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Homogeneous Catalysis

Facile, Catalytic Dehydrocoupling of Phosphines Using β-Diketiminate Iron(II) Complexes

Andrew K. King, Antoine Buchard, Mary F. Mahon, and Ruth L. Webster*[a]

Abstract: Catalytic dehydrocoupling of primary and secondary phosphines has been achieved for the first time using an iron pre-catalyst. The reaction proceeds under mild reaction conditions and is successful with a range of diarylphosphines. A proton acceptor is not needed for the transformation to take place, but addition of 1-hexene does allow for turnover at 50 °C. The catalytic system developed also facilitates the dehydrocoupling of phenylphosphane and dicyclohexylphosphane. A change in solvent switches off dehydrocoupling to allow hydrophosphination of alkenes.

Catalytic dehydrocoupling (DHC) is an attractive and efficient method to synthesize P–P bonds,[1] evolving H_2 as the only by-product. The resulting substrates are of great synthetic interest and have found a wide range of applications in coordination chemistry[2] and through further functionalization to produce a diverse range of P–C[3] and P-element bonds.[4] Although DHC to make P–P bonds is less well explored than the P–B and N–B counterparts, a handful of elegant examples mediated by a small selection of platinum group,[5] group 4,[6] and main group catalysts[7] along with Lewis acid catalysts[8] and carbenes[9] exist. Given the ubiquity of the β-diketiminate Fe^{II} motif, it is surprising to note that, although well explored in terms of coordination chemistry and stoichiometric reactivity,[10] only a handful of examples of catalysis have been reported using these iron complexes.[11] However, these complexes evidently lend themselves to very important and challenging catalytic transformations including C–F bond activation[11b] and hydroamination.[11c] An ideal scenario would be to use synthetically simple and inexpensive iron pre-catalysts to develop desirable transformations, in this case the preparation of key phosphorus motifs, without the need for expensive ligands, exogenous reductants, or additives. We herein report the first example of catalytic homo-DHC of phosphines using iron.[12] DHC of a range of activated and deactivated phosphines proceeds under mild conditions with simple β-diketiminate Fe^{II} complexes.

[a] *A. K. King, Dr. A. Buchard, Dr. M. F. Mahon, Dr. R. L. Webster*
Department of Chemistry
University of Bath
Claverton Down, Bath, BA2 7AY (UK)
E-mail: r.l.webster@bath.ac.uk

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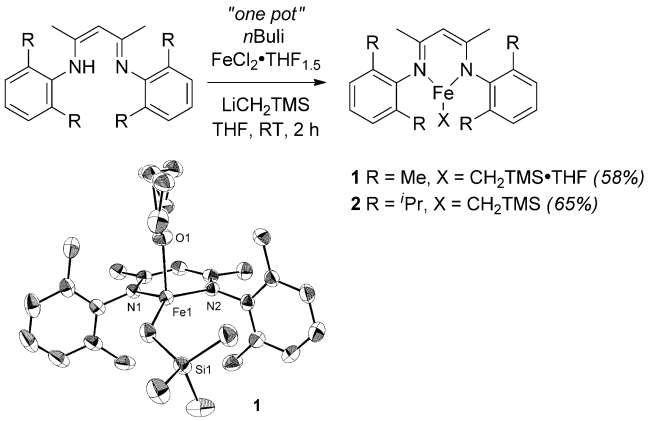
Following the work of Hessen and co-workers,[13] we found that sterically varied β-diketiminate iron(II) (trimethylsilyl)-methylene complexes could be easily synthesized in one pot and isolated as red (**1**) or yellow solids (**2**) in good yield (Scheme 1). The 2,6-dimethyl complex (**1**) forms the formal



Scheme 1. Synthesis of β-diketiminate complexes **1** (thermal ellipsoids set at 50% probability) and **2** used to catalyze dehydrocoupling.

four-coordinate adduct with THF,[14] adopting a distorted tetrahedral geometry around the iron center, whereas the 2,6-diisopropyl complex (**2**) is three-coordinate.[13,15]

Our initial studies show that complexes **1** and **2** are exceptional stoichiometric reagents for the dehydrocoupling of $HPPh_2$ at RT with complete conversion after only 30 mins (Table 1, entries 1 and 4). Pleasingly, both complexes also show excellent catalytic activity upon heating to 70 °C in C_6H_6 (entries 3, 6, and 7). The increase in steric bulk around the metal center, changing from complex **1** to **2**, delivers an improvement in reactivity (compare entries 3 and 7).

An exogenous hydrogen acceptor is not needed to facilitate the transformation but when 1-hexene is added to the reaction mixture, there is further improvement in reactivity, with 100% conversion to the DHC product after 24 h at 50 °C (entry 8). This is in line with observations made by Stephan and co-workers,[16] where an equilibrium is believed to exist; addition of an alkene removes hydrogen from the reaction mixture and pushes the equilibrium in favor of DHC. Only trace amounts of anti-Markovnikov hydrophosphination product are observed when the reaction is performed in the presence of styrene where the spectroscopic yield of **3a** is 100% after 24 h at 70 °C. However, this latter transformation is highly

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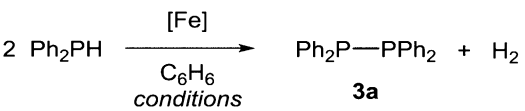
Table 1. Optimization of DHC of $HPPh_2$ using **1** and **2**.[a]



Entry	[Fe]	Loading [mol%]	Conditions	$HPPh_2$ consumption [%][b]
1	**1**	100	RT, 30 min	100
2	**1**	5	50 °C, 24 h	22
3	**1**	5	70 °C, 24 h	71
4	**2**	100	RT, 30 min	100
5	**2**	5	50 °C, 24 h	48
6	**2**	5	70 °C, 18 h	68
7	**2**	5	70 °C, 24 h	100
8[c]	**2**	5	50 °C, 24 h	100
9	$FeCl_2{\cdot}THF_{1.5}$	5	70 °C, 24 h	trace

[a] Conditions: $HPPh_2$ (0.5 mmol), C_6H_6 (0.35 mL). [b] Based on loss of P–H signal from ^1H NMR, using 1,3,5-trimethoxybenzene as an analytical standard and evidenced by $^{31}P\{^1H\}$ NMR spectroscopy.[15] [c] 1 mmol 1-hexene added.

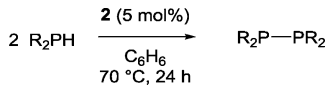
solvent dependent and a change to CH_2Cl_2 results in hydrophosphination (see below). Only a trace amount of **3a** is observed when $FeCl_2{\cdot}THF_{1.5}$ is used (Table 1, entry 9).

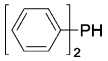
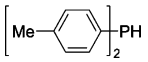
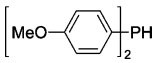
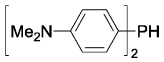
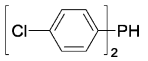
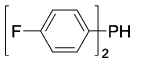
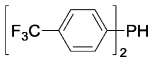
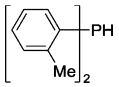
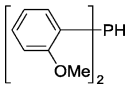
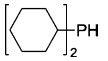
We proceeded to test the scope and extent of reaction using pre-catalyst **2**. We were pleased to observe that a range of electronically activated, deactivated and sterically demanding secondary phosphines dehydrocouple (Table 2). Phosphines bearing a halogen are excellent substrates for DHC, with no evidence for dehalogenation. The presence of an *N*- or *O*-substituent reduces reactivity and higher reaction temperatures are necessary (Table 2, entries 3, 4, and 9), whereas in the case of the *ortho*-methoxy substrate (entry 9), this combination of steric bulk and heteroatom gives very little turnover even with heating at high temperature. Under more forcing reaction conditions, $HPCy_2$ proceeds cleanly through to the DHC product in modest yield (entry 10).

We then investigated the proficiency of pre-catalyst **2** in the DHC of primary phosphines; H_2PCy and H_2PPh (Scheme 2). H_2PPh undergoes DHC to form the P–P dimer **4a** cleanly in 60% spectroscopic yield (catalyzed by 5 mol% **2** at 100 °C for 24 h), with no evidence for the formation of cyclic species. The product is observed as a 1:1 ratio of the *meso* and *rac* isomers (Scheme 2a). When more forcing conditions are applied (10 mol% **2**, 120 °C, 72 h, Scheme 2b), although more of the H_2PPh starting material is consumed (89%), a mixture of products form. $^{31}P\{^1H\}$ NMR analysis of the reaction shows a mixture of **4a**, the cyclic pentamer and an unknown species in approximately 2:4:1 ratio (using inverse gated $^{31}P\{^1H\}$ NMR calibrated against a PPh_3 standard). In comparison, after 24 h at 100 °C using 5 mol% **2** only a trace amount of 1,2-dicyclohexyldiphosphane (**4b**) is observed. Although an increase in loading of **2**, reaction temperature and time (10 mol%, 120 °C, 72 h) allows the DHC of H_2PCy, the reaction mixture is complex and consists of an intractable mixture of products.

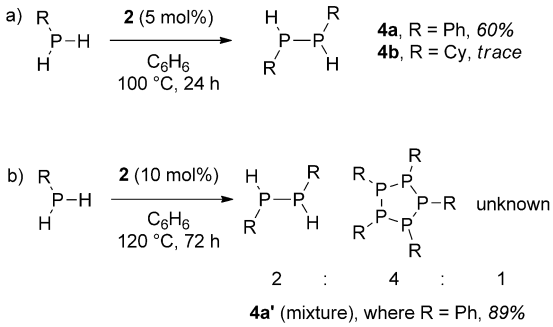
The extreme reactivity when employing a stoichiometric amount of either **1** or **2** is such that no catalytic intermediates

Table 2. Extent of DHC reactivity of secondary phosphines using pre-catalyst **2**.[a]



Entry	R_2PH	Product	Substrate consumption[b] [Isolated yield of product] [%]
1		**3a**	100 [85]
2		**3b**	95 [76]
3[c]		**3c**	33 [–]
4[c]		**3d**	100 [60]
5		**3e**	90 [82]
6		**3f**	100 [90]
7		**3g**	72 [57]
8		**3h**	36 [–]
9[c]		**3i**	10 [–]
10[d]		**3j**	28 [–]

[a] Conditions: Phosphine (0.5 mmol), **2** (5 mol%), C_6H_6 (0.35 mL), 70 °C, 24 h. [b] Based on loss of P–H signal from ^1H NMR, using 1,3,5-trimethoxybenzene as an analytical standard.[15] [c] 100 °C, 24 h. [d] 10 mol%, 120 °C, 72 h.



Scheme 2. DHC of primary phosphines.

can be isolated from their reaction with $HPPh_2$ in C_6H_6. Attempts to isolate an iron phosphido complex from a salt metathesis route (using either the iron μ-chloroate complex[17] or dinuclear μ-bromo complex[18] in the presence of $LiPPh_2$ or $KPPh_2$) did not proceed cleanly through to the desired product. We presume that catalysis is initiated by loss of $Si(CH_3)_4$ on formation of an iron-phosphido intermediate. Indeed, $^{31}P\{^1H\}$ NMR analysis of the catalytic mixture shows the formation of a new species at 110 ppm,[15] this downfield signal is consistent with

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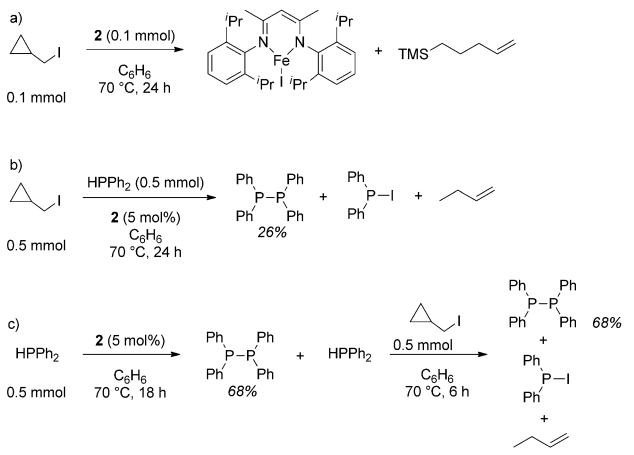
an Fe–PR_2 bond, in line with seminal independent reports from Carty, Seyferth, and Wojcicki on studies of phosphido-bridged iron carbonyl complexes,[19] but in this case the complex is anticipated to be mononuclear due to steric hindrance.[20] This is substantiated by DFT calculations[15] along with inert atmosphere ESI mass spectrometry of the crude catalytic mixture, which shows the presence of a monomeric iron-phosphido complex (*m/z* 659.3161, consistent with M+H where M = $C_{41}H_{51}FePN_2$), with no evidence for the presence of a dimer. Following phosphido formation, reaction with phosphine could allow elimination of the DHC product along with the potential formation of an iron hydride,[21] which could then react with another equivalent of phosphine releasing H_2 and regenerating the iron phosphido, similar to previous reports with Zr catalysts.[6b,22]

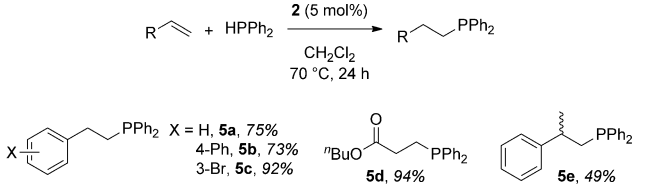
Addition of 10 mol% TEMPO to the catalytic reaction mixture inhibits reactivity (20% **3a**), suggesting that these steps may be radical mediated. Reaction of a stoichiometric amount of radical clock ((iodomethyl)cyclopropane) with **2** results in the quantitative formation of a bright orange iron–iodide complex and 5-(trimethylsilyl)pent-1-ene (Scheme 3a). Addition of



Scheme 3. Reactions with a radical clock.

the radical clock to a catalytic reaction of **2** and $HPPh_2$ results in the formation of 26% **3a**, diphenylphosphinous iodide and 1-butene (Scheme 3b). This would suggest that, during the catalytic reaction, both off-cycle catalyst activation and on-cycle DHC processes are radical mediated, with evidence for this provided by addition of (iodomethyl)cyclopropane to the catalytic reaction after 18 h where no further reactivity is observed and 68% **3a** is obtained along with diphenylphosphinous iodide and 1-butene (Scheme 3c). $HPPh_2$ does not react with (iodomethyl)cyclopropane in the absence of **2**. Based on the radical nature of the reaction, ligand non-innocence cannot be ruled out.[15,23]

As previously mentioned, a change in solvent results in a substantial change in reactivity. Under standard DHC conditions (cf. Table 1, entry 7) only a trace amount of **3a** is observed when CH_2Cl_2 is employed as the solvent, but in the presence of 1.8 equiv styrene 75% spectroscopic yield of the anti-Markovnikov hydrophosphination product, **5a**, is obtained.[24] Indeed, these hydrophosphination conditions[25] can be applied to a range of activated alkenes, furnishing the phosphine products in good to excellent yields (Scheme 4).



Scheme 4. Hydrophosphination of alkenes using **2** as the pre-catalyst.

Unfortunately, less active alkenes, such as allyl benzene and 1-hexene yield only trace amounts of product under these conditions, likewise reaction of styrene with $HPCy_2$ and H_2PPh is poor.

It is not surprising that anti-Markovnikov hydrophosphination of activated substrates can be achieved under these catalytic conditions, but this dramatic change in reactivity on change in solvent is fascinating; moreover, addition of 10 mol% TEMPO is not detrimental to reactivity with no reduction in spectroscopic yield.

In summary, iron(II) β-diketiminate complexes possessing a labile co-ligand prove to be excellent pre-catalysts for the dehydrocoupling of a range of primary and secondary phosphines. No additives are necessary for the transformation to take place and an exogenous proton acceptor is not needed to sequester the H_2 released. Although synthetically simple, the reaction mechanism is not trivial but appears to proceed via a radical pathway. A detailed spectroscopic and electronic study of the mechanism, along with investigations into the substantial change in reactivity on change in solvent, is underway and will be reported in due course.

Experimental Section

General method for the dehydrocoupling of phosphines: all steps were performed under an inert atmosphere. To a Schlenk tube 5 mol% (0.025 mmol) of pre-catalyst **1** or **2** was added in 0.35 mL of benzene. Phosphine (0.5 mmol) was then added to the reaction vessel and the corresponding solution was stirred at 70 °C for 24 h (or otherwise stated). To obtain spectroscopic yield and/or isolated yield the reaction mixture was passed through a short silica plug, eluting with CH_2Cl_2. To obtain spectroscopic yield, the solution was charged with a known quantity of 1,3,5-trimethoxybenzene, concentrated, then an NMR sample prepared using C_6D_6. This isolation method was necessary to remove the paramagnetic component from the reaction mixture, allowing analysis by ^{1}H NMR spectroscopy.

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Keywords: homogeneous catalysis · iron · phosphanes · phosphorus · radicals

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[14] Crystal data for $C_{29}H_{44}FeN_2OSi$, **1**: $M = 520.60$, $\lambda = 0.71073$ Å, monoclinic, space group $C2/c$, $a = 29.1850(4)$, $b = 11.0540(1)$, $c = 18.3670(3)$ Å, $\beta = 98.750(1)^\circ$, $U = 5856.43(14)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.181$ g cm^{-3}, $\mu = 0.578$ mm^{-1}, $F(000) = 2240$. Crystal size $= 0.25 \times 0.25 \times 0.20$ mm, unique reflections = 6693 [R(int) = 0.0599], observed reflections [$I > 2\sigma(I)$] = 4995, data/restraints/parameters = 6693/0/335. Observed data; $R1 = 0.0376$, $wR2 = 0.0853$. All data; $R1 = 0.0612$, $wR2 = 0.0957$. Max peak/hole = 0.435 and −0.373 e Å^{-3}, respectively. CCDC 1060002 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[15] See the Supporting Information.

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