[(Arene)(Diene)Fe] and [(Arene)(Diazadiene)Fe] Complexes: Preparation, Reactivity, and Catalytic Properties☆

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Two different routes to novel [(diene)(η^6-2,6-dimethylpyridine)Fe] complexes are reported, both of which utilize metal vapour reactions. The presence of two small substituents on the 2,6-position of pyridine is essential for the η^6-coordination of the heterocycle. Investigations on the reactivity and stability of the [(diene)(η^6-arene)Fe] complexes are presented, including those of the benzene, phosphinine, and pyridine derivatives. These investigations give some hints to the relevant factors for determining the interaction between an iron atom and a π-coordinated neutral arene ligand, and their modification by a nitrogen or a phosphorus atom. Selective substitution of the 1,5-cyclooctadiene (COD) ligand of [(COD)(η^6-arene)Fe] complexes by some 1,4-diaza-1,3-diene (DAD) derivatives is possible in the case of the benzene or phosphinine arene ligands, and [(DAD)(η^6-arene)Fe] complexes are formed, but all DAD derivatives tested so far cause the complete disintegration of [(COD)(η^6-2,6-dimethylpyridine)Fe]. [(DAD)(η^6-arene)Fe] complexes exhibit a catalytic potential, which was evaluated by experiments on the catalytic cyclodimerization of 1,3-butadiene in the presence of [(Et_2AlOEt)$_2$] as a co-catalyst. This reaction yields up to 92% of 1,5-cyclooctadiene, and an almost quantitative butadiene conversion is possible in the presence of less than 0.1% of the catalyst. Structural investigations on [(*N,N′*-bis(cyclohexyl)ethylenediimine)(η^6-toluene)Fe] **5a** reveal some details of the Fe-DAD interaction. An effective electron back-donation from occupied iron d-orbitals into the π*-LUMO of the DAD is indicated.

Diazadienes (DAD, **1**) exhibit a rich coordination chemistry[1], as they can formally act as 2-, 4-, 6-, or 8-electron donors. Metal coordination of the heterodiene is possible in different conformations since rotation of the central C−C-bond is only slightly energetically hindered (20−28 $kJmol^{-1}$). The most frequent case is coordination in the end-on chelate ligating mode, where the σ-lone pairs of the two nitrogen atoms are donated to a metal atom. A high catalytic potential has been found for such σ-diazadiene iron complexes in connection with unsaturated hydrocarbons. For example [(DAD)$_2$Fe] (**2**) derivatives[2] are catalysts for the cyclodimerization of 1,3-dienes in the presence of alkyl aluminium co-catalysts, to form vinylcyclohexene and 1,5-cyclooctadiene derivatives. [(DAD)$FeCl_2$] is activated by Grignard reagents. It allows efficient cyclodimerization, or co-dimerization, reactions of dienes and alkenes under mild conditions, and a Diels-Alder type reaction of 1,3-dienes with alkynes[3].

Both catalytically active species have the 12 valence electron (VE) fragment [(DAD)Fe] in common, which is believed to be part of the true catalyst[4]. With the aim of finding new catalytically active species with complementary properties to the known ones, and as the influence of the leaving ligand of a pro-catalyst may be decisive for such a process, we are interested in (DAD)Fe complexes with labile co-ligands.

On the basis of our own work on arene iron complexes, we have some knowledge about the conditions necessary to replace an arene ligand by other substrates at ambient or slightly elevated temperatures[5], and thus we decided to prepare the novel [(η^6-arene)(DAD)Fe] complexes. Attempts to prepare this class of compounds have been reported, but no full evidence was presented[6]. We found convenient synthetic routes for their preparation, including the iron complexes of heteroarenes. Some initial experiments on their catalytic potential demonstrated the merits of the concept.

Our synthetic approach to these complexes is that of an alkene ligand exchange reaction by diazadiene derivatives, which are allowed to react with [bis(alkene)(η^6-arene)Fe] or the corresponding diene complexes. Such compouds are known for benzene[7] and phosphinine[8] derivatives acting as the η^6-arene ligand, but no report about a pyridine derivative of this type has yet appeared in the literature. As

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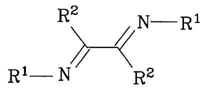
pyridine derivatives are believed to be decisively different in their π-ligand properties in respect to the other arenes, [(diene)(η^6-pyridine)Fe] complexes were our first synthetic goal. As for the phosphinines, the σ-lone pair of the hetero atom has to be shielded by one, or better two, *o*-substituents attached to the ring ligand in order to prevent the kinetically preferred σ-coordination[9][10]. The most simple pyridine derivative fulfilling this condition is 2,6-dimethylpyridine, which we therefore included in our studies.

The diazadiene derivatives **1a−g** used in this study are shown in Table 1.

Table 1. Diazadiene derivatives used

1a − g



	R^1	R^2
1a	Cyclohexyl	H
1b	*iso*-Propyl	H
1c	*tert*-Butyl	H
1d	*p*-Tolyl	Me
1e	*p*-Tolyl	Ph
1f	*p*-Anisyl	Me
1g	2,6-Dimethylphenyl	Me

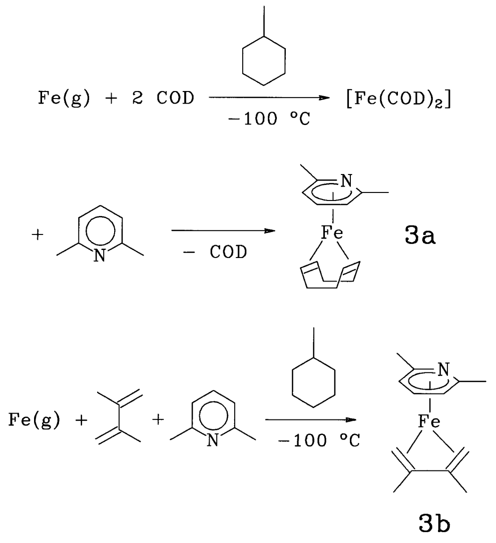
[(Diene)(η^6-2,6-Dimethylpyridine)Fe] Complexes and their Reactivity Towards Diazadienes

Highly reactive [$(COD)_2Fe$] was prepared in situ by reacting 1,5-cyclooctadiene (COD) with iron atoms in a metal vapour reaction[11]. Addition of 2,6-dimethylpyridine to the mixture at low temperatures results in the substitution of one COD ligand, and the desired product [(COD)(η^6-2,6-dimethylpyridine)Fe] **3a** is formed in a moderate yield. The same experiments have been performed with [$(COD)_2Fe$] and 2-trimethylsilylpyridine, 2,6-bis(trimethylsilyl)pyridine, or 2,6-bis(chloromethyl)pyridine. According to NMR studies of the crude product, the monosilylated heterocycle gave around a 5% yield of the corresponding [(COD)(η^6-2-trimethylsilylpyridine)Fe]. Due to the small amounts formed, no workup was attempted. The other pyridine derivatives failed completely to produce any observable π-complexes.

[(2,3-Dimethylbutadiene)(η^6-2,6-dimethylpyridine)Fe] **3b** is accessible directly, but only in poor yield, by a three-component reaction of stoichiometric quantities of iron vapour, 2,3-dimethylbutadiene and 2,6-dimethylpyridine. To the best of our knowledge, **3a** and **3b** represent the first examples of (η^6-pyridine)iron complex derivatives.

3a and **3b** are soluble in polar and apolar organic solvents, but strong donor solvents, such as acetonitrile, rapidly destroy the COD complex **3a**. Solutions of **3a** decompose slowly even in apolar solvents at room temp., whereas **3b** is stable under these conditions, probably due to the stabilizing effect of the conjugated diene ligand. Therefore the NMR spectroscopic characterization of **3a** has to be done at −10°C or lower. This problem does not exist for **3b**.

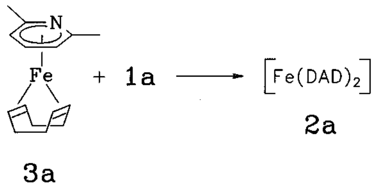
Scheme 1



Both compounds exhibit all the characteristics of π-complexes. There is no hint of σ-coordination of the nitrogen atom. For example the NMR data of **3a** and **3b** are closely related to those of their carbacyclic analogues [(COD)(η^6-toluene)Fe] and [(2,3-dimethylbutadiene)(η^6-toluene)Fe], respectively[12]. The observation of high-field coordination shifts for all ring nuclei investigated are a proof for the π-coordination of the heterocycle in both cases. In contrast to the otherwise much more reactive arene iron species [$(ethene)_2$(η^6-toluene)Fe] (**4**) (vide infra), the reaction of 2,6-dimethylpyridine complex **3a** and *N*,*N′*-bis(cyclohexyl)ethylenediimine **1a** results in a complete exchange of ligands and [(*N*,*N′*-bis(cyclohexyl)ethylenediimine)$_2$Fe] (**2a**) is formed as the only isolable species. This a known compound[2][4].

As expected, the reactivity of the η^6-coordinated 2,6-dimethylpyridine ligand of the iron atom is different from that of the carbacycle toluene. As hoped for, it is enhanced, but to such an extent that the replacement of the heterocycle by **1a** occurs parallel with the desired substitution of the diene ligand. [(DAD)(η^6-2,6-dimethylpyridine)Fe] complexes cannot therefore be made in this way.

Scheme 2

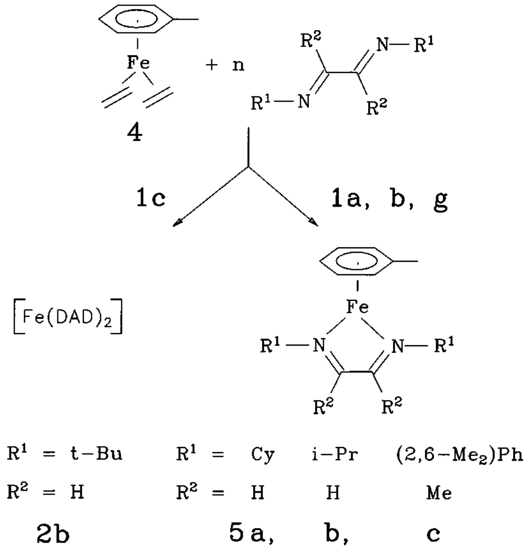


[(DAD)(η^6-Toluene)Fe] Complexes

[$(Ethene)_2$(η^6-toluene)Fe][7] **4** is well known as a highly reactive starting material which gives convenient access to many (η^6-toluene)Fe complexes, or FeL_n species, at low temperatures, depending on the reaction partners[5][13]. In contrast to the significantly more stable pyridine π-complex **3a** only the two ethene ligands of **4** are substituted by **1a**,

b, and **g** around −20°C, and [(DAD)(η^6-toluene)Fe] derivatives **5a−c** are formed in satisfactory to good yields.

Scheme 3



To our surprise, the complete coordination sphere of **4** was substituted under the same reaction conditions by the bis(*tert*-butyl) species **1c**, and the corresponding [(DAD)$_2$Fe] derivative **2b**[4] is the only isolable product of this reaction. Finally, the tolyl compounds **1d**, **e** and the anisyl derivative **1f** produce multicomponent reaction mixtures, which we have not been able to work up yet. Compared to the others, which substitute only the ethene ligands of **4**, **1c** contains bulkier *N*-alkyl substituents, but the increase in bulk is small compared to the cyclohexyl substituents of **1a**, and the 2,6-dimethyl phenyl substituents of **1g.** Therefore, the reason for this selective reactivity of DAD derivatives towards **4** is not yet clear and this point is currently under investigation.

Solid or dissolved **5a−c** are stable at room temp. and the solutions start decomposing around 40°C. Workup by column chromatography, however, requires low temperatures in order to prevent heavy losses. As was the case for **3a** and **b** the interpretation of the spectroscopic data of **5a−c** is straightforward and the desired products are definitely formed.

As **5** represents only the second class of compounds observed where arene iron fragments are combined with N-donor co-ligands in stable complexes, we are interested in more detailed information about the bonding situation between the metal and its ligands. In particular the Fe-DAD interaction is of interest. This fragment should be closely related to the active species of the diene dimerization (DAD)Fe catalysts.

An X-ray structure determination of crystalline [(*N,N*′-bis(cyclohexyl)ethylenediimine)(η^6-toluene)Fe] **5a** was accomplished. The molecular structure in the solid state is shown in Figure 1 and some selected bond lengths are summarized in Table 2.

Figure 1. Molecular structure of **5a** in the solid state

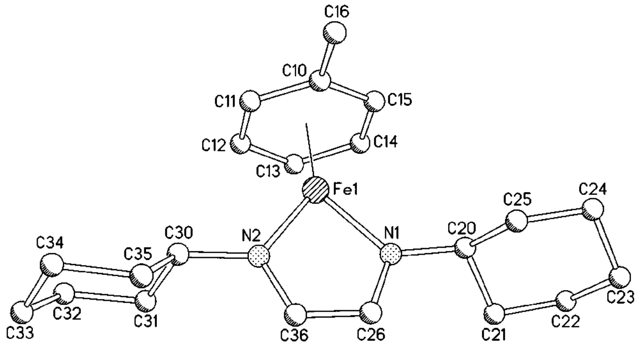


Table 2. Selected bond lenghts (pm) of **5a**

Fe−C10	208.1(3)	Fe−C11	209.4(3)
Fe−C12	208.7(3)	Fe−C13	208.9(3)
Fe−C14	210.0(3)	Fe−C15	210.1(3)
Fe−N1	189.9(2)	Fe−N2	190.1(2)
N1−C20	146.6(3)	N2−C30	146.4(3)
N1−C26	134.4(4)	N2−C36	133.6(4)
C26−C36	137.9(4)		

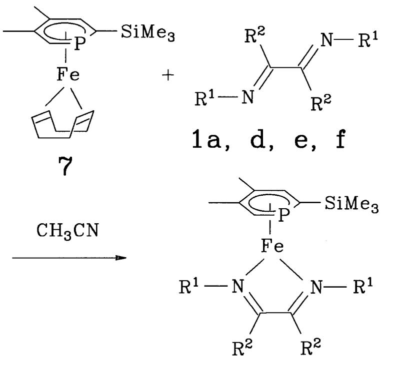
There are no unusually short intermolecular distances detectable in the unit cell. As a consequence, the details of the molecular structure have to be discussed mainly on the basis of intramolecular considerations. In full accord with the spectra, the DAD ligand acts as a chelate ligand, donating its N-lone pair electrons to the iron atom, and all ring carbon atoms of the planar toluene ligand are within bonding distance to the metal. The variation of the Fe−C bond lenths is small (208−210 pm), thus the metal is symmetrically bonded to the carbacycle. The Fe-DAD chelate ring is also planar, and both rings are oriented perpendicular to each other (90.4°). The bond distances within the ferradiazacyclobutadiene substructure of **5a** reflect the bonding situation between the iron atom and the DAD ligand, which is our main point of interest in this context. There is only one study dealing with related structural and electronic features of an arene iron complex. The authors who investigated [(2,2′-bipyridyl)(η^6-toluene)Fe] **6**[14] point out the significant role of back-donation of π-electron density from the iron atom into the π*-orbitals of the bipyridyl ligand which they deduced from C−C- and C−N bond length variations within the bipyridyl ligand. This effect reduces the d-electron density of the occupied orbitals of the metal involved in this interaction.

If we compare the bond lenghts between free[15] and coordinated **1a** within **5a,** the distance C26−C36 is reduced by 7.8 pm, whereas the average of the distances C26−N1 and C36−N2 is increased by 4.3 pm. Exactly the same trends are observed for the corresponding parts of the molecule **6,** but the effect is slightly smaller (−7.3 and +3.9 pm, respectively)[14]. As a consequence the same interpretation seems to be appropriate for both compounds and we have to state that there is a slightly stronger electron back-donation from the iron atom of **5a** into the π*-LUMO of **1a**, which is antibonding in respect to the C=N double bonds, but bonding in respect to the central C26−C3 single bond. This synergetic metal−ligand interaction creates a partial double bond character of the Fe−N bonds as well, which manifests itself in extremely short Fe−N bonds in the case of **5a** and **6** in relation to other examples of N-donor ligands complexed to iron[14]. We can thus classify the DAD as a very good π-acceptor of Fe d-electrons, and this interpretation is confirmed by independent NDDO calculations[16]. The decisive role of back-bonding for complexes of the type [(arene)(N−N−donor)Fe] is demonstrated by the experiments which aimed to produce [(toluene)(TMEDA)Fe], but which resulted in a completely different chemistry[17]. Being the formal hydrogenation product of a DAD derivative, the saturated N−N donor ligand TMEDA forms a closely related chelate ring with a complexed metal atom, but it completely lacks an appropriate π*-orbital and therefore cannot act as an π-acceptor.

[(DAD)(η^6-2-Trimethylsilyl-4,5-Dimethylphosphinine)Fe] Complexes

From earlier work we know about the activating role of nitriles in initiating reactions of stable [(COD)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] **7**, which require the dissociation of the Fe−COD π-bond[8]. Because of a close relation between imine and nitrile N-donor ligands, DAD derivatives have first been reacted with **7** in the absence of nitriles. The reaction works, but requires elevated temperatures and the yields, as well as the purity of the products obtained, are not convincing. Running the same reaction with acetonitrile as the solvent, the substitution of COD by the DAD derivatives **1a, d, e, f** takes place at room temp. and moderate yields of the desired products are obtained. The [(DAD)(η^6-2-trimethylsilyl-4,5 dimethylphosphinine)Fe] derivatives **8a−d** have been prepared in this way.

Scheme 4



R^1 =	Cy	p−Tol	p−Tol	p−Anis
R^2 =	H	Me	Ph	Me
	8a,	b,	c,	d

8a−d are much more robust than the other π-complexes reported in this paper. Workup by column chromatography, for example, is possible at room temp. without losses.

Some Considerations on the Stability of Arene Iron Complexes

The preparative results of this study give an improved insight into the relative stability and reactivity of π-arene iron complexes of pyridine, benzene, and phosphinine derivatives. All three allow the preparation of [(arene)(diene)Fe] complexes[18]. Their stability as pure compounds, as solvated complexes in solution, or during workup by chromatography always increases in the sequence: pyridine < benzene < phosphinine.

In reacting such complexes with DAD derivatives, the same order is reproduced. The pyridine complex is disintegrated completely by DADs, even at temperatures below room temp. In spite of the fact that we did not react a diene, but the bis(ethene)Fe complex **4,** with different DADs, we can state that there is a differentiated behaviour, depending on the DAD substituents. However, in several cases the DAD derivative substitutes the ethene ligands in the presence of a π-toluene spectator ligand. The phosphinine complex **7**, however, requires either elevated temperatures, or the presence of nitriles as activating solvents, for the desired substitution reaction. Up to now, we found no indication of a substitution of the P-heterocycle of **7** parallel to the replacement of the COD ligand.

Without thermochemical data it is difficult to differentiate between thermodynamic and kinetic factors of complex stabilization. We believe in the predominance of the first factor, as the accessibility of the iron atom is not very different for the investigated substances.

Details of the electronic structures of the free arenes have been investigated for the unsubstituted rings[19] and these data have been used for comparing the π-ligand properties of benzene and phosphinine. Phosphinine is an equivalent π-donor but is the better π-acceptor ligand for transition metal atoms compared to benzene[20]. The two highest occupied orbitals of phosphinine are energetically close to the degenerate HOMO (e_{1g}) of benzene, but the LUMO (b_1) of phosphinine is significantly stabilized with respect to the LUMO (e_{2u}) of benzene. For pyridine the situation is different. Due to the higher electronegativity of the nitrogen atom combined with good π-orbital overlap, the LUMO (a_2) of pyridine is stabilized, but the HOMO is closer in its energy to the HOMO of benzene[19]. Consequently pyridine can be classified as a weaker π-donor, but a comparable π-acceptor ligand, with respect to benzene. From the combined data, we can rank the donor and acceptor capabilities of the arenes as follows:

π-Donor strength: phosphinine ≅ benzene > pyridine.

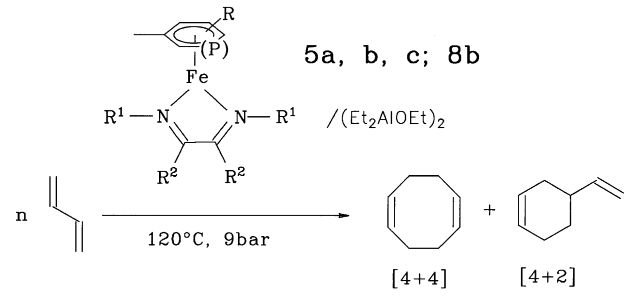
π-Acceptor potential: phosphinine > benzene ≅ pyridine.

For electron-rich transition metals such as iron, the combination of both factors determine the bonding energy of the metal to the π-ligand of such complexes. Thus the experimental findings, and this interpretation of the bonding situation of arene iron complexes, are in a good agreement.

Catalytic Properties

The catalytic potential of the [(DAD)(arene)Fe] complexes was tested by experiments on the catalytic cyclodimerization of 1,3-butadiene. For the purpose of comparison analogous reaction conditions to those for the [$(DAD)_2Fe$] catalysts were initially chosen, including the use of the [$(Et_2AlOEt)_2$] co-catalyst[4]. The cyclodimerization of 1,3-butadiene yields two main products, and [4 + 2] and [4 + 4] cyclic addition reactions are the favoured processes, which result in the formation of vinyl cyclohexene (VCH) and COD, respectively.

Scheme 5



5a−c and **8b** have been tested as catalysts for this reaction and control experiments have been carried out with [(COD)(toluene)Fe][12]; all in the presence, as well as in the absence, of the [$(Et_2AlOEt)_2$] co-catalyst. To rule out an independent role for [$(Et_2AlOEt)_2$], this also was used (without an iron complex). Product analysis was done by gas chromatography. Some selected data are summarized in Table 3.

Table 3. Selected data of catalytic cyclodimerization of 1,3-butadiene

Experiment No.	Catalyst / mmol	[$(Et_2AlOEt)_2$] / mmol	COD TON[a]	VCH TON[a]	Selectivity % COD[c]
1	**5a** / 0.062	0.4	972[b]	240	80.2
2	**5a** / 0.062	0.8	503	159	76.0
3	**5a** / 0.062	0.2	455	166	73.3
4	**5c** / 0.062	0.4	1479[b]	130	91.9
5	**8a** / 0.062	0.4	94	54	63.7

[a] TON = Turnover number, mole product per mole catalyst. − [b] Almost quantitative butadiene conversion. − [c] Percentage of the volatile products COD + VCH.

As hoped for, **5a−c** and **8b**, all in combination with the co-catalyst only, are cyclodimerization catalysts for the formation of COD and smaller amounts of VCH, whereas the combination [(COD)(toluene)Fe]/[$(Et_2AlOEt)_2$] yields only a little VCH. Product yield and chemoselectivity of the [(arene)(COD)Fe] catalysts are closely related to those of the other (DAD)Fe systems[2][3][4], a first indication of comparable catalytic processes for the complete family of catalysts. The main difference is the lower reactivity of the [(arene)(DAD)Fe] complexes. The optimal temp. here is 120°C, whereas [DAD)$_2$Fe] requires less elevated temperatures, and the in situ reduction of [(DAD)$FeCl_2$] results in the formation of an active species which already transfoms butadiene at room temp. A strong argument for the (DAD)Fe fragment to be part of the catalytically active species is deduced from the control experiments. Neither [(COD)(toluene)Fe] or [$(Et_2AlOEt)_2$] alone, nor a mixture of both components, are able to induce the formation of COD, the main product of the catalytic reaction. As mentioned above, the presence of the co-catalyst in the reaction mixture is essential. The best results have been obtained with a molar ratio of catalyst/co-catalyst ≅ 2:13. In some experiments the butadiene was almost completely converted into the products, thus the maximal number of turnovers is most probably higher than the greatest number given in Table 3. Complete reaction of butadiene was also found, in some cases, with the other (DAD)Fe catalysts[21].

Toluene complexes **5,** and the phosphinine species **8b,** differ slightly in their selectivity of COD formation. Depending on the reaction conditions, 76−92% COD are formed by the derivatives of **5**, whereas **8b** produces 64% COD, but the difference in their reactivity is much more pronounced. Under the same conditions the catalysts **5** act approximately ten times faster than **8b**. We believe the higher turover frequency of the toluene complexes to be the main reason for their almost quantitative butadiene conversion.

The much higher reactivity of the complexes **5a−c** nicely parallels our findings on the substitution reactions of iron complexes with toluene or phosphinine π-arene ligands (vide supra). Obviously, the stronger Fe−phosphinine interaction hampers the generation of the true (DAD)Fe catalyst from the pro-catalyst **8b**. On the other hand, closed shell 18 valence electron (VE) species like **5a−c** are relatively stable. In contrast to the paramagnetic 16 VE [(DAD)$_2$Fe] derivatives, for example, hydrolysis does not play a role here. Thus the reactivity of the catalytically active systems follows the stability of the different types of (DAD)Fe complexes, another hint that there are analogous reaction mechanisms in all cases.

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Experimental Section

All reactions were carried out under a dry, oxygen free, nitrogen atmosphere. Solvents were purified by conventional methods, distilled and stored under nitrogen. − Unless otherwise stated, NMR spectra were recorded around room temp. on a Jeol FT-JNM-EX 270 spectrometer (269.6 MHz for ^1H, 67.7 MHz for ^{13}C, and 109.4 MHz for ^{31}P NMR), using dimethylpolysiloxane and solvent signals as internal standards for ^1H and ^{13}C, and 85% H_3PO_4/water as an external standard for ^{31}P NMR. The degree of substitution of the C-atoms was determined by DEPT spectra. − Mass spectra were recorded on a varian MAT 212 spectrometer (EI, 70 eV). − Microanalyses were peformed at the analytical department of the institute, using a Carlo Erba Elemental Analysers Mod. 1106. − Gas chromatography was done with a Philips PYE UNICAM PU 4500 chromatograph equipped with a supelcowax 10 capillary column l = 60 m, dia. = 0.75 mm. Column chromatography (15 × 1 cm) was accomplished with neutral degassed alumina or silica (Merck), deactivated with 5% degassed water. − Metal vapour reactions were carried out in a locally constructed rotating metal atom reactor[22], which uses resistively heated alumina crucibles in tungsten baskets as metal evaporators. The reactor allows low temp. reactions of metal vapours with liquid substrates, or solutions of substrates in low melting point solvents, and the transfer of cold solutions with complete exclusion of air and moisture.

The following starting materials have been prepared according to published procedures: DAD derivatives **1a**[23a], **1b**, **c**[23b], **1d**, **e**, **f**[23c], **1g**[23d], [(ethene)$_2$(η^6-toluene)Fe] **4**[7] , and [(COD)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] **7**[8]. All other substances have been purchased from commercial sources in synthetic quality and have been purified by distillation and saturation with pure nitrogen gas. Prior to use, 1,3-butadiene was condensed from a gas cylinder in a Schlenck tube at −78°C and stored there for several hours on a molecular sieve (0.5 nm).

[(COD)(η^6-2,6-dimethylpyridine)Fe] (**3a**): 8 g of iron gas (0.14 mol) was distilled into a mixture of 26,4 g of 1,5-*cis-cis*-cyclooctadiene (COD) (0.24 mol) and 300 ml of methylcyclohexane. During the course of reaction the gas pressure and the temp. of the liquid phase were held below 10^{-2} Pa and −100°C, respectively. The colour of the reaction mixture turned to dark green, while [(COD)$_2$Fe] was formed[11]. After completion of the metal vapour reaction, the cooling bath was removed. When close to −50°C the mixture was transferred to a round bottom flask and 921 mg 2,6-dimethylpyridine (8.6 mmol) was added at −40°C. It was then stirred and allowed to warm up slowly in air. Around −5°C the colour turned to red and the reaction was completed by stirring for 3 h at room temp.. Solvent and excess of COD were stripped off in vacuum and the residue was diluted in light petroleum ether (PE). Column chromatography (−30°C; alumina/5% water) resulted in two red fractions eluted by PE and toluene/THF (1:2), respectively. The toluene/THF solution contained red **3a**. Removal of the solvents and recrystallization from *n*-pentane yielded 716 mg (30,7%) of the dark red crystalline solid. − ^{1}H NMR ([D$_8$]toluene, −10°C): δ = 5.45 (d, J_{HH} = 10 Hz, 2 H, CH-pyr.), 3.05 (m, 1 H, CH-pyr.), 2.85 (m, 4 H, CH-COD), 2.55 (m, 4 H, CH$_2$-COD/*endo*); 2.35 (s, 6 H, CH$_3$-pyr.), 1.85 (m, 4 H, CH$_2$-COD/*exo*). − ^{13}C{^{1}H} NMR ([D$_8$]toluene, −10°C): δ = 115.8 (C-pyr.), 86.2 (CH-pyr.), 78.2 (s, CH-pyr.), 68.0 (CH-COD), 31.4 (CH$_2$-COD); 20.4 (CH$_3$-pyr.). − MS (70 eV) *m*/*z*: 271 [M$^+$], 163 [M$^+$ − COD]. − $C_{15}H_{21}FeN$ (271.10): calcd. C 66.44, H 7.81, N 5.17, found: C 66.50, H 7.90, N 5.03.

Reaction of **3a** *with DAD* **1a**: 222 mg of **3a** (0.82 mmol) was added to a solution of 180 mg of *N,N′*-bis(cyclohexyl)ethylenediimine **1a** (0.82 mmol) in 30 ml of toluene at −10°C. The mixture was stirred for 15 h without cooling, thus the temp. increased slowly to room temp.. Then the resulting dark suspension was filtered at −60°C through 3 cm alumina on a frit and a red solution was obtained. After removal of the solvent and recrystallization from *n*-pentane 123 mg (64.1%) of analytically pure, dark crystalline [bis(*N,N′*-bis(cyclohexyl)ethylenediimine)iron] was afforded. Within the experimental limits, all data on this compound are identical with those published in the literature[4].

[(η^4-2,3-Dimethylbutadiene)(η^6-2,6-dimethylpyridine)Fe] (**3b**): 8 g of iron gas (0.14 mol) was distilled into a mixture of 11.7 g of 2,3-dimethylbutadiene (0.14 mol), 15.3 g of 2,6-dimethylpyridine (0.14 mol), and 300 ml of methylcyclohexane as described before. The reaction mixture darkened until it was finally almost black. After completion of the metal vapour reaction, the cooling bath was removed to allow slow warming up. At −25°C the mixture was filtered through 3 cm alumina/5% H$_2$O on a frit, the alumina was extracted with toluene/THF, the liquid phases united, and the solvent removed in vacuo. Redilution in PE and column chromatography (−30°C; alumina/5% water) resulted in the formation of two red fractions (PE and toluene/THF, 1:4). The second fraction contained the desired product **3b**. Recrystallization from *n*-pentane gave 584 mg (1,7%) of red needles. − ^{1}H NMR ([D$_6$]benzene): δ = 5.12 (m, 1 H, CH-pyr.), 4.57 (m, 2 H, CH-pyr.), 2.30 (s, 6 H, CH$_3$), 1.93 (s, 6 H, CH$_3$), 1.04 (s, 2 H, CH$_2$-butad.), −0.53 (s, 2 H, CH$_2$-butad.). − ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 113.4 (C-pyr.), 91.2 (CH-pyr.), 84.7 (s, CH-pyr.), 78.9 (C-butad.), 39.8 (CH$_2$-butad.), 23.3 (CH$_3$), 19.3 (CH$_3$). − MS (70 eV) *m*/*z*: 245 [M$^+$], 163 [M$^+$ − butad.], 138 [M$^+$ − pyr.]. $C_{13}H_{19}FeN$ (245.14): calcd. − C 63.69, H 7.81, N 5.71, found: C 63.76, H 7.75, N 5.52.

[(N,N′-Bis(cyclohexyl)ethylenediimine)(η^6-toluene)Fe] (**5a**): 292 mg of *N,N′*-bis(cyclohexyl)ethylenediimine (**1a**) (1.33 mmol) was suspended by stirring in 50 ml of toluene (1.35 mmol), and a solution of 275 mg of (1.35 mmol) [(ethene)$_2$(η^6-toluene)Fe] **4** in 10 ml of toluene was added, both were at −40°C. A badly isolated cooling bath (three plastic bowls of the same size, one put into the other) containing ca. 200 ml of ethanol at a temp. of , originally, ca. −40°C, allowed a slow increase in the temp. At −20°C the reaction mixture turned dark. The reaction was completed by stirring overnight at room temp.. After removal of the solvent, the residue was dissolved in PE. Column chromatography (−30°C; alumina) yielded two fractions (PE and PE/toluene, 3:1). The second fraction contained the desired red brown product **5a**. It was recrystallized twice, from acetonitrile and *n*-pentane, yielding 234 mg (47.7%) of dark crystals. − ^{1}H NMR ([D$_6$]benzene): δ = 6.76 (s, 2 H, CH-imine), 5.58 (t, *J* = 6 Hz, 1 H, CH-tol.), 5.20 (t, *J* = 6 Hz, 2 H, CH-tol.), 5.11 (d, *J* = 7 Hz, 2 H, CH-tol.), 4.47 (m, 2 H, CH-cy.), 2.30 (s, 3 H, CH$_3$-tol.), 2.24 (s, 4 H, CH$_2$-cy.), 1.55 (m, 14 H, CH$_2$-cy.), 1.10 (m, 2 H, CH$_2$-cy.). − ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 133.9 (CH-imine), 92.2 (C-tol.), 80.9 (CH-tol.), 79.4 (CH-tol.) 79.3 (CH-tol.), 70.0 (CH-cy.), 35.5 (CH$_2$-cy.); 27.1 (CH$_2$-cy.), 26. 5 (CH$_2$-cy.), 21.4 (CH$_3$-tol.). − MS (70 eV) *m*/*z*: 368 [M$^+$], 276 [M$^+$ − **1a**]. − $C_{21}H_{32}FeN_2$ (368.19).

[(N,N′-Bis(2-propyl)ethylenediimine)(η^6-toluol)Fe] (**5b**): Preparation as described for **5a** from 266 mg (1.90 mmol) of **1b** and 387 mg (1.90 mmol)of **4**. Recrystallization from *n*-pentane yielded 315 mg (57.6%) of **5b**. − ^{1}H NMR ([D$_6$]benzene): δ = 6.75 (s, 2 H, CH-imine), 5.55 (t, *J* = 6 Hz, 1 H, CH-tol.), 5.08 (t, *J* = 6 Hz, CH-tol.), 5.01 (d, *J* = 6 Hz, 2 H, CH-tol.), 4.80 (sept, *J* = 6 Hz, 1 H, CH-isopr.), 2.27 (s, 3 H, CH$_3$-tol.), 1.40 (d, *J* = 7 Hz, 12 H, CH$_3$-isopr.). − ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 133.4 (CH-imine), 92.8 (C-tol.), 81.1 (CH-tol.), 79.8 (CH-tol.), 79.7 (CH-tol.), 60,4 (CH-isopr.), 24,6 (CH$_3$-isopr.), 21.8 (CH$_3$-tol.). − MS (70 eV) *m*/*z*: 288 [M$^+$], 196 [M$^+$ − **1b**]. − $C_{15}H_{24}FeN_2$ (288.21).

[(N,N′-Bis(2,6-dimethylphenyl)-2,3-butanediimine)(η^6-toluene)Fe] (**5c**): Preparation as described for **5a** from 316 mg (1.08 mmol) of **1g** and 265 mg (1.30 mmol) of **4**. Recrystallization from *n*-pentane yielded 161 mg (33.9%) of **5c**. − ^{1}H NMR ([D$_6$]benzene): δ = 7.2 (m, 6 H, CH-phenyl), 5.30 (t, *J* = 5 Hz, 1 H, CH-tol.), 4.52 (t, *J* = 5 Hz, 2 H, CH-tol.), 4.46 (d, *J* = 5 Hz, 2 H, CH-tol.), 2.26 (s, 12 H, CH$_3$-phenyl), 1.95 (s, 3 H, CH$_3$-tol.), 1.00 (s, 6 H, CH$_3$-imine). − ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 157.1 (C-phenyl), 141.6 (C-phenyl), 131.0 (CH-phenyl), 129.2 (C-imine), 124.5 (CH-phenyl), 94.5 (C-tol.), 82.0 (CH-tol.), 81.3 (CH-tol.), 80.7 (CH-tol.), 20,1 (CH$_3$-tol.), 18,3 (CH$_3$-phenyl); 15,6 (CH$_3$-imine). − MS (70 eV) *m*/*z*: 277 [**1g**$^+$−CH$_3$]. − $C_{25}H_{32}FeN_2$ (368.19).

[(N,N′-Bis(cyclohexyl)ethylenediimine)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] (**8a**): 179 mg (0,81 mmol) of **1a**, 293 mg (0,81 mmol) of [(COD)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] **7** and 50 ml of acetonitrile were mixed at room temp. and stirred for 20 h. The orange reaction mixture slowly darkens and finally was nearly black. After removal of the solvent in vacuo the residue was dissolved in PE and subjected to column chromatography on silica/5% water. PE eluted some unreacted **7** and free phosphinine, whereas PE/toluene (1:1) gave a dark red fraction. Removal of the solvent and recrystallization afforded 146 mg (28.1%)

of dark red **8a**. − ^{1}H NMR ([D$_6$]benzene): δ = 6.75 (s, 2 H, CH-imine), 5.43 (d, J_{PH} = 10 Hz, 1 H, CH-phosp.) 4.70 (d, J_{PH} = 36 Hz, 1 H, CH-phosp.), 4.25 (m, 2 H, CH-cy.), 2.55 (m, 5 H, CH-cy. + CH$_3$ -phosp.), 2.35 (s, 3 H, CH$_3$ -phosp.), 2.00 (m, 2 H, CH-cy.), 1.52 (m, 14 H, CH-cy.), 1.06 (m, 2 H, CH-cy.), 0.45 [s, 9 H, Si(CH$_3$)$_3$]. − ^{13} C{^{1}H} NMR ([D$_6$]benzene): δ = 137,8 (CH-imine), 99.0 (d, J_{PC} = 12 Hz, CH-phosp.), 95.2 (d, J_{PC} = 8 Hz, CH-phosp.), 93.6 (d, J_{PC} = 78 Hz, C-phosp.), 90.0 (d, J_{PC} = 8 Hz, C-phosp.), 89.2 (d, J_{PC} = 68 Hz, CH-phosp.), 69.8 (CH-cy.), 43.6 (CH$_2$-cy.), 34.6 (CH$_2$-cy.), 27.0 (CH$_2$-cy.), 26.8 (CH$_2$-cy.), 26.4 (CH$_2$-cy.), 23.4 (CH$_3$-phosp.), 22.4 (CH$_3$-phosp.), 1,4 [Si(CH$_3$)$_3$]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = −17.7. − MS (70 eV) *m/z*: 472 [M$^+$]. − C$_{24}$H$_{41}$FeN$_2$PSi (368.19).

[(N,N′-Bis(4-tolyl)-2,3-butanediimine)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] (**8b**): Preparation as described for **8a** from 279 mg (1.06 mmol) of **1d** and 381 mg (1.06 mmol) of **7**. Recrystallization from *n*-pentane, yielded 219 mg (30.4%) of dark red **8b**. − ^{1}H NMR ([D$_6$]benzene): δ = 7.75 (d, J_{HH} = 8 Hz, 2 H, CH-tolyl), 7.10 (d, J_{HH} = 8 Hz, 2 H, CH-tolyl), 7.0 (m, 4 H, CH-tolyl), 5.05 (d, J_{PH} = 9 Hz, 1 H, CH-phosp.), 3.99 (d, J_{PH} = 36 Hz, 1 H, CH-phosp.), 2.50 (s, 3 H, CH$_3$-phosp.), 2.24 (s, 3 H, CH$_3$-phosp.), 2.22 (s, 6 H, CH$_3$-tolyl), 1.00 (s, 6 H, CH$_3$-imine), 0.36 [s, 9 H, Si(CH$_3$)$_3$]. − ^{13} C{^{1}H} NMR ([D$_6$]benzene): δ = 157.1 (C-tolyl), 146.1 (C-tolyl), 134.0 (C-imine), 125.6 (CH-tolyl), 124.3 (CH-tolyl), 99.0 (d, J_{PC} = 13.5 Hz, C-phosp.), 97.3 (d, J_{PC} = 6.6 Hz, CH-phosp.), 96.6 (d, J_{PC} = 77.9 Hz, C-phosp.), 91.2 (d, J_{PC} = 67.7 Hz, CH-phosp.), 90.2 (d, J_{PC} = 10.1 Hz, C-phosp.), 23.1 (CH$_3$-phosph.), 22.6 (CH$_3$-phosph.), 21.1 (CH$_3$-tolyl), 17.7 (CH$_3$-imine), 1.4 [Si(CH$_3$)$_3$]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = −12.85 (s). − MS (70 eV) *m/z*: 516 [M$^+$], 320 [M$^+$ − phosp.]. − C$_{28}$H$_{37}$FeN$_2$PSi (516.18).

[(N,N′-Bis(4-tolyl)-1,2-diphenylethylenediimine)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] (**8c**): Preparation as described for **8a** from 870 mg (2.23 mmol) of **1e** and 792 mg (2.20 mmol) of **7**. Chromatography was done with PE/toluene (3:1) and toluene. Toluene eluted the product. Recrystallization from PE yielded 270 mg (19.1%) of dark red **8c**. − ^{1}H NMR ([D$_6$]benzene): δ = 8.13 (dd, J_{HH} = 7 / 1 Hz, 2 H, CH-aryl) 7.05 (dd, J_{HH} = 7 / 1 Hz, 2 H, CH-aryl), 6.88 (dd, J_{HH} = 8 / 1 Hz, 2 H, CH-aryl), 6.70 (m, 6 H, CH-aryl), 6.60 (m, 6 H, CH-aryl), 5.48 (d, J_{PH} = 10 Hz, 1 H, CH-phosp.), 4.43 (d, J_{PH} = 34 Hz, 1 H, CH-phosp.), 2.55 (s, 3 H, CH$_3$-phosp.), 2.15 (s, 3 H, CH$_3$-phosp.), 2.03 (s, 6 H, CH$_3$-diimine), 0.25 [s, 9 H, Si(CH$_3$)$_3$]. − ^{13} C{^{1}H} NMR ([D$_6$]benzene): δ = 157.0 (C-aryl), 152.4 (C-aryl), 138.9 (C-aryl or C-imine), 133.6 (C-aryl or C-imine), 130.4 (C-aryl or C-imine), 127.3 (C-aryl), 126.9 (C-aryl), 126.0 (C-aryl), 125.6 (C-aryl), 103.2 (br., C-phosp.), 99.6 (br., C-phosp.), 99.0 (br., C-phosp.), 94.5 (br., C-phosph.), 90.6 (br., C-phosph.), 22.8 (CH$_3$-phosph.), 22.7 (CH$_3$-phosph.), 21.0 (CH$_3$-tolyl), 1.2 [Si(CH$_3$)$_3$]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = −11,7 (s). − MS (70 eV) *m/z*: 641 [M$^+$]. − C$_{38}$H$_{41}$FeN$_2$PSi (640.21): calcd. C 71.24, H 6.45, N 4.37, found C 71.12, H 6.81, N 3.94.

[(N,N′-Bis(4-anisyl)-2,3-butanediimine)(η^6-2-trimethylsilyl-4,5-dimethylphosphinine)Fe] (**8d**): Preparation as described for **8a** from 241 mg (0.81 mmol) of **1f** and 290 mg (0.87 mmol) of **7**. Recrystallization from *n*-pentane yielded 145 mg (32.5%) of dark red **8d**, which was always contaminated with traces of a second uncharacterized product. − ^{1}H NMR ([D$_6$]benzene): δ = 7.75 (d, J_{HH} = 8 Hz, 2 H, CH-anisyl), 7.01 (d, J_{HH} = 8 Hz, 2 H, CH-anisyl), 6.88 (d, J_{HH} = 8 Hz, 2 H, CH-anisyl), 6.79 (d, J_{HH} = 8 Hz, 2 H, CH-anisyl), 5.05 (d, J_{PH} = 9 Hz, 1 H, CH-phosp.), 4.01 (d, J_{PH} = 31 Hz, 1 H, CH-phosp.), 3.40 (s, 6 H, CH$_3$-anisyl.), 2.50 (s, 3 H, CH$_3$-phosp.), 2.20 (s, 3 H, CH$_3$-phosp.), 1.03 (s, 3 H, CH$_3$-imine), 0.35 [s, 9 H, Si(CH$_3$)$_3$]. − ^{13} C{^{1}H} NMR ([D$_6$]benzene): δ = 157.3 (C-anisyl), 152,6 (C-anisyl), 146.3 (C-imine), 126.0 (CH-anisyl), 125.1 (CH-anisyl), 99.1 (d, J_{PC} = 12 Hz, C-phosp.), 97.3 (d, J_{PC} = 8 Hz, C-phosp.), 96.5 (d, J_{PC} = 78 Hz, C-phosp.), 91.2 (d, J_{PC} = 68 Hz, C-phosp.), 90.1 (d, J_{PC} = 9 Hz, C-phosp.), 55.0 (CH$_3$-anisyl), 23.1 (CH$_3$-phosp.), 22.7 (CH$_3$-phosp.), 17.7 (CH$_3$-imine, 1,4 [Si(CH$_3$)$_3$]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = −13.4 (s). − MS (70 eV) *m/z*: 546 [M$^+$]. − C$_{28}$H$_{37}$FeN$_2$O$_2$PSi (548.17).

General Procedure of Catalytic Cyclodimerization and Gas Chromatographic Product Analysis: Ca. 30 ml of purified 1,3-butadiene was condensed at −20°C into a glass tube, and defined solutions of catalyst and co-catalyst in a few ml of toluene are added. In some of the experiments 15 ml of additional solvents (toluene or diethylether) have been used with negligible effects on product formation. The tube was then put into a 250-ml stainless steel autoclave which contained an argon atmosphere. After closing the autoclave, the bottom half of it was placed in an oil bath and heated up to the reaction temp. for 3 h, whilst butadiene built up a gas pressure inside. At 80°C reactor temp. the volatile components of the reaction mixture were transferred in vacuo into a cold (77 K) trap and the content of the trap was analysed by gas chromatography later.

The volatile components butadiene, COD, VCH, and toluene of the product mixture were separated by the capillary down to the base line. For quantitative determinations defined amounts of THF were added. A complete calibration procedure was done for the integrated peaks of COD and THF and the VCH was then related to the COD. In all cases a linear correlation was observed. The data allow us to relate the molar amounts of product formed to the amounts of catalysts used in the experiments. These results are presented as the "turnover number of substrate molecules per molecule catalyst" (TON). The precise ratio of butadiene conversion, however, was undeterminable in our experimental setup, as the exact amounts of butadiene which have had contact with the catalysts remained unknown. In cases where we detected only traces of remaining butadiene in the product mixture, an almost quantitative conversion is assumed. Higher oligomers of butadiene are formed to some extent, but no analysis was attempted. An summary of the experimental data is given in Table 3.

Crystal Structure Determination: Suitable crystals of **5a** were grown in *n*-pentane at −40°C. The data were collected on a Sie-

Table 4. Crystal data of **5a**

Empirical formula	C$_{21}$H$_{32}$FeN$_2$
Colour, form	almost black cube
Size [mm]	0.7×0.6×0.6×0.6
Crystal system	monoclinic
Space group	*P* 2$_1$/c
Unit cell dimensions [Å]	*a* = 10.629(3)
Unit cell dimensions [Å]	*a* = 10.629(3)
	b = 14.181(3)
	c = 13.398(4)
	β = 103.83(3)
Volume [Å^3]	1961(1)
Z	4
Molecular mass	368.19
Density (calcd.)	1.248 gcm^{-3}
Absorption coefficient	0.773 mm^{-1}
Number of refined parameters	217
F(000)	792
Reflections measured	6343
Independent reflections	3217
Goodnesss-of-fit at *F*^{2}	1.110
*R*1	0.0389
wR$_2$	0.1048

mens P4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator (Table 4.). The crystal structures were solved by direct methods (SHELXS-86[24]) and refined by SHELXL-93[25]. 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 a least squares refinements. Other experimental details are given in Table 4. Crystallographic data (excluding structure factors) for the structure report in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary pubilication no. CCDC-100543. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB12 1EZ [Fax: (internat.) + 44(0)1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Gottfried Huttner* on the occasion of his 60th birthday.

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