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S. J. Connon, M. O. Senge et al.
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The Ambiguous Behaviour of Diphosphines Towards the Quasilinear Iron(I) Complex [Fe(N(SiMe₃)₂)₂]⁻ – Between Inertness, P–C Bond Cleavage and C–C Double Bond Isomerisation

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Chelating phosphines are widely used as robust and reliable ligands in catalysis. We show, that the anionic iron(I) complex [Feᴵ(N(SiMe₃)₂)₂]⁻ is able to selectively cleave a P-aryl bond of 1,2-bis(diphenylphosphino)benzene. Further, the related *cis*-1,2-bis(diphenylphosphino)-ethylene (dppee) binds not by the P donors but by the ethylene unit, and is (catalytically) transformed to the *trans*-isomer.

Tertiary phosphines are common ligands in organometallic chemistry that are mainly used to stabilize metal centres in medium to low oxidation states. They are usually seen as robust spectator ligands that can be easily modified concerning its electronic and steric properties. As such they are widely used as co-ligands in many catalytic transformations.[1] However, the cleavage and/or scrambling of the P–aryl and to a lesser extent P–alkyl bonds in ligating phosphines is sometimes observed and can pose an unwanted deactivation pathway in catalysis.[2,3] This is mainly the case for 2nd and 3rd row transition metals (especially Pd).[4] For 3d-metals less is known about P–C bond cleavage, and is mainly observed for metal carbonyls upon prolonged heating.[3,5] Rare exceptions for reported conversions under mild conditions involve (di)cobalt,[6,7] diiron[8] and dinickel[7,9] carbonyl compounds and the bis(diphenylphosphino)methane ligand resulting in bridged phosphide complexes. P–C bond cleavage for carbonyl free 3d-metal systems was only seen in case of a nickel complex.[10]

Recently we reported on the synthesis of the quasi-linear iron(I) complex K{18-crown-6}[Fe(N(SiMe₃)₂)₂], **1**.[11] Despite a sterically unhindered metal centre, preliminary examinations showed that it is unaffected by monodentate lewis bases like PPh₃, PCy₃, P(OEt)₃ or the N-hetero cyclic carbene IMes. This behaviour is peculiar for two-coordinate metal(I) ions,[12] and might be result of the anionic state of the complex anion in **1**. We were thus

interested if the observed inertness of compound **1** towards pure Lewis bases holds true for a variety of commonly used (chelating) Lewis base additives used in catalysis, especially diphosphines. This would shed light onto the behaviour of these additives towards low-coordinate, low-valent 3d-metal species observed or postulated in a variety of catalytic transformations, especially those where anionic metallates are likely such as in Grignard based C–C cross-coupling.[13]

When compound **1** is subjected to regular O- or N-Donors such as simple ethers (THF, dimethoxy ethane), N-methyl-2-pyrrolidone (NMP), amines (NEt₃, TMEDA) or pyridine derivatives (4-dimethylaminopyridine, 4-tert-butylpyridine) no reaction is observed. This holds also true for carbenes (IDipp, SIMes, SIDipp), PEt₃ and larger monodentate phosphines as well as chelating phosphines like Xanthphos, 1,2-bis(diethylphosphino)ethane or 1,2-bis(diphenylphosphino) methane/ethane as well as propane. This implicates, that low-coordinate, low-valent *anionic* iron complexes might display only weak interactions with mono- and bidentate phosphines, which is emphasized by the lack of respective complexes.[14]

Employing 1,2-bis(diphenylphosphino) *benzene* (dppbz), a further commonly used ligand framework, it reacted with complex **1** under formation of a dark red solution within 30 minutes. Workup afforded a mixture of colourless as well as blood red crystals. The former turned out to be K{18c6}[Feᴵᴵ(N(SiMe₃)₂)₃], **2**, (18c6 = 18-crown-6) whereas the latter is the tetrahedral phenyliron(II) complex **3** (Scheme 1), whose equimolar formation was shown by ¹H NMR spectroscopy. The phenyl group is result of the P–C bond cleavage of one P–Ph units of the dppbz ligand which now acts as an anionic phosphine/phosphanide ligand (ppbz* = 1-(diphenylphosphino)-2-(phenylphosphido)benzene)). The Fe1–P1 and Fe1–P2 bond lengths amount 2.4557(6) Å and 2.4096(5) which reflects the difference between the phosphine and phosphide unit. Together with the tetrahedral geometry of the phosphide moiety, whereas the free lone pair points away from the iron ion, it indicates the absence of significant double bond character of the iron-phosphide bond.

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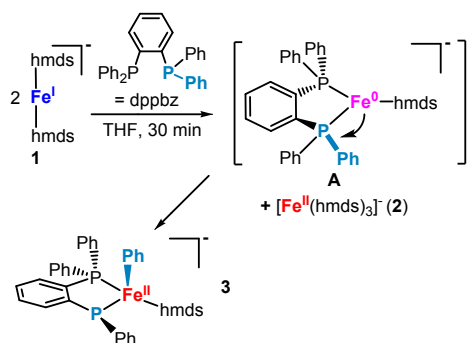
Scheme 1. Reaction of **1** with 1,2-bis(diphenylphosphino)benzene (dppbz) and proposed iron(0) intermediate responsible for the P–aryl bond cleavage. K⁺{18c6} was omitted.
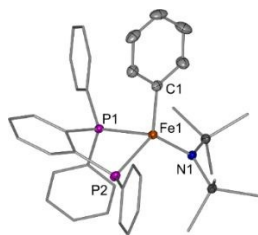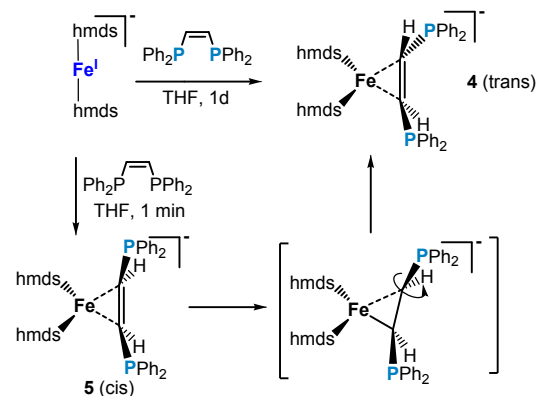

Figure 1. Section of the crystal structure of complex **3**. The K{18c6} cation was omitted. Selected bond lengths (Å) and angles (°): Fe1–P1 2.4557(6), Fe1–P2 2.4096(5), Fe1–N1 1.9886(13), Fe1–C1 2.068(2), P1–Fe1–P2 77.32(2), P1–Fe1–C1 101.15(5), P1–Fe1–N1 114.47(4), P2–Fe1–C1 117.93(5), P2–Fe1–N1 115.16(4), C1–Fe1–N1 120.75(6).

Complex **3** exhibits a number of paramagnetic ¹H NMR signals owing to the asymmetric nature of the formed ppbz* ligand. The magnetic susceptibility of compound **3** of μ_{eff} = 5.29 μ_B is expected for a high spin iron(II) complex. This example of an iron mediated P–aryl bond cleavage at mild conditions is rare (vide supra). Moreover, the use of the asymmetric ppbz* as a ligand is unknown so far and its parent protonated form was only detected as a side product in the unselective reaction of dppbz with alkali metals.[15] The inertness of **1** towards other aryl phosphines, and the stability of the related complexes [Feᴵ(dppbz)₂(X)] (X = Br, Cl, *p*-tolyl)[16] implicated that the presence of an iron(I) ion is not necessarily sufficient in P–aryl bond rupture. Thus, we hypothesized that the formation of **3** is result of a disproportionation of **1** into the observed iron(II) complex **2** as well as the proposed iron(0) species **A** via formal e⁻/hmds exchange (Scheme 1) which is triggered by dppbz, due to the additional presence of the unsaturated ligand backbone. **A** would then facilitate the formal intramolecular oxidative addition of a P–Aryl unit to the iron centre. This behaviour is similar the one of the nickel(0) complex [Ni⁰(IMe₄)₂(PPh₃)] which rapidly transforms into [Niᴵᴵ(IMe₄)₂(Ph)(PPh₂)] (IMe₄=l,3,4,5- tetramethylimidazol-2-ylidene) and contrasts the behaviour of phosphine stabilized iron(0) species which prefer cyclometallation via adjacent C–H bonds of the phosphine substituents, especially in case of aryl groups.[17]

Given the observed reactivity of dppbz with **1**, which contrasts the inertness of arylated diphosphines with a saturated backbone such as dppe, we speculated about some degree of back donation or partial electron transfer from the metal to the ligand backbone that might initiate redox disproportionation and formation of **3**. As such we turned our attention to *cis*-1,2-

bis(diphenylphosphino) *ethylene* (dppee). Reaction of dppee with complex **1** in THF gave a rapid colour change to brown. After stirring over night the reaction mixture was filtered and then layered with pentane to give reddish violet crystals after storage at −40°C for a few days (Scheme 2). X-Ray diffraction analysis revealed the presence of the dppee iron complex **4** (Figure 2). The iron centre, besides two hmds ligands, exhibits a diphosphine ligand, which astonishingly binds *not* via the phosphine atoms but solely by the C–C double bond of the backbone. This behaviour is unprecedented for any mononuclear transition metal complex with dppee or a related diphosphine ligand. Such an ethylene coordination was only observed for binuclear complexes where the ethylene bridged diphosphine already coordinated to a second metal ion via the P donor atoms or when it is enforced by the backbone of the diphosphine.[18] Further, in complex **4** the phosphine atoms are situated in a *trans*-arrangement, revealing a *cis*–>*trans* double bond isomerisation. The C1–C2 bond length amounts to 1.438(2) Å which is between the values of free dppee (1.334(4) Å)[19] and 1,2-bis(diphenylphosphino) ethane (1.521(7) Å).[20] The planes span by N1–Fe1–N2 and C1–Fe1–C2 are twisted by approximately 26° towards each other.

Scheme 2. Synthesis of complexes **4** and **5** and proposed isomerisation mechanism.
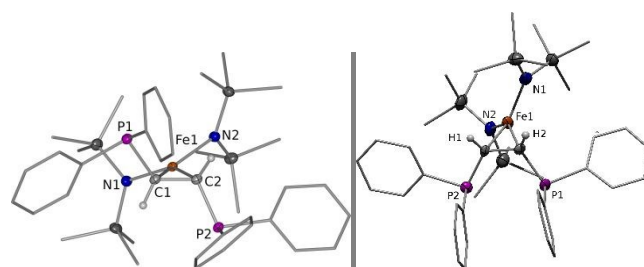
Figure 2. Sections of the crystal structure of complexes **4** and **5**. K{18c6} cations, disorders and hydrogen atoms are omitted (with the exception of the ethylene H atoms). Selected bond lengths (Å) and angles (°): (**4**) Fe1–C1 2.085(2), Fe1–C2 2.064(2), Fe1–N1 2.009(2), Fe1–N2 2.000(2); C1–C2 1.438(3), N1–Fe1–N2 116.33(7). (**5**) Fe1–C1 2.153(12), Fe1–C2 2.1187(12), Fe1–N1 2.001(6), Fe1–N2 1.998(6), C1–C2 1.463(15); N1–Fe1–N2 116.4(2).

The ¹H NMR spectrum of isolated **4**, which can also directly be obtained when reacting **1** with *trans*-dppee, shows one set of paramagnetically shifted signals, with the signal attributed for the hmds protons at −4.53 ppm which is similar to the value observed for iron(II) bound hmds ligands.[21] The magnetic

susceptibility of compound **4** amounts to μ_{eff} = 4.38 μ_B and corresponds to the values of other low-coordinate iron(I) alkene complexes.[22] However, given the strong elongation of the C=C double bond it implicates significant charge transfer from iron to the alkyne.

An immediately recorded ^{1}H-NMR spectrum of the reaction of compound **1** with *cis*-dppee gave a single set of paramagnetic signals attentively attributed to the *cis*-isomer **5** (δ_{hmds} = −2.67 ppm), which transformed completely to compound **4** over the course of three days (45% after 16 h). The identity of the *cis*-dppee complex **5** was confirmed by X-ray diffraction analysis. In complex **5** The C1−C2 bond length of the iron bound dppee amounts to 1.463(15) Å which is even more elongated than in case of the *trans*-complex **4**. The planes spanned by N1−Fe1−N2 and C1−Fe1−C2 are also more twisted (56.6(7)°), which is probably due to the different steric demand of *cis*-dppee.

The observed metal mediated *cis*–>*trans* C−C double bond isomerisation is rather unexpected. It is commonly seen during olefin metathesis, mediated by a metal hydride via 1,2-addition to a C−C double bond or scrambling of a metal (hydride) bound allylic species.[23] However, in our case such possibilities can be excluded due to the absence of a metal hydride species or allylic substrate positions. The only comparable example is an iron mediated stilbene isomerisation, although the mechanism and the identity of the iron species remained elusive.[24] As in complex **5** the C=C bond of *cis*-dppee is significantly elongated this very bond could be sufficiently weakened to allow for the rotation of the substituents. A more speculative mechanism would be a reversible formal 1e$^-$-transfer from the metal(I) ion to the substrate (similar to complex **1** mediated irreversible reduction of 2,2'-bipyridine)[25] under intermittent formation of a formally metal(II) ion bound η_1-*cis*-alkenyl radical anion. Alkenyl radical anions are calculated to exhibit no rotational barrier, however were so far not observed in the proximity of a metal ion.[26] As the C=C isomerisation is an electroneutral process, we aspired a catalytic transformation. Indeed, when employing 10% of compound **1** *cis*-dppee is slowly isomerized over the course of several days, (66%, r.t. 6 d, Scheme 3). However, the catalysis is limited by simultaneous decomposition of complex **1** within this timeframe.
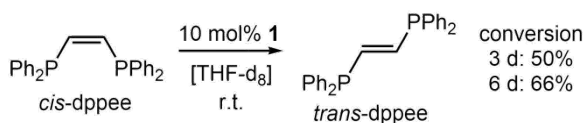
Scheme 3. Catalytic *cis*->*trans* isomerisation of *cis*-dppee mediated by complex **1**.

Concluding, we presented the peculiar behaviour of the two-coordinate iron(I) complex **1** towards commonly used phosphine and diphosphine ligands. Thereby it shows, that most phosphines (as well as various N/O donor ligands) do *not* interact with the anionic iron(I) complex **1**, despite its accessible metal ion. However, in case of dppbz the facile rupture of a P−Aryl bond is observed leading to the formation of an iron(II) phenyl complex ligated by a novel bidentate mixed phosphine/phosphide ligand. For *cis*-dppee the unprecedented sole coordination via the C=C bond of the ethylene linker but not the phosphorous atoms is observed. Further, an unusual *cis*–>*trans* isomerisation of this very bond took place, that involved no apparent metal hydride or allyl species, and could be performed on a catalytic scale. Overall, it shows that for low-coordinate, anionic iron complexes (and potentially of other metals) the role of phosphines as a simple and robust P donor ligand should not be readily assumed.

Conflicts of interest

There are no conflicts to declare.

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COMMUNICATION

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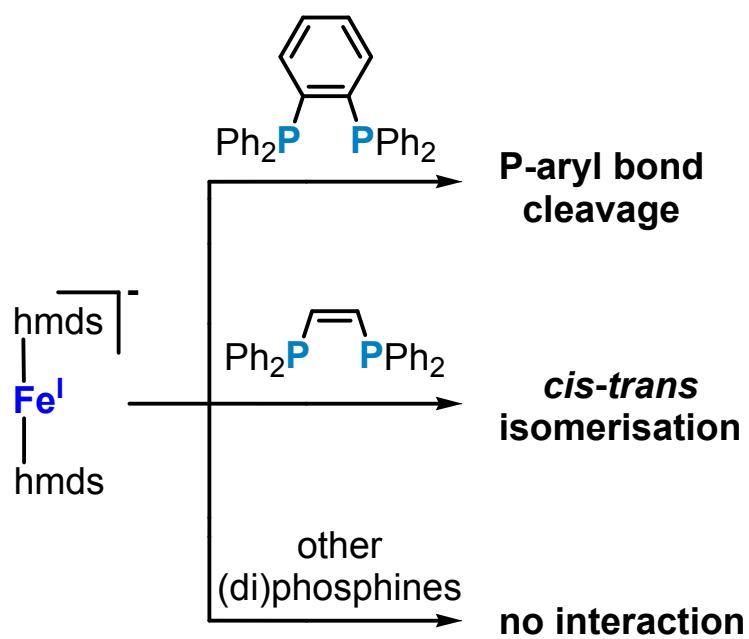
A quasilinear iron(I) complex facilitates C-C bond isomerisation or P-aryl bond cleavage of diphosphines but is otherwise inert to simple phosphine coordination.