Synthesis and Reactivity of *cis*-FeH₂(dcpe)₂ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane)

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ABSTRACT: A new six-coordinate iron dihydride *cis*-FeH₂(dcpe)₂ (**1**) has been synthesized (dcpe = 1,2-bis(dicyclohexylphosphino)ethane). It has been found to react with either 1,4-cyclohexadiene or *tert*-butylethylene in toluene to give the respected hydrogenated hydrocarbon and the zerovalent species Fe(dcpe)(toluene) (**2**). When this reaction with acceptor olefins was performed in methylcyclohexane, transfer dehydrogenation was observed to give low-yields of iron-bound toluene in **2**.

Selective C-H activation and functionalization of alkanes continues to be a longstanding challenge for chemists.¹ This is despite demand from industry to develop more effective methods for transforming simple hydrocarbons such as methane into liquid fuels or basic building blocks for pharmaceutical synthesis.

Single-site, molecular species, e.g. organometallic and transition metal coordination compounds, have shown some remarkably selective activities towards the breaking of C-H bonds in hydrocarbons, and in a few cases, methane, at ambient temperatures and pressures.²⁻⁴ Notably, the iron complex FeH₂(dmpe)₂ (dmpe = 1,2-bis(dimethylphosphino)ethane) has been shown to C-H activate a variety of alkanes – including methane via a photolytic method in liquid xenon at -100°C, presumably via the transient zerovalent Fe(dmpe)₂ species (Scheme 1).⁵⁻⁸ Roddick et al. demonstrated that a thermolytic method could be used to effect aliphatic C-H activation for similar

ruthenium dihydrides – e.g. $\text{RuH}_2(\text{dfepe})_2$ (dfepe = 1,2-bis(dipentafluoroethanephosphino)ethane) will dehydrogenate methylcyclohexane at 180°C to give metal-bound toluene and dihydrogen.⁹

Scheme 1. C-H activation of alkanes with an iron and ruthenium bis-diphosphine dihydride species.

Although the dmpe ligand promotes intermolecular alkane activation in the iron system, other diphosphine ligands used ($\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$; $\text{R} = \text{Et}$ (depe), ^iPr (dnppe), Ph (dppe)) give rise to unwanted intramolecular cyclometallation reactions.¹⁰⁻¹² Nonetheless, it is possible that further modification of this system may provide the sought-after intermolecular CH activation reactivity of the dmpe system combined with a less facile loss of methane from the methyl hydride species. Therefore we have investigated other diphosphine ligands for the $\text{FeH}_2(\text{L})_2$ system – specifically, $\text{L} = \text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ (where $\text{R} = \text{Cy}$ (dcpe), C_6F_5 (dfppe)); $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppp).

Our experiments showed that two equivalents of the larger diphosphine dcpe cannot bind to FeCl_2 to form “ $\text{FeCl}_2(\text{dcpe})_2$ ” presumably because they create too much steric crowding around the metal center (formation of complexes of the type $\text{FeCl}_2(\text{L})_2$ has been previously shown for smaller ligands $\text{L} = \text{dmpe}$ and depe).¹³ Even with heating, the only product from the reaction of FeCl_2 and two or more equivalents of dcpe is the known species $\text{FeCl}_2(\text{dcpe})$.¹⁴ Nonetheless, we found that

the reaction of paramagnetic $\text{FeCl}_2(\text{dcpe})$ with two equivalents of NaBEt_3H and one additional equivalent dcpe successfully yielded the diamagnetic, bis-ligated species $\text{cis-FeH}_2(\text{dcpe})_2$ (**1**) as a pale yellow powder in 59% yield (Scheme 2). Presumably this reflects the smaller radius of the hydride ion, and shorter bond length to the iron center, versus the equivalent values for the chloride ion.

Using the analogous preparative route with ligands dfppe , dppp , dcpm and dppm unfortunately failed to produce the bis-ligand dihydride species, and instead typically resulted in formation of metallic iron and free ligand.

Scheme 2. Preparation of **1**.

The observed diamagnetism of complex **1** is indicative of a low-spin Fe(II) center, and consistent with an octahedral coordination environment. ^1H NMR spectroscopy (C_6D_6) revealed a broad, distinctive peak at δ -17.59 to -17.17 ppm assigned to the metal-bound hydride, split into a multiplet by coupling to four phosphorus centers. This is very similar to the broad hydride peak reported for $\text{Fe}(\text{dippe})_2\text{H}_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane) at δ -17.4 ppm (d_8 -toluene).¹⁵ The $^{31}\text{P}\{^1\text{H}\}$ spectrum revealed two peaks at δ 87.25 and 106.50 ppm, consistent with *cis*-geometry and similar to shifts reported previously for similar complexes.¹⁶

1 was found to be unreactive towards a variety of hydrocarbons under ambient conditions (toluene, hexane, *tert*-butyl ethylene (TBE), 1,4-cyclohexadiene (CHD), 9,10-dihydroanthracene). These solutions were subsequently heated to explore the possibility of generating a reactive low-valent species (e.g. “ $\text{Fe}(\text{dcpe})_2$ ”) by thermolytic loss of H_2 . Decomposition of **1** to give iron metal and free ligand in most cases, however it was found that when **1** is heated in toluene at 100°C in the presence of equimolar amounts of either CHD or TBE, a new 18-electron species is formed (η^6 -toluene) $\text{Fe}(\text{dcpe})$ (**2**) in quantitative yield along with an equivalent of free dcpe and either

cyclohexane or 3,3-dimethylbutane, respectively (Scheme 2). This formation was indicated by a color change from yellow to dark orange and evidenced by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. **2** gives a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) at δ 102.0 ppm, very similar to the related π complexes $(\eta^6\text{-naphthalene})\text{Fe}(\text{dcpe})$, $(\text{toluene})\text{Fe}(\text{dippe})$ and $(\eta^6\text{-benzene})\text{Fe}(\text{dcpe})$ (δ 94.6, 109.1 & 102.2 ppm).¹⁷ Repeating the reaction in benzene solvent rather than toluene gave a similar result, with a peak at δ 102.2 ppm, consistent with formation of $(\eta^6\text{-benzene})\text{Fe}(\text{dcpe})$.¹⁷ A distinctive C-H (aromatic) stretch was observed in the IR spectrum of **2** at 3041 cm^{-1} .

2 could not be obtained in a pure form, as it co-crystallized with the free ligand impurity. In order to fully characterize this species, a rational synthesis was followed: $\text{Fe}(\text{dcpe})\text{Cl}_2$ was reduced with two equivalents of sodium metal in toluene to give pure samples of **2** in moderate yields. $^{31}\text{P}\{^1\text{H}\}$ NMR data were identical to those obtained from the reactions above.

Scheme 3. Formation of the iron(0) complex **2** from **1**.

Crystals of **2** (red) and dcpe (colorless) co-crystallized from the reaction mixture – the red crystals could be separated by hand and subjected to single crystal X-ray diffraction analysis. The structure of **2** was solved in monoclinic $P 2_1/n$ and shows a “piano-stool” complex with a pi-bound toluene ligand and a single diphosphine ligand (Figure 1), similar to that found for $(\eta^6\text{-naphthalene})\text{Fe}(\text{dcpe})$. Average C-C distances within the toluene moiety (average 1.414(2) Å) indicate that no formal reduction has occurred.

Figure 1. Thermal ellipsoid plot of the structure of **2** (hydrogen atoms omitted; ellipsoids at 50% probability).

When this reaction is carried out either in the absence of hydrogen acceptor (CHD/TBE in pure toluene in a sealed vessel at 180°C), or in the absence of toluene (pure CHD/TBE at 100°C), metallic iron and free ligand are the only detectable products. Therefore it appears that the hydrogen acceptor olefin is necessary as an acceptor for the hydride ligands and concomitant reduction to Fe(0), and the arene solvent is necessary to trap this low-valent species before it decomposes to metallic iron. It is also evident that the dcpe ligands are easily lost in these processes.

Given that the reaction between **1** and hydrogen acceptor produces an Fe(0) complex – possibly of the type which Fields et al. have previously shown to be effective for C-H activation – we were interested to see if this species would perform C-H activation in the absence of an arene solvent which can trap it. Methylcyclohexane was chosen as a substrate because the anticipated product

of dehydrogenation – toluene – would be favored due to the driving force of aromatization and expected to form **2**, which could be easily characterized due to the signature signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Reaction of **1** with excess CHD/TBE in methylcyclohexane at 140 °C was monitored by $^{13}\text{P}\{^1\text{H}\}$ NMR and showed partial formation of **2**, as indicated by the signature peak at 102.0 ppm – however in low yield (ca. 10% by NMR). Significant decomposition was also observed, with a large amount of free ligand generated. Attempts to change stoichiometry and reaction conditions did not improve the yield of this reaction, and no reaction was observed with **1** and neat methylcyclohexane at elevated temperatures (i.e. a hydrogen acceptor is required to initiate the reaction). ^1H NMR and GC-MS analysis of the methylcyclohexane solvent did not give evidence for any toluene impurities.

This transfer dehydrogenation of methylcyclohexane to toluene presumably proceeds via a molecular Fe(0) complex formed immediately following reaction of **1** with the acceptor. Homogeneous transfer dehydrogenation of cycloalkanes to arenes using an acceptor olefin has been documented, in particular for Pt, Pd, Ir and Rh systems with stoichiometric and catalytic turnovers¹⁸⁻²² – however, we could not find any literature precedent for this type of reaction for homogeneous iron complexes. Considering the low yield and facile loss of ligand, this iron system is currently not practical, however it does demonstrate that transfer dehydrogenation can occur with this metal. Heterogeneous reaction cannot be completely ruled out – mercury is often used to test heterogeneous reactions that proceed with metallic elements, by forming an amalgam and suppressing any heterogeneous reactivity, however it has been shown that this is not viable in the case of iron which forms a poor amalgam with Hg.^{23,24} With further modification it is possible that iron complexes may show catalytic activity for these type of reactions. This chemistry is similar to that demonstrated for $\text{RuH}_2(\text{dfepe})_2$ – which also loses an equivalent of ligand, however proceeds in high yields⁹ – with the exception that an olefin acceptor is required, in contrast to the “acceptorless” C-H activation displayed by ruthenium.

Presumably the major driving force for this reaction comes from the aromatization of the six-membered ring, and the resultant iron(0)-arene π bonding interactions, which are typically very strong. Reactions in hexane rather than methylcyclohexane gave only metallic iron and free ligand.

Finally, similar experiments between $\text{RuH}_2(\text{L})_2$ ($\text{L} = \text{dcpe}, \text{dppp}, \text{dppm}$)²⁵ and a variety of hydrocarbons (toluene, hexane, TBE, 9,10-dihydroanthracene, CHD) under thermolytic conditions (up to 200°C) failed to yield any reactions.

In summary, a new iron(II) dihydride **1** was synthesized via salt metathesis supported by two dcpe ligands, despite the corresponding bis-ligand dichloride being inaccessible. Several other diphosphine ligands were also examined, but complexes of the type $\text{FeH}_2(\text{L})_2$ could not be synthesized, presumably owing to steric constraints. **1** was shown to effect stoichiometric hydrogenation of olefins, and transfer dehydrogenation using **1** was observed in low yields with acceptor olefins and elevated temperatures, with no evidence of unwanted intramolecular C-H activation. Nonetheless, the ligands are very easily lost from the metal center. Future work should explore photolytic methods of activating complex **1** for C-H activation.

Experimental Section

Unless noted otherwise, all operations were performed under a purified argon atmosphere in a standard MBraun UniLab drybox or under an argon atmosphere using high-vacuum and Schlenk techniques. Hydrocarbon solvents were purchased anhydrous from Sigma-Aldrich, and further dried over activated 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratory, and dried over 4 Å molecular sieves. Unless noted, chemicals were purchased from commercial sources and used without further purification. $\text{Fe}(\text{dcpe})\text{Cl}_2$,¹⁴ $\text{RuH}_2(\text{dcpe})_2$,^{25,26} $\text{RuH}_2(\text{dppp})_2$,²⁵ $\text{RuH}_2(\text{dppm})_2$ ²⁵ were prepared according to literature procedures. FeCl_2 , NaBEt_3H (1.0M in THF), 1,4-cyclohexadiene, tert-butyl ethylene, dcpe, dppp, dppm and 9,10-dihydroanthracene were purchased from Sigma-Aldrich and used as received. H_2 gas was provided by the LANL in-house gas facility at 99.9% grade. CeCl_3 was purchased anhydrous from Strem and used as received. All NMR spectra were recorded using a Bruker 400 Ultra Shield spectrometer. ^1H NMR spectra were referenced to solvent residual peaks (δ 7.15 ppm for C_6D_6). Infrared spectra were measured as KBr discs using a Perkin Elmer Spectrum Two FTIR spectrometer. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

***cis*-Fe(dcpe) $_2$ H $_2$ (1).** A suspension of FeCl_2 (45 mg, 0.355 mmol) and dcpe (300 mg, 0.710 mmol) was stirred in tetrahydrofuran. After 2 hours a clear solution was produced. This was cooled to -

30°C and two equivalents of NaBEt₃H (0.71 ml of 1.0M solution in THF, 0.710 mmol) was added, whereupon the solution immediately changed to a dark blue color. After stirring overnight, the solution became red with precipitate and was filtered (celite) and all volatiles removed in vacuo. This tacky red solid was washed with hexane (2x10ml) on a frit to leave the product as a pale light yellow solid which was dried in vacuo (m= 141 mg, 0.156 mmol). Further product was obtained by recrystallization from the mother liquor at -30°C for several days (m = 189 mg, 0.209 mmol; total 59% yield). ¹H NMR (C₆D₆) δ -17.592 to -17.170 (m, Fe-*H*), 1.191-2.300 (m, 88H, Cy-*H*), 2.470 (s, br, 4H, CH₂CH₂), 2.818 (s, br, 4H, CH₂CH₂); ¹³C{¹H} 14.70 (s), 23.39 (s), 23.84 (s), 25.41 (s), 27.22 (m), 27.74 (m), 28.35-29.63 (m), 30.02 (m), 31.35 (m), 32.27 (s), 40.06 (m), 40.81 (m), 44.31 (m); ³¹P{¹H} NMR (C₆D₆) δ 87.3, 106.5 ppm. IR (KBr / cm⁻¹) 2929 (s), 2851 (s), 1882 (w, br), 1447 (m), 1176 (w), 1109 (w), 1003 (w), 892 (w), 850 (w), 736 (w), 530 (w). CH for C₅₂H₉₈P₄Fe Calc. % (found) C 69.16 (69.46) H 10.94 (11.12)

(toluene)Fe(dcpe) (2) from FeCl₂(dcpe). Cold toluene (30 mL) was added to a mixture of **1** (100 mg, 0.18 mmol) and sodium metal (9.2 mg, 0.40 mmol) and stirred overnight. The following day, the blood red solution was reduced to dryness under vacuum and extracted into hexane (20 mL). The product was recrystallized from this solution at -30°C (m = 51 mg, 0.09 mmol, 49 % yield). ¹H NMR (C₆D₆) δ 56.0 (br, tol), 12.3 (br, tol), 5.87 (s, br, tol), 4.54 (d, 4H, dcpe-Et), 1.07-2.41 (m, 44H, dcpe-Cy), -0.50 (br, tol); ¹³C{¹H} 91.2, 78.3, 75.9, 72.9, 39.7, 29.6, 29.4, 28.3, 27.9, 27.4; ³¹P{¹H} NMR (C₆D₆) δ 102.0 ppm. IR (KBr / cm⁻¹) 3041 (m), 2917 (s), 2851 (s), 1447 (s), 1176 (m), 1109 (m), 1003 (m), 850 (w), 736 (w), 530 (w), 470 (w). CH for C₃₃H₅₆P₂Fe Calc. % (found) C 69.46 (69.12) H 9.89 (10.12)

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