of a transition metal. [6]

Results

In spite of the fact, that bis(1,5-cyclooctadiene)iron (COD_2Fe) [7] has never been used successfully for the preparation of arene(COD)Fe complexes by ligand exchange, we tried this route with phosphinine derivatives. The reaction produces excellent yields of (η^6-phosphinine)(COD)Fe derivatives 1, if the lone pair of the phosphorus atom is shielded by a big ortho substituent (TMS, **1a**), or if it is blocked by a σ-bonded transition metal fragment like $Cr(CO)_5$ (**1b**). Alternatively **1** can be made by three-component metal vapour reactions of $Fe_{(gas)}$, COD and the phosphinines, but the yields are somewhat lower. The molecular structure of **1a** has been proven by X-ray.

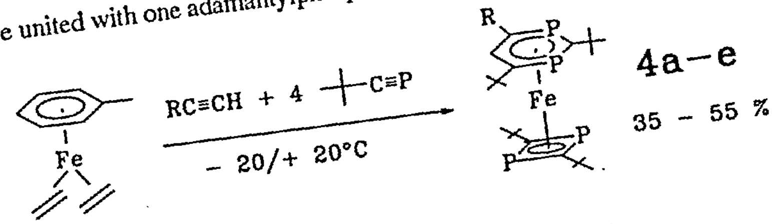


1a



1b

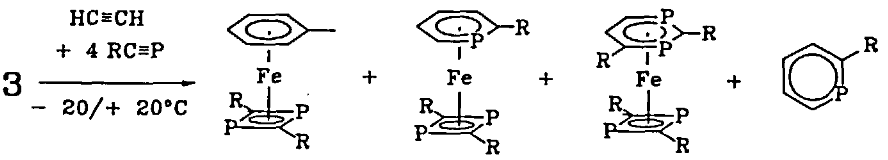
As di- or triphosphinines are not available yet, only $(CF_3)_4$-1,4-diphosphinine has been identified in solution so far, [8] a new synthetic approach to these aromatic heterocycles is necessary. We solved this synthetic problem by a [2+2+2] cocyclization of alkynes and phosphaalkynes. Compared to the so far unsuccessful cyclic trimerization of *tert*-butylphosphaethyne **2a** at most transition metal complexes, the inclusion of acetylene or terminal alkynes with small substituents into the process, leads to lesser sterical hindrance of transition states, yielding six membered rings. The reaction proceeds well with the highly reactive metal vapour product bis(ethylene)(toluene)iron **3** [9], yielding (η^6-1,3-diphosphinine)(1,3-diphosphete)iron complexes **4a-e** as the main product. Functional groups as parts of the alkyne substituents do not hinder the reaction. [10] If adamantylphosphaethyne **2b** is reacted with **3** and acetylene, the product spectrum changes significantly. The 1,3-diphosphinine complex **5** is only a side product in this case, while adamantylphosphinine complex **6** and free 2-adamantylphosphinine dominate the products. Thus still [2+2+2] cyclic addition reactions are the main route, however, two alkynes are united with one adamantylphosphaethyne only.



3

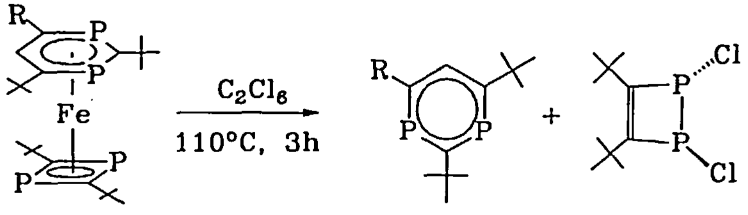
4a−e

R = H, CH_2OH, CH_2OCH_3, n-C_4H_9, $CH_2OC(O)CH_3$



R = Adamantyl 18% **6** 19% **5** 4% 20%

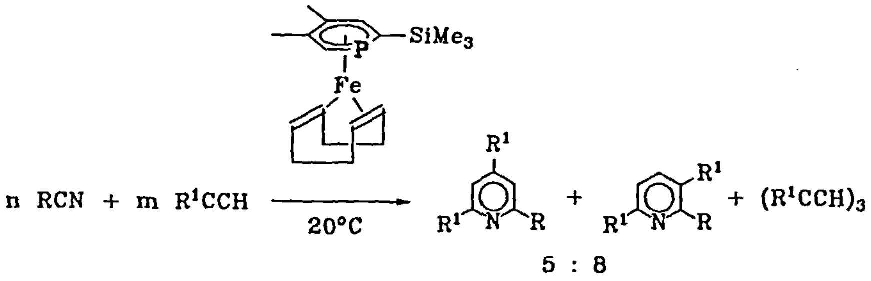
The formation of **4a-e** is strictly regiospecific. Exclusively 1,3-diphosphinines are formed and the substituent, introduced with the alkyne, ends up always neighbouring the P atom. All arene(cyclobutadiene)iron derivatives, including those containing up to four P-ring atoms instead of C-R fragments, are extremely stable, if compared with other arene iron complexes (air stable for some time, thermal decomposition beyond +300°C, no ligand substitution reaction), thus they are not useful as catalysts. To make use of the novel 1,3-diphosphinines in this sense, decomplexation is necessary. Oxidizing agents at elevated temperatures can be used for this purpose. $FeCl_3$ or CCl_4 deliberate the 1,3-diphosphinine ligands **7a,b** only, whereas C_2Cl_6 gives access to both free rings. However, the 1,4-diphosphete is oxidized partly and transformed into a *trans*-1,2-dichloro-1,2-phosphetene derivative **8** completely. All spectra recorded of **7a,b** so far, are in perfect agreement with viewing the free rings as stable π^6 heteroarenes. This structure has been proven for the co-ordinated rings. The formation of the rings in the co-ordination sphere of iron(0) and the 1,3 → 1,2-rearrangement of the four membered ring upon decomplexation cast interesting mechanistic questions.



4a,e 7a,b 8

R = H, $CH_2OC(O)CH_3$

We are engaged in the moment in recomplexation experiments of **7a,b** with more promising coligands as 1,3-diphosphetes, aiming for potentially catalytic active complexes. The proposed benefit of phosphinine iron complexes as catalysts for pyridine formation was confirmed for **1a**. Conveniently it is active at room temperature, the optimal temperature for laboratory and industrial scale catalytic processes. As the turnover numbers (TON) and the chemoselectivity are still far away from technical requirements, more experiments are necessary to optimize the reaction. Complexes of **7** are promising, as the replacement of toluene by phosphinine ligands of the catalyst prototype (arene)FeL_2 leads to a significant improvement. Therefore the introduction of a second P atom as part of the arene ligand of iron(0) is believed to have an additional positive effect on pyridine formation as well.



$c(Cat.) = 5 \times 10^{-4}$ mol/l $R^1 = CH_2OCH_3$

Chemoselectivity	Benzenes : Pyridines = 1.4 – 4
TON (max.)	Benzenes 470, Pyridines 160
Alkyne conversion	4 – 84%

Acknowledgements

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