(η^4-1,5-Cyclooctadiene)(η^6-phosphinine)iron(0): Novel Room-Temperature Catalyst for Pyridine Formation[†,1]

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Two routes are described for the synthesis of (η^4-1,5-cyclooctadiene)(η^6-phosphinine)iron-(0) complexes. A three-component reaction of iron vapor with COD and 2-(trimethylsilyl)-4,5-dimethylphosphinine at low temperature yields 20% (COD)(2-(trimethylsilyl)-4,5-dimethylphosphinine)Fe(0) (**3**), whereas ligand exchange of one COD ligand of the in situ prepared metal vapor product $(COD)_2Fe$ by 2-(trimethylsilyl)-4,5-dimethylphosphinine or (η^1-2-chloro-4,5-dimethylphosphinine)$Cr(CO)_5$ gives corresponding (COD)(phosphinine)Fe(0) complexes in more than 80% isolated yield. As the phosphinine derivatives are prochiral, complexation leads to the racemate of two enantiomers. Both enantiomers are found in the unit cell of single crystalline **3** and are related by an inversion center. Complex **3** is a novel room-temperature catalyst for the [2 + 2 + 2] cyclic addition reaction of one molecule of butyronitrile with two molecules of methyl propargyl ether giving up to 160 mol of pyridine derivatives/mol **3**. A chemically robust species, **3** is an air-stable crystalline material, but exposure to oxygen in solution causes slow decomposition.

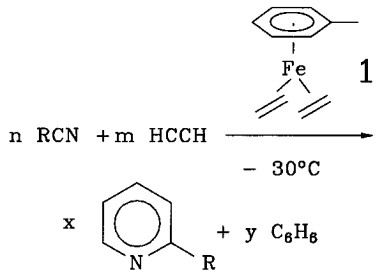
Introduction

Complexes capable of generating 14-electron fragments are widely used in catalysis. Prominent examples are (cyclopentadienyl)CoL_2 species, which are catalysts for the formation of substituted pyridine derivatives.[2] (Arene)iron complexes are isoelectronic to CpCo species and exhibit the same principal reaction pattern, but significantly milder reaction conditions are used. Catalytic pyridine synthesis can be carried out (Scheme 1); however, the turnover numbers observed are smaller than for the CpCo-based systems.[3]

As the CpCo system failed to fulfill the requirement of industrial use, we were motivated to systematically investigate (arene)iron complexes for catalytic pyridine synthesis.

To improve the turnover numbers of the catalysts, reactions leading out of the catalytic cycle must be disfavored. We believe both classes of catalysts operate by similar mechanisms. As a consequence, the results of the fundamental studies of Bönnemann,[2,4] Wakatsuki, and Yamazaki[5] on reactions of alkynes and nitriles in the coordination sphere of Co(I) are regarded as indicative of the corresponding reactions at iron(0) centers. We thus believe that metallacyclopentadienes are key intermediates. This proposal is supported by isolation and characterization of a ferrole derivative.[3,6] Like Cp the arene ligand should remain π-complexed to the iron throughout the catalytic cycle; however, loss of the arene is much more likely than loss of Cp. Arenes are highly stable neutral molecules; thus, many (arene)-iron complexes decompose at ambient to slightly elevated temperatures by forming metallic iron and free ligands.[3] The splitting of a Cp−Co bond requires charge separation, and higher stabilities for those species are

Scheme 1



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† Dedicated to Professor Hans Jürgen Bestmann, University of Erlangen-Nürnberg on the occasion of his 70th birthday.

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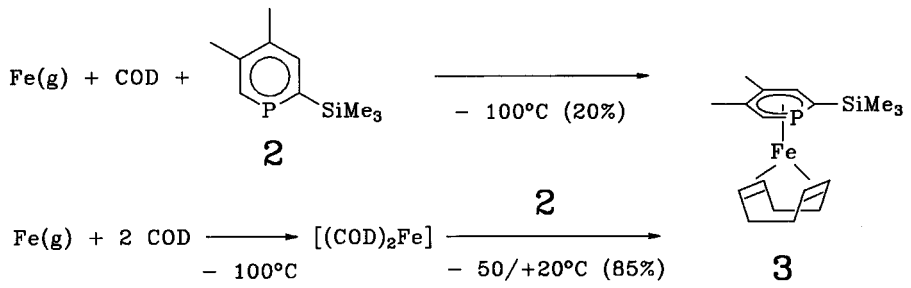
Scheme 2



observed in most cases. From preliminary studies we learned that substituted variations of the arene ligands do not provide a very promising approach to the problem.

In contrast to (arene)(diene)Fe good stability for (arene)FeL_2 complexes is observed in the case of phosphite ligands L = $P(OR)_3$, and these do not form metallic iron upon thermal decomposition.[7] The phosphorus atom of the ligands interact strongly with the metal and seem to remain bound to iron even during thermal disintegration of the complexes. Such an effect also seems possible with iron-coordinated P-heterocycles. We thus decided to test heteroarenes as π-ligands, especially phosphinines, but (η^6-phosphinine)Fe(0) complexes have not yet been reported in the literature. If complexes of this sort are still catalytically active, an increase in the turnover numbers is expected.

Highly reactive catalyst **1** ($T_{decomp} \approx -20$ °C) was used for our first experiments.[8] Because of its thermolability, it is of no practical use. To approach the problem of excessive reactivity, we need to take two factors into consideration, the reaction temperature and the reaction rate. Temperatures near room temperature are preferred, as energy costs and handling of reaction mixtures of any size is optimal. The reaction rate, however, is optimal in the case of catalyst **1** and should be maintained upon variation of the arene ligand. But the catalytic process is not fully understood yet, leaving no chance of influencing the reaction rate systematically at a given temperature. On the other hand, the reaction temperature can be influenced in the desired direction. The reaction definitely starts with the substitution of one ethylene ligand of **1** by either an alkyne or a nitrile. If we stabilize this part of a potential precatalyst, the activation energy of the substitution process would increase and higher temperatures would be required. To do so, a connection of the two olefinic ligands is a good choice and dienes have to be considered instead of two alkenes. Because of practical reasons we concentrated on 1,5-cyclooctadiene (COD) in the beginning; thus, (COD)(η^6-phosphinine)Fe(0) complexes were our first synthetic goal.

Reactions with unsubstituted phosphinine and organoiron compounds have already been attempted, but only $\eta^1(\sigma)$-complexation of the heterocycle was identified.[9] The same is true for other transition metal complexes;[10] only vanadium vapor and phosphinine directly yield (η^6-phosphinine)$_2$V.[11] Substituted phosphinines, however, offer several coordination modes. Complexation to the metal may either involve the σ-electron pair of the phosphorus atom,[12] the π-electrons of the ring (η^6),[13] or both kinds of electrons.[14] If bulky groups are present at the ortho positions of the phosphinine ring,[16] σ-complexation is strongly disfavored and (η^6-phosphinine)metal complexes are the main product.[15]

In this paper we describe experiments with 2-chloro and 2-(trimethylsilyl)phosphinine derivatives. The bulky silyl group shields the P-lone pair, whereas the chloro substituent is less bulky and σ-complexation is also possible. In addition to the sterical demands the different electronegativities of each group were considered.

Results and Discussion

Preparation of (η^4-1,5-Cyclooctadiene)(η^6-phosphinine)iron Complexes. (COD)(2-(trimethylsilyl)-4,5-dimethylphosphinine)Fe (**3**) can be synthesized by two different routes (Scheme 2). The three-component reaction of stochiometric amounts of iron vapor, COD, and 2-(trimethylsilyl)-4,5-dimethylphosphinine (**2**) yields 20% **3**, whereas the reaction of an excess of the metal vapor product $(COD)_2Fe$[17] with phosphinine **2** leads to the formation of **3** in more than a 80% yield.

Solutions of **3** can be stored for months at room temperature in an inert-gas atmosphere; exposure to oxygen of this solution leads to slow decomposition. Crystals of **3** are air stable.

The excellent yield of **3** with respect to the phosphinine **2** utilizing a highly reactive organometallic intermediate is consistent with the results of other thermo-

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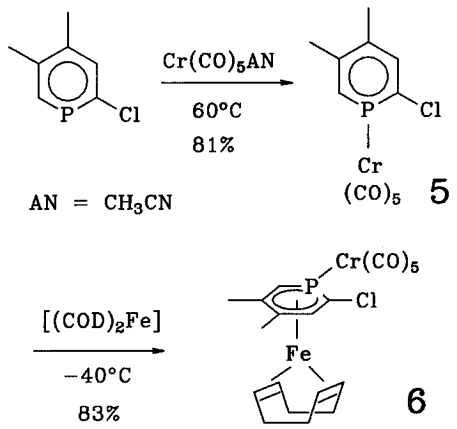
Scheme 3



labile metal vapor products like bis(toluene)iron.[3] $(COD)_2Fe$ is easily prepared using standard metal vapor apparatuses[17−19] in 0.1−0.2 mol quantities from very cheap educts within 1 h.

Therefore, the introduction of a large excess of the reagent is not a problem. It should be noted that no successful ligand displacement reactions of $(COD)_2Fe$ by arenes are present in the literature, despite much effort.[20] The reverse reaction of $(arene)_2Fe$ with COD directly leads to (arene)(COD)Fe derivatives in high yields.[19,21] Our initial proposal for the role of the phosphorus lone pair has been proven wrong (vide infra). It is likely that the modified energies of the π- and π*-orbitals of the heteroarene stabilize transition states with η^2- and η^4-coordination to the metal. Phosphinines are better π-acceptors than their carbacyclic analog, but the π-donor strength remains the same.[22] This argument explains the recently successful ligand displacement experiments on $(COD)_2Fe$ by naphthalene derivatives that yield (COD)(η^6-naphthalene)Fe complexes.[23]

Analogous experiments with 2-chloro-4,5-dimethylphosphinine (**4**) provide spectroscopic evidence of σ-(three-component reaction) and π-complexation (ligand displacement of $(COD)_2Fe$), but the stabilitiy of these products is poor and the attempts to purify them therefore failed. In order to direct the reaction to a single product, we blocked the lone pair of **4** by σ-complexation to a $Cr(CO)_5$ fragment. In analogy to the preparation of (η^1-2-chloro-4,5-dimethylphosphinine)W-$(CO)_5$,[16d] **4** readily reacts with $Cr(CO)_5(CH_3CN)$ forming (η^1-2-chloro-4,5-dimethylphosphinine)$Cr(CO)_5$ (**5**) in high yield. Chemical and spectroscopic properties of the Cr- and W-σ-complexes are closely related. Like the silyl-substituted phosphinine **2**, the σ-complex **5** effectively replaces one ligand of $(COD)_2Fe$ to form the binuclear species (COD)(η^6-[(η^1-μ-2-chloro-4,5-dimethylphosphinine)$Cr(CO)_5$])Fe (**6**) (Scheme 3).

As for **3**, the isolated yield of **6** exceeds 80%, if an excess of $(COD)_2Fe$ is used. This observation rules out a decisive role of the phosphorus lone pair in the substitution reactions of $(COD)_2Fe$ with the phosphinine derivatives employed here. In contrast to **3**, solutions of **6** are very air sensitive and can be stored for only a few hours at room temperature even in the absence of oxygen. Crystalline **3** is slightly air sensitive, too. The reason for this dramatic loss of stability is not fully understood at the moment. The electron-withdrawing nature of the chlorine substituent and the donation of the lone pair of the phosphorus atom to the $Cr(CO)_5$ group without an additional bonding interaction between the two metal atoms provide two possible reasons.

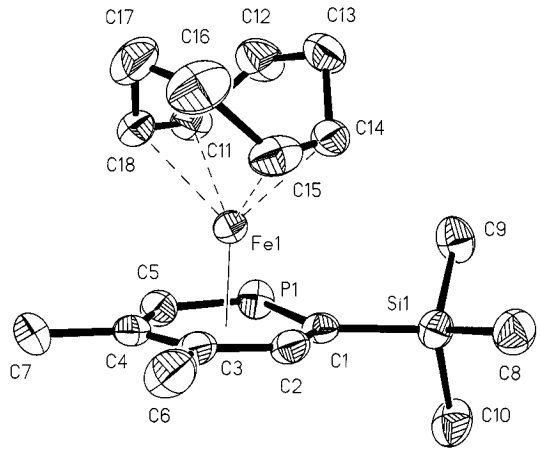


Figure 1. Molecular structure of **3** in the solid state (one enantiomer). Thermal ellipsoids have been drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Spectroscopic Properties. As mentioned, the Cr complex **5** is very closely related to the corresponding $W(CO)_5$ complex,[16d] and this is documented in all spectra. η^6-Coordination of the phosphinine derivatives **2** and **5** to the iron atom causes the characteristic upfield shifts in the NMR spectra observed for all nuclei that are either part of the ring ligand (P, C_{ring}) or directly attached to the ring (H_{ring}).[24] The shifts observed are in the range found for corresponding diamagnetic η^6-phosphinine complexes.[13,14] In addition to the upfield shift, the $P-H_{ring}$ and $P-C_{ring}$ coupling constants are reduced upon complexation. Again this is a well-documented phenomenon.[14,25]

Due to the low symmetry of the prochiral heterocycles, **2** and **5**, π-complexation causes the formation of racemic mixtures of two enantiomers. The asymmetry of complexes **3** and **6** is proven by the splitting of the ^1H- and ^{13}C-NMR resonances of the COD ligand. This part of the spectra is unambiguously different from that of (arene)(COD)Fe complexes containing a vertical mirror plane within the arene ligand.[21]

As expected, the C−O bonding modes in the vibrational spectra of **5** and **6** are almost identical. Thus π-complex formation causes no significant interaction between the iron and chromium atoms of **6**.

Structural Description of 3. Because of the stability of **3** and the quality of the crystals obtained, an X-ray structure determination of **3** could be accomplished. The molecular structure of one of the two symmetry-related enantiomers is shown in Figure 1, and selected bonding

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Lengths					
Fe−P	2.328(2)	Fe−C(1)	2.192(3)	Fe−C(2)	2.106(3)
Fe−C(3)	2.131(3)	Fe−C(4)	2.167(4)	Fe−C(5)	2.110(3)
Fe−C(11)	2.085(4)	Fe−C(14)	2.077(3)	Fe−C(15)	2.058(3)
Fe−C(18)	2.073(4)	P−C(1)	1.749(3)	P−C(5)	1.749(4)
C(1)−C(2)	1.406(4)	C(2)−C(3)	1.427(5)	C(3)−C(4)	1.401(5)
C(4)−C(5)	1.409(5)	C(14)−C(15)	1.406(5)	C(11)−C(18)	1.383(5)
Bond Angles					
P−C(1)−C(2)	122.8(2)	C(1)−C(2)−C(3)	127.2(3)	C(2)−C(3)−C(4)	120.8(3)
C(3)−C(4)−C(5)	120.2(3)	P−C(5)−C(4)	129.7(3)	C(1)−P−C(5)	99.1(2)

distances and angles are listed in Table 1.

As deduced from the consideration of the low symmetry of the ligands and observed in the NMR spectra, the X-ray structure determination of **3** provides further evidence for the formation of enantiomers upon π-complexation of **2** to a (COD)Fe fragment. Complex **3** crystallizes in the monoclinic space group, $P2_1/c$, and each unit cell contains both enantiomers of **3**, which are related by an inversion center. The phosphinine ligand remains planar; the largest deviation from planarity within the ring is ±0.03 Å. Even the silyl atom (+0.04 Å) and the two carbon atoms of the methyl substituents (+0.07 and −0.04 Å, respectively) lie essentially within this plane. The average distance between iron and the six atoms of the heterocycle is 2.17 Å. This distance is only slightly shorter than the value of 2.29 Å found in (η^6-2,4,6-triphenylphosphinine)$Cr(CO)_3$[25] but is identical to the value found in Cp(η^6-2,4,6-triphenylphosphinine)-Mn.[26] The bonding distances and angles within the phosphinine ring of **3** are also similar to the values found for coordinated 2,4,6-triphenylphosphinine in the CpMn complex. Obviously neither the identity of the transition metal nor the presence of alkyl, aryl, or silyl substituents on the phosphinine ring can cause significant structural changes in (η^6-phosphinine)metal complexes.

The mean bonding distance between Fe and the olefinic carbon atoms in **3** is 2.07 Å and the mean $C{=}C_{olefinic}$ double bond distance of the COD ligand is 1.39 Å, but the exact values vary slightly, due to the asymmetry of the molecule. These distances are similar to those found for bis(ethylene)(η^6-toluene)iron[8] (2.07 and 1.41 Å, respectively) and indicate that no substantial change results in the bonding situation of (arene)-FeL_2 complexes if a C−H unit is replaced by a P atom within the aromatic π-ligand. The calculated plane containing the four olefinic carbon atoms is only slightly tilted with respect to that one of the phosphinine. The perpendiculars of the two planes intersect at an angle of 2.8°.

Reactivity Studies with 3. Due to its poor stability, no systematic reactivity studies have been undertaken with **6**; **3**, on the other hand, is easily accessible and robust as described above and proved suitable for systematic reactivity studies. All substitution reactions attempted to date show a strong preference for the COD ligand to be replaced rather than the phosphinine ligand. Reactions with diazadienes, for example, lead to (diazadiene)(phosphinine)Fe complexes. These reactions will be reported in detail at a later date; however, these reactions do demonstrate the stability of the (arene)iron fragment that results from the introduction of the phosphorus atom in the arene ligand. Corresponding reactions with related (toluene)iron complexes often lead to homoleptic (diazadiene)iron complexes, showing that the toluene ligand is not inert toward substitution by diazadienes, but phosphinine **2** is.[27] Initial attempts to test the ability of **3** to act as a catalyst in cyclic addition reactions have been successful. The addition of the electron-poor alkyne $C_2(COOCH_3)_2$ to solutions of **3** result with the catalytic formation at ≈ 80°C of the aromatic cyclotrimer $C_6(COOCH_3)_6$. On the other hand, the catalytic formation of benzene derivatives with catalyst **1** takes place at around 0°C;[28] the increase of the reaction temperature by 80 °C nicely demonstrates the built-in stabilization effect of the chelating leaving group, COD. As nitriles activate (arene)iron complexes,[3b,27] the relatively high reaction temperature does not exclude the desired room-temperature formation of pyridine derivatives by **3**.

3 as a Catalyst for Pyridine Formation by Cocyclization of Alkynes and Nitriles. In order to access regiochemical information and because of analytical reasons, the monosubstituted acetylene derivative, methyl propargyl ether, was reacted with butyronitrile in a toluene solution of the potential catalyst, **3**. The reaction proceeds well at room temperature, but relatively long reaction times are required to obtain good yields. Four main cyclization products are formed, pyridine derivatives **7a**,**b** as well as benzene derivatives **8a**,**b** (Scheme 4).

The symmetric 2,4,6-substituted pyridine derivative (**7b**) is preferred over the 2,3,6-derivative (**7a**), but the symmetric 1,3,5-substituted benzene derivative **8b** is produced in a lower yield than the asymmetric **8a**; however, this regioselectivity was not very pronounced (ca. 1.6:1). Only small traces of two other pyridine regioisomers have been detected by GC, but **8a**,**b** are the only cyclotrimerization products of the alkyne. Diazines or triazines have not been identified in the reaction mixtures.

For the initial screening of the catalytic properties of **3**, the concentrations of all three reaction components (butyronitrile, alkyne, and catalyst **3**) were changed systematically. A fourth significant factor is the polarity of the reaction mixture, which is strongly dependent on the nitrile concentration. Selected results of these experiments are summarized in Table 2. The concentration of butyronitrile used was increased stepwise from 5.7 to 103.5 mmol/10 mL of reaction mixture containing 5.9 mmol of alkyne and 0.003 mmol of **3**. The addition of the alkyne has varied from 1.2 to 11.8 mmol (51.7 mmol of butyronitrile, 0.003 mmol of **3**) as well as

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Scheme 4

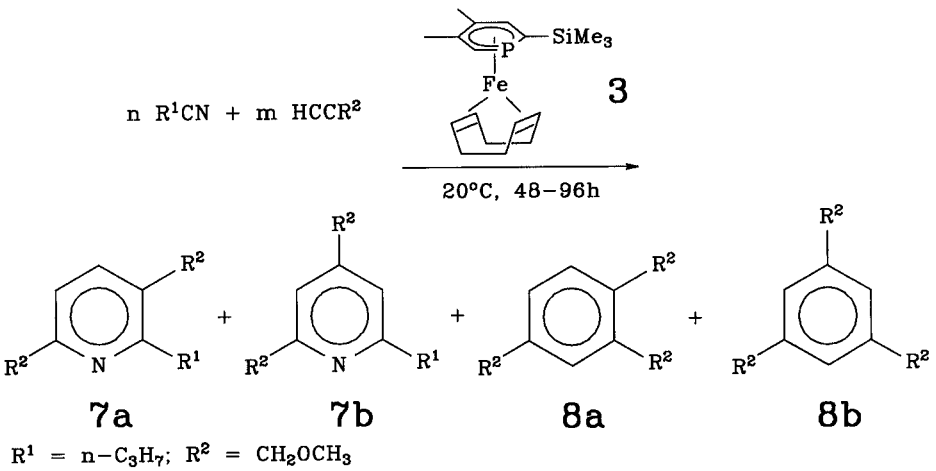

Table 2. Selected Data for Catalytic Pyridine Formation

(A) Composition of Reaction Mixtures (mmol)

expt	catal **3**	alkyne[a]	butyronitrile	toluene[b]
E1	0.003	5.92	23.0	65.9
E2	0.003	5.92	57.4	37.6
E3	0.003	5.92	103.5	
E4	0.003	1.92	51.7	41.4
E5	0.003	11.8	51.7	32.9
E6	0.005	11.8	51.7	37.6
E7	0.019	11.8	51.7	24.5

(B) Cyclic Addition Products

expt	pyridines[c] **7a** + **7b**	benzenes[c] **8a** + **8b**	chemo selectivity[d]	alkyne consumptn (%)
E1	99	145	0.69	32
E2	160	326	0.49	66
E3	117	427	0.25	84
E4	41	174	0.24	95
E5	102	160	0.64	17
E6	55	102	0.54	*e*
E7	52	96	0.54	*e*

[a] Methyl propargyl ether. [b] The amount of toluene used to yield 10 mL of reaction mixture. [c] In mol of product/mol of catalyst = TON. [d] TON(**7a** + **7b**):TON(**8a** + **8b**). [e] Not determined.

catalyst **3** which was varied from 0.003 to 0.019 mmol (11.8 mmol of alkyne, 51.7 mmol of butyronitrile). The reaction volume was maintained in all cases at 10 mL of reaction mixture with the solvent toluene as the fourth component.

In addition to the number of turnovers with respect to the amount of catalyst used (TON), the consumption of the alkyne and the chemoselectivity (number of moles of **7a** + **7b** formed divided by the number of moles of **8a** + **8b**) are also important data.

The best values obtained in this series of experiments are as follows: TON for pyridine formation (**7a** + **7b**), 160; alkyne consumption, 95%; chemoselectivity, 0.69. As for **1**, benzene derivatives are formed in higher yields compared with the pyridine derivatives, but their excess is significantly diminished. To our surprise, the optimal chemoselectivity and the maximal TON for pyridine formation are not found at the highest concentration of butyronitrile but are found at intermediate values (chemoselectivity, 23 mmol; TON, 57.4 mmol of butyronitrile). This effect is currently under investigation; one possible reason is the difference in polarity of these mixtures.

If we compare the data for **3** with the results of catalyst **1**,[3b] the following can be concluded: As anticipated, **3** is a room-temperature catalyst. The reaction temperature is elevated from −30 to +20 °C. The optimal catalyst concentration of **3** (0.3 mmol L^{-1}) is a factor of 10 smaller than that of **1,** but the reaction takes a much longer time. The turnover per mole of catalyst and second is slightly better for **1** at the respective chosen temperatures. The maximal TON for the pyridine derivatives increases from 22 to 160. Chemoselectivity for pyridine formation increases from 0.16 to 0.69. Regiospecifity is observed for the ortho positions of the pyridine derivatives of **7**. One of the two substituents is introduced with the nitrile and thus positioned necessarily there, and the other one stems from an alkyne molecule. The third substituent may occupy a *m*- or a *p*-position with no strong preference. The same principal results are found with CpCo catalysts, an additional argument for the close mechanistical relations of the two systems.[2,4,5]

In summary, we can conclude that a real improvement in the catalytic reaction results from the introduction of phosphinine **2** as a π-ligand to Fe(0). This improvement, however, is not yet sufficient to match the requirements of industrial processes or even to compete successfully with CpCo catalysts.[2] On the other hand, this paper demonstrates the possibility of systematically developing (arene)iron catalysts for a desired function. The system is far from being fully optimized. Variation of the solvent and reaction temperature and use of different alkynes and nitriles are currently under investigation. Heterocycles with other suitable heteroatoms or multiple P atoms are also being considered. Recently we developed a convenient route to the novel 1,3-diphosphinines, either as a free aromatic heterocycle or as a π-ligand to iron(0).[29]

Experimental Section

General Information. All reactions were carried out under an atmosphere of purified and dried nitrogen using Schlenk-type glassware. Solvents and educts were dried and saturated with nitrogen according to standard procedures.

Instruments used: ^{1}H-, ^{13}C-NMR, JEOL-GX 270 operating at 270 MHz (^{1}H) and 67.7 MHz (^{13}C), respectively; ^{31}P-NMR,

(29) Böhm, D.; Knoch, F.; Kummer, S.; Schmidt, U.; Zenneck, U. *Angew. Chem.* **1995,** *107*, 251; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 198. Knoch, F.; Böhm, D.; Zenneck, U. *Z. Kristallogr.* **1995**, *210*, 801.

JEOL-EX 270 operating at 109.3 MHz; mass spectra, Varian MAT 212 (EI-mode, 70 eV); IR, Perkin-Elmer FT-IR Model 16; Gas chromatography, Philips PYE UNICAM PU 4500 chromatograph equipped with a Supelcowax 10 capillary column.

Elemental analyses were performed at the microanalytical laboratory of the Institut für Anorganische Chemie, University of Erlangen-Nürnberg. The column chromatography material used was silica gel (70−230 mesh) deactivated with 5% degassed water. Metal vapor reactions were carried out in a locally constructed rotating metal atom reactor[17] (V = 6 L), which uses resistively heated alumina cruicibles in tungsten baskets as metal evaporators. The reactor allows low-temperature reactions of metal vapor with the ligands and the transfer of cold solutions with the exclusion of both air and moisture.

(η^4-1,5-cyclooctadiene)(η^6-2-(trimethylsilyl)-4,5-dimethylphosphinine)iron (3). (A) By Three-Component Reaction of Iron Vapor and the Ligands. Iron (1.5 g, 26.9 mmol) is distilled at a pressure of 10^{-2} Pa into a cold (−100 °C) solution of 3.92 g (20 mmol) of 2-(trimethylsilyl)-4,5-dimethylphosphinine[16b] and 2.21 g (20.4 mmol) of 1,5-*cis*,*cis*-cyclooctadiene in 400 mL of methylcyclohexane. The reaction mixture turns dark brown. After the complete evaporation of the metal, the temperature is raised to −30 °C and the mixture is filtered through alumina/5% H_2O, yielding a dark red solution which is stable at room temperature. After removal of the solvent in vacuo, the residue is recrystallized from light petroleum ether yielding 1.44 g of **3** (4 mmol, 20% based on 2-(trimethylsilyl)-4,5-dimethylphosphinine) as deep red crystals.

^{31}P-NMR (C_6D_6): δ 17.5. ^{1}H-NMR (C_6D_6): δ 0.4 (s, 9H, $SiMe_3$), 1.55 (m, 2H, CH_{2exo}), 1.89 (s, 3H, Me), 2.06 (m, 2H, CH_{2exo}), 2.14 (d, 1H, H_6, ^2J(P,H)) = 34.7 Hz), 2.26 (m, 2H, CH_{2endo} and m, 2H, H_{olef}), 2.69 (s, 3H, Me), 2.78 (m, 2H, CH_{2endo}), 3.14 (m, 2H, H_{olef}), 3.88 (d, 1H, H_3, ^3J(P,H) = 8.4 Hz). ^{13}C-NMR (C_6D_6): δ 0.07 (s, $SiMe_3$), 20.43 (s, Me), 21.08 (s, Me), 30.58 (s, CH_2), 34.18 (s, CH_2), 67.76 (s, C_{olef}), 68.35 (s, C_{olef}), 84.31 (d, C_5, ^1J(P,C) = 68.6 Hz), 93.61 (d, $C_{3/4}$, $^{2/3}J$(P,C) = 6.09 Hz), 99.44 (d, C_2, ^2J(P,C) = 7.92 Hz), 105.72 (d, C_1, ^1J(P,C) = 79.21 Hz), 109.39 (d, $C_{3/4}$, $^{2/3}J$(P−C) = 10.7 Hz). (Designation of nuclei corresponds to Figure 1 and Table 1.) MS [m/z (%)]: 360 (M^+, 86), 252 (M^+ − COD, 98), 196 (2^+, 84), 181 (2^+ − Me, 100). Anal. Calcd for $C_{18}H_{29}PSiFe$: C, 60.00; H, 8.12. Found: C, 59.67; H, 8.13.

(B) By a Ligand Exchange Reaction of Bis(1,5-cyclooctadiene)iron. Iron (4 g, 72 mmol) is evaporated at p = 10^{-2} Pa into a cold (−100 °C) solution of 1,5-cyclooctadiene in methylcyclohexane (35.3 mL, 288 mmol of COD in 350 mL of methylcyclohexane). A deep green color indicates the formation of $(COD)_2Fe$.[17] After the complete evaporation of the metal, the temperature is raised to −50 °C and a solution of 392 mg (2 mmol) of 2-(trimethylsilyl)-4,5-dimethylphosphinine in 25 mL of methylcyclohexane is added slowly. While the mixture is stirring, the temperature is slowly increased to room temperature over the course of 3 h, and the mixture is left at ambient temperature overnight. Filtration through alumina/5% H_2O yields a deep red solution. After removal of the solvent in vacuo, the residue is recrystallized from light petroleum ether yielding 612 mg (1.70 mmol, 85% based on to 2-(trimethylsilyl)-4,5-dimethylphosphinine) of **3** as deep red crystals. The product **3** obtained both ways, methods A and B, is identical.

(η^1-2-Chloro-4,5-dimethylphosphinine)$Cr(CO)_5$ (5). 2-Chloro-4,5-dimethylphosphinine (555 mg, 3.5 mmol)[16d] and $Cr(CO)_5(CH_3CN)$ (816 mg, 3.5 mmol) are heated in 50 mL of dry THF at 60 °C for 1 h. After cooling and evaporation of the solvent, the residue is chromatographed. A yellow fraction can be eluted with light petroleum ether. After removal of the solvent, the residue is recrystallized from light petroleum ether, yielding 992 mg of **5** (81% based on 2-chloro-4,5-dimethylphosphinine) as yellow crystals.

^{31}P-NMR ($CDCl_3$): δ 209. ^{1}H-NMR ($CDCl_3$): δ 2.34 (d, 3H, Me, ^4J(P,H) = 7.9 Hz), 2.39 (s, 3H, Me), 7.77 (d, 1H, H_3, ^3J(P,H) = 12.5 Hz), 8.1 (d, 1H, H_6, ^2J(P,H) = 27.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 21.83 (d, Me, ^4J(P,C) = 4.06 Hz), 22.88 (d, Me, ^3J(P,C) = 9.41 Hz), 138.48 (d, C_1, ^1J(P,C) = 22.82 Hz), 140.14 (d, C_2, ^2J(P,C) = 9.41 Hz), 145.65 (d, $C_{3/4}$, $^{2/3}J$(P,C) = 17.47 Hz), 151.49 (d, C_5, ^1J(P,C) = 13.47 Hz), 158.32 (d, $C_{3/4}$, $^{4/5}J$(P,C) = 17.47 Hz), 214.16 (d, CO_{trans}, ^2J(P,C) = 17.47 Hz), 220.54 (d, CO_{cis}, ^2J(P,C) = 4.06 Hz). (Designation of nuclei is analogous to that for **3**.) IR (toluene): ν_{CO} 2072, 1999, 1957. MS [m/z (%)]: 349 (M^+, 18), 209 (M^+ − 5CO, 85), 173.6 (M^+ − 5CO − Cl, 52). Anal. Calcd for $C_{12}H_8ClCrPO_5$: C, 41.09; H, 2.3. Found: C, 40.57; H, 2.36.

(η^4-1,5-Cyclooctadiene)(η^6-[(η^1-μ-2-chloro-4,5-dimethylphosphinine)$Cr(CO)_5$]Fe (6) by Ligand Exchange Reaction of Bis(1,5-cyclooctadiene)iron. A solution of (η^1-2-chloro-4,5-dimethylphosphinine)$Cr(CO)_5$ (**5**) (350 mg, 1 mmol) in 25 mL of methylcyclohexane is added at −50 °C to 350 mL of a $(COD)_2Fe$ solution in the same solvent prepared in situ from 4 g of Fe (72 mmol) and 35.3 mL of COD (288 mmol) as described above. The reaction mixture is stored at −40 °C for 3−10 days until the green color of $(COD)_2Fe$ disappears and the solution turns red. The mixture was then stirred at −10 °C for 8 h and stored at −40 °C overnight. Filtering of the solution through alumina/5% H_2O at 0 °C yielded an extremely air sensitive red solution that can be handled at room temperature only for a few hours. After removal of the solvent in vacuo, the residue was diluted in light petroleum ether; column chromatography (−30 °C, silica gel) with light petroleum ether resulted in the elution of a red fraction, which is recrystallized from the same solvent yielding 427 mg of **6** (0.83 mmol, 83% based on **5**) as red crystals.

^{31}P-NMR (C_6D_6): δ 72.3. ^{1}H-NMR (C_6D_6): δ 1.2 (s, 3H, Me), 1.62 (m, CH_{2exo}), 1.81 (m, CH_{2exo}), 2.11 (d, 1H, H_6, ^2J(P,H) = 26.9 Hz), 2.18 (m, 2H, CH_{olef}), 2.35 (m, 2H, CH_{2endo}), 2.35 (s, 3H, Me), 2.54 (m, 2H, CH_{2endo}), 2.9 (m, 2H, CH_{olef}), 4.16 (d, 1H, H_3,^3J(P,H) = 10 Hz). ^{13}C-NMR (C_6D_6): δ 19.38 (d, Me, ^3J(P,C) = 6.1 Hz), 19.81 (s, Me), 31.33 (s, CH_2), 33.04 (s, CH_2), 71.1 (s, C_{olef}), 77.27 (s, C_{olef}), 80.19 (d, C_5, ^1J(P,C) = 6.1 Hz), 92.28 (d, C_4, ^2J(P,C) = 4.6 Hz), 101.81 (d, C_2, ^2J(P,C) = 3.1 Hz), 109.42 (s, C_3), 110.36 (d, C_1, ^1J(P,C) = 9.14 Hz), 215.89 (d, CO, ^2J(P,C) = 16.8 Hz), 221.17 (d, CO, ^2J(P,C) = 3.05 Hz). (Designation of nuclei is analogous to that for **3**.) IR (toluene): ν_{CO} 2068, 1993, 1950 cm^{-1}. MS [m/z (%)]: 513 (M^+, 18), 373 (M^+ − 5CO, 25), 265 (M^+ − 5CO − COD, 100). Anal. Calcd for $C_{20}H_{20}ClCrFePO_5$: C, 46.68; H, 3.92. Found: C, 46.32; H, 4.05.

X-ray Structure Determination of 3. Data were collected on a Siemens P4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structure was solved by direct methods and refined by the full-matrix least-squares method with weights $\omega = 1/\sigma^2$. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were taken from a difference fourier calculation and included as fixed contributions in the final stages of least-squares refinements.

Crystals of **3** were grown at −40 °C from a light petroleum ether solution. **3** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters a = 11.781(7) Å, b = 10.713(7) Å, c = 14.518(7) Å, β = 95.21°, V = 1825(2) Å^3, Z = 4, d(calcd) = 1.31 g/cm^3, and F(000) = 768. A total of 5602 reflections were recorded in the range 3° ≤ 2θ ≤ 54° at 200 K of which 2797 were considered as observed ($F \geq 4\sigma(F)$) for solution and refinement. The final refinement yielded R = 0.035 and R_w = 0.033. Selected bond lengths and angles are given in Table 1.

General Procedure for the Catalytic Cocyclization of Butyronitrile and Methyl Propargyl Ether. (COD)(η^6-2-(trimethylsilyl)-4,5-dimethylphosphinine)iron (**3**) is dissolved in toluene and added at room temperature to a mixture of butyronitrile, toluene, and methyl propargyl ether. The light yellow solution is stirred at room temperature under nitrogen

for 48 h. Product formation was analyzed by gas chromatography using independently prepared compounds as standards. Selected data for these experiments are listed in Table 2.

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Supporting Information Available: Tables giving the complete set of data for the catalytic pyridine formation by catalyst **3** and the complete set of structural data for **3** (description of the structure determination, atomic coordinates, isotropic and anisotropic thermal factors, bond angles and distances) (11 pages). Ordering information is given on any current masthead page.

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