Synthesis of [bis(hexamethylene)cyclopentadienone]iron tricarbonyl and its application to catalytic reductions of C=O bonds

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Abstract: Herein, we report the synthesis of [bis(hexamethylene)cyclopentadienone]iron tricarbonyl (**1b**) by reaction of cyclooctyne with $Fe(CO)_5$, and the investigation of its catalytic properties in C=O bond reduction. Owing to the peculiar reactivity of cyclooctyne, complex **1b** was formed in good yield (56%) by intermolecular cyclative carbonylation/complexation with $Fe(CO)_5$. Compound **1b** was fully characterized, and its crystal structure was determined by X-ray analysis. Catalytic tests revealed that, upon in situ activation with Me_3NO, complex **1b** promotes the hydrogenation of ketones, aldehydes and activated esters, as well as the transfer hydrogenation of ketones, showing higher activity compared to the classical "Knölker complex" (**1a**). Studies on the hydrogenation kinetics in the presence of **1a** and **1b** (respectively) suggest that this difference in terms of activity is probably due to the better stability of the **1b**-derived complex compared to the in situ generated Knölker-Casey catalyst.

Introduction

In recent years there has been a growing interest for developing efficient homogeneous base metal catalysts[1] with the ultimate goal to replace the precious and often toxic noble metals (e.g., Ir, Pd, Pt, Rh) in homogeneous catalysis. In this context, iron is particularly appealing for its abundancy (2nd most abundant metal in the Earth's crust) and for its low toxicity, which stems from being ubiquitous in biological systems.[2] The accepted limits for residual iron traces in fine chemicals and pharma intermediates are significantly higher compared to noble metals,[3] which makes iron a very attractive candidate for the development of cheap and sustainable catalysts.[4] Besides the well-established applications in oxidation and cross-coupling processes, increasing efforts have been recently put in the development of homogeneous Fe-catalytic reduction methodologies as hydrogenation,[5, 6, 7] transfer hydrogenation [5, 7, 8] and hydrosilylation.[5, 9] However, most of these methodologies suffer from serious drawbacks, such as difficult synthesis and lack of robustness of the catalyst, moderate activity/selectivity and/or high cost/poor atom economy of the catalysed process.

A promising class of pre-catalysts which is partially exempt from this limitations is represented by (cyclopentadienone)iron complexes (**1** in Figure 1),[10] firstly reported by Reppe and Vetter in 1953.[11] These compounds, which were studied in more detail much later by Knölker[12] and Pearson,[13] can be easily synthesized and purified owing to their stability to air, moisture and chromatography. In 1999, Knölker and co-workers synthesized and isolated the first (hydroxycyclopentadienyl)iron hydride complex (**2a**, Figure 1 B) from the corresponding (cyclopentadienone)iron complex (**1a**) using the Hieber reaction.[14]

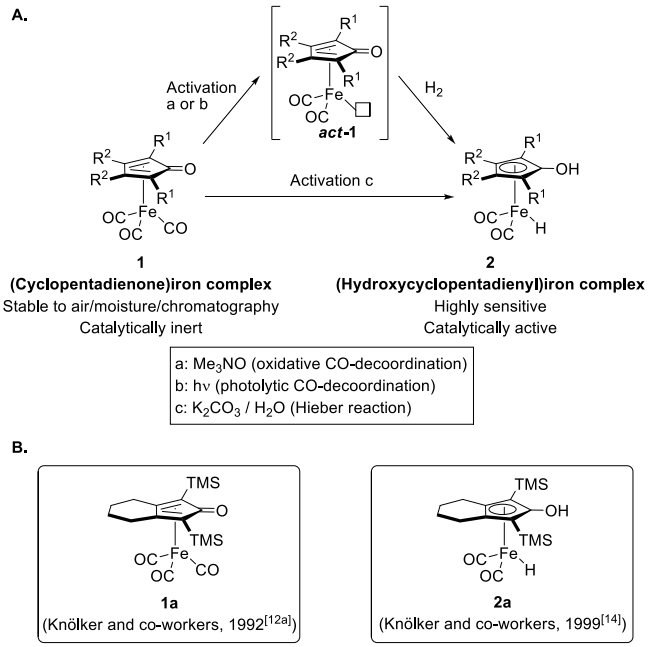

Figure 1. A: (Cyclopentadienone)iron complexes (**1**), and their activation to the catalytically active complexes ***act*-1** and **2**. B: the so-called "Knölker complexes" **1a** and **2a**.

The catalytic potential of (hydroxycyclopentadienyl)iron complexes (**2**) remained concealed until 2007, when Casey and Guan[15] reported that complex **2a** is a highly efficient catalyst for the hydrogenation of aldehydes and ketones under mild conditions. The main drawback of the active hydride **2a** is its sensitivity to air and moisture, which makes glovebox essential

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for its synthesis and manipulation. Later contributions demonstrated that (hydroxycyclopentadienyl)iron complexes **2** can be formed in situ upon decoordination of one CO ligand from **1** (by oxidative cleavage with Me_3NO,[16] or under UV irradiation[17]) in the presence of H_2 (Figure 1 A, Activation a and b).

Analogous to frustrated Lewis pairs, the (cyclopentadienone)iron complexes ***act*-1**, bearing a vacant coordination site, are able to split H_2 and form the active hydrides **2**. Alternatively, hydrides **2** can be generated in situ from the (cyclopentadienone)iron complexes **1** by Hieber reaction in the presence of aqueous bases (Figure 1 A, Activation c).[18] In situ activated (cyclopentadienone)iron complexes have found application in several reactions involving transfer of H_2, such as hydrogenation (of ketones,[16b,h,i,18a] aldehydes,[18a] imines,[16b] CO_2/$NaHCO_3$[16d,17b] and, very recently, activated esters[16k]), transfer hydrogenation of ketones,[16e,g] reductive amination (of aldehydes and ketones),[16a,c,d] alcohol dehydrogenation[16g,n] and amination of benzylic alcohols.[16f,l,m]

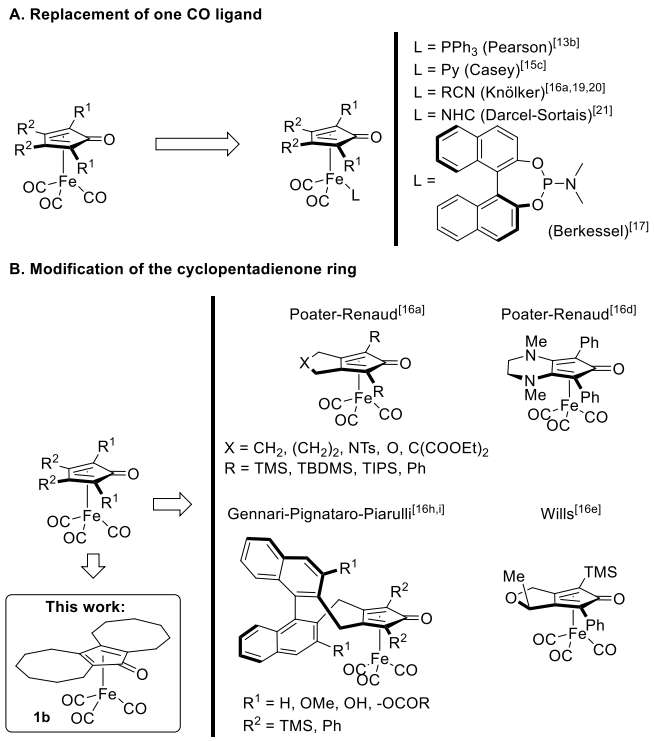


Figure 2. Examples of structural variation of (cyclopentadienone)iron complexes **1**, and the new [bis(hexamethylene)cyclopentadienone]iron complex **1b** reported in this paper.

A number of variations were introduced in the structure of the (cyclopentadienone)iron complexes **1**, both before the discovery of their catalytic applications,[12,13] and afterwards, with the goal to improve their catalytic activity and to expand the application scope. To this end, a first approach (Figure 2 A) consisted in the replacement of one of the three carbon monoxide moieties with other types of ligands such as nitriles[16a,19,20] pyridines,[15c] N-heterocyclic carbenes,[21] phosphines[13b] and chiral phosphoramidites.[16g,17] In a second approach (Figure 2 B) the structural elements of the cyclopentadienone ligand, such as the substituents at the 2,5-positions[16a,d,f,i,18a] and/or the 3,4-positions of the cyclopentadienone were modified.[16a,b,e-i] Following this strategy, several chiral complexes were also synthesized by Wills and co-workers[16e,g] and also by our group,[16h,i] and these complexes were used in the asymmetric hydrogenation and transfer hydrogenation of ketones.

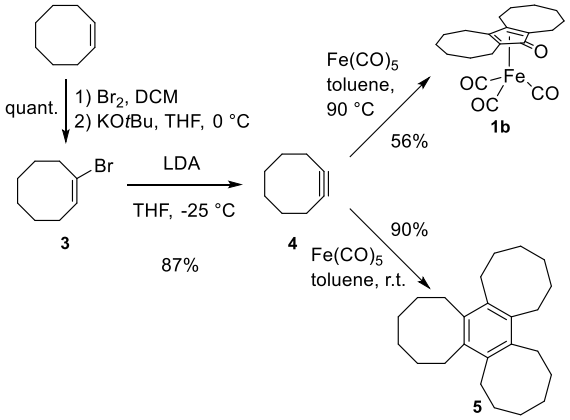
In line with this latter approach, we report herein the first efficient synthesis and the full characterization of [bis(hexamethylene)cyclopentadienone]iron tricarbonyl **1b** (Figure 2 B), a Knölker-type complex featuring cyclooctene rings fused to the 2,3 and 4,5 positions of the cyclopentadienone ring,[22] as well as its application as pre-catalyst for the reduction of C=O bonds.

Results and Discussion

(Cyclopentadienone)iron complexes are usually synthesized by one-pot tethered cyclative carbonylation of diynes with large excesses of iron pentacarbonyl, $Fe(CO)_5$ or diiron nonacarbonyl $Fe_2(CO)_9$, which results also in complexation of the iron tricarbonyl moiety. It should be noted that $Fe(CO)_5$ is inexpensive, so the use of a large excess is acceptable. This approach requires a significant synthetic effort to obtain the diyne precursor with the proper functionalization, thus somehow limiting the possibility to tune the substitution pattern at the cyclopentadienone ring. In principle, an intermolecular cyclative carbonylation/complexation reaction could also be envisioned, starting from two discrete alkynes in the presence of the iron carbonyl reagent [$Fe(CO)_5$ or $Fe_2(CO)_9$]. However, this approach has a limited scope, as it has been reported to occur in good yields only with very specific types of alkyne substitution, such as silyl groups[12a] or some electron withdrawing substituents (e.g., Cl, O*t*Bu and CF_3).[23] Very low yields (< 15%) were reported for the cyclization of more common alkynes such as, for example, phenylacetylene and diphenylacetylene.[24]

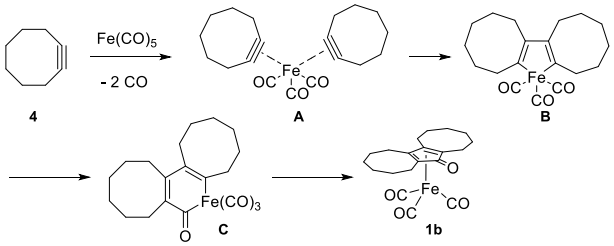
Cyclooctyne (**4** in Scheme 1), the smallest isolated cyclic alkyne, is known to be very reactive, undergoing degradation upon prolonged standing. The compound is not commercially available, but can be easily synthesized in very good yields starting from cyclooctene (Scheme 1):[25] first the alkene is brominated with Br_2 to form the corresponding 1,2-dibromoalkane, from which HBr is eliminated by addition of KO*t*Bu to yield 1-bromocyclooctene (**3**). Then, a second elimination reaction in the presence of LDA allows to obtain the desired product (**4**). According to the literature, when cyclooctyne (**4**) was reacted with Ni, W, Co and Fe carbonyl complexes,[22] several products were isolated, among which were, in the case of iron, substantial amounts of tris(hexamethylene) benzene **5** (derived from cyclotrimerization), and minor quantities of the bis(hexamethylene)cyclopentadienone iron complex **1b** (Scheme 1). This peculiar behavior raised our attention, and induced us to investigate the reaction, in order to optimize the

formation of complex **1b**. The cyclative carbonylation of cyclooctyne (**4**) was then performed in toluene using $Fe(CO)_5$ and carefully controlling the temperature. Much to our delight, the reaction at 90 °C afforded complex **1b** in a respectable 56% yield.



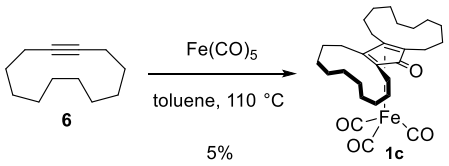
Scheme 1. Synthesis of the bis(hexamethylene)cyclopentadienone iron complex **1b**.

Control of the temperature is important to minimize the formation of the trimerization product **5**, and 90 °C seems to be the optimal value. Indeed, when the reaction was performed at r.t., **5** was the only observed product, but also setting the temperature to 110 °C led to an increased formation of trimer **5** at the expense of the desired complex **1b**, which was obtained in only 45% yield. The proposed mechanism for the formation of **1b** (Scheme 2) consists of a stepwise iron-mediated [2+2+1] cycloaddition which is initiated by the sequential replacement of two carbon monoxides by the two alkyne molecules, thus generating the tricarbonyl[bis-η^2-alkyne] iron complex **A**. At this stage, iron(0) promotes the oxidative coupling of the two bound alkynes to form the intermediate ferrocyclopentadiene structure **B**. Insertion of a molecule of carbon monoxide into the iron-carbon bond followed by a subsequent rearrangement of the ferrohexadienone structure **C** affords the tricarbonyliron-complexed cyclopentadienone **1b**.



Scheme 2. Proposed mechanism for the formation of complex **1b**.

Release of the ring strain of cyclooctyne probably plays an important role in facilitating the intermolecular cyclative carbonylation/complexation process. To confirm this hypothesis, we subjected cyclododecyne **6**,[26] which mainly differs from **4** for the lesser ring strain, to the same reaction conditions adopted in the synthesis of **1b** (Scheme 3). As expected, the reaction of compound **6** in the presence of $Fe(CO)_5$ afforded the desired complex **1c** only in very poor yield (5%, together with unreacted cyclododecyne), and no improvement could be obtained by changing the solvent (toluene, xylene) or varying the reaction temperature.



Scheme 3. The low-yielding synthesis of bis(decamethylene)cyclopentadienone iron complex **1c**.

Complex **1b** was thoroughly characterized spectroscopically, and crystals suitable for X-ray diffraction analysis could be grown by cooling a saturated solution of the bis(hexamethylene) cyclopentadienone iron complex **1b** in *n*-hexane/DCM. The X-ray structure reveals the usual piano-stool geometry with a significant deviation from planarity of the cyclopentadienone ring (see the Supporting Information, Tables S1 and S2, for the relevant parameters).

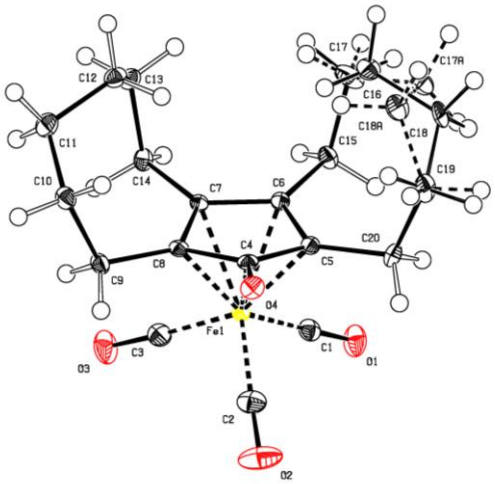
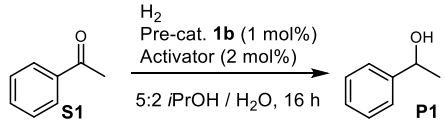


Figure 3. Crystal structure of the [bis(hexamethylene)cyclopentadienone]iron complex **1b**.

We then set to investigate the catalytic activity of complex **1b** in the hydrogenation of acetophenone (**S1**). We firstly screened the above-mentioned methodologies for the in situ activation of the pre-catalyst (Table 1). Use of K_2CO_3 (in situ Hieber reaction)[18] only led to a moderate conversion (Table 1, entry 1), while the other activation strategies (entries 2-3) were more successful: photolysis of a CO ligand by UV irradiation[17] allowed to obtain full conversion, and oxidative cleavage with Me_3NO[16] gave 52% conversion. Increasing the hydrogen pressure to 30 bar allowed to reach 51% conversion in the presence of K_2CO_3 (entry 4) and full conversion in the presence of Me_3NO (entry 5).

Table 1. Test of pre-catalyst **1b** in the hydrogenation of acetophenone **S1** and screening of different activators.[a]

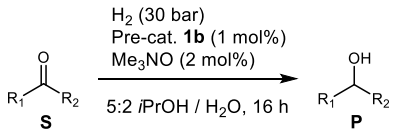


Entry	Activator	P_{H2} [bar]	T [°C]	Conv. [%][b]
1	K_2CO_3	10	70	< 5
2	*hv*[c]	10	40	> 99
3	Me_3NO	10	70	52
4	K_2CO_3	30	70	51
5	Me_3NO	30	70	> 99

[a] Reaction conditions: **S1**/**1b**/activator = 100:1:2, solvent: 5:2 *i*PrOH/H_2O, c_0 (**S1**) = 1.43 M, reaction time = 16 h. [b] Determined by GC (see the Supporting Information). [c] Reaction vessel irradiated at λ_{max} = 352 nm and 8 W; solvent: toluene.

For investigating the substrate scope of pre-catalyst **1b**, we decided to adopt the activation protocol with Me_3NO, which is compatible with standard hydrogenation equipment as it does not require UV irradiation. A number of substrates were screened, giving the results shown in Table 2. Several 4-, 3- and 2-substituted acetophenones were fully hydrogenated (Table 2, entries 2-6), regardless the electron withdrawing or electron donating nature of the substituent. Notably, reducible groups such as carbon-halogen bonds (entries 4 and 6) or nitro group (entry 2) were not affected under the reaction conditions. 2-Acetylpyridine (**S7**) was also hydrogenated with full conversion (entry 7), despite the presence of a coordinating nitrogen atom that - in principle - could poison the catalyst. α-Tetralone (**S8**) was the only aryl ketone to be hydrogenated with less than quantitative yield (entry 8). Aliphatic ketones **S9-10** showed quantitative conversion (entries 9-10), as did the α,β-unsaturated ketone **S11** (entry 11) which, however, gave a 1:1 mixture of 4-phenyl-3-buten-2-ol (from C=O reduction) and 4-phenylbutan-2-ol (from reduction of both C=O and C=C). As – in a control experiment – 4-phenyl-3-buten-2-ol itself did not react at all under the same experimental conditions, we assume that 4-phenylbutan-2-ol was formed by 1,4-reduction of **S11** followed by hydrogenation of the C=O double bond. The cyclic α,β-unsaturated ketone isophorone (**S12**), instead, formed only the C=O reduction product with a modest conversion (entry 12). Quite expectedly, the aldehyde substrates **S14**-**S17** were smoothly hydrogenated to the corresponding alcohols (Table 2, entries 14-17). In the case of cinnamaldehyde (**S17**), some 3-phenyl-1-propanol (from reduction of both C=O and C=C) was also obtained, together with the expected cinnamyl alcohol (entry 17). However, the amount of over-reduction product (5%) was much lower than in the case of the corresponding α,β-unsaturated ketone **S11**. This difference is explained by the fact that – in the case of **S17** – 1,2-reduction of C=O competes more efficiently with the 1,4-reduction pathway due to the higher reactivity of the aldehyde compared to the keto group.

Table 2. Substrate screening for C=O hydrogenation in the presence of pre-catalyst **1b**.[a]



Entry	Substrate	Conv. [%][b]
1	**S1**	> 99 (98)[c]
2	**S2**	> 99
3	**S3**	> 99 (98)[c]
4	**S4**	> 99 (98)[c]
5	**S5**	> 99
6	**S6**	> 99
7	**S7**	> 99
8	**S8**	80
9	**S9**	> 99
10	**S10**	> 99
11	**S11**	> 99[c]
12	**S12**	15
13	**S13**	> 99 *cis : trans* = 60:40
14	**S14**	> 99 (94)[c]
15	**S15**	> 99 (86)[c]
16	**S16**	> 99
17	**S17**	> 99[d]
18	**S18**	99
19	**S19**	0

[a] Reaction conditions: substrate/**1b**/Me_3NO = 100:1:2, P_{H2} = 30 bar, solvent: 5:2 *i*PrOH/H_2O, c_0 (substrate) = 1.43 M, T = 70 °C, reaction time = 16 h. [b] Determined by GC or ^{1}H-NMR of the crude reaction mixture. [c] In brackets, isolated yields of 2 mmol-scale reactions. [d] 1:1 4-phenyl-3-buten-2-ol / 4-phenylbutan-2-ol. [e] 95:5 cinnamyl alcohol / 3-phenyl-1-propanol.

Activated ester **S18** was also hydrogenated (to the corresponding alcohol products) with full conversion (entry 18) under the conditions that we have recently reported (with pre-catalyst **1a**) for the hydrogenation of trifluoroacetates.[16k] Finally, amide **S19** (entry 19) was not reduced, consistent with what was reported for the other Knölker-Casey-type complexes.[10]

The catalytic activity of the [bis(hexamethylene)cyclopentadienone]iron complex **1b** and that of the "classical" (cyclopentadienone)iron complex **1a** in the hydrogenation of acetophenone (**S1**) were then tested at low catalyst loading (0.1 mol%). As can be seen in Table 3, higher turnover numbers (TON) and turnover frequencies (TOF) were observed for complex **1b** compared to **1a**.

Table 3. Comparison between complexes **1a** and **1b** in the hydrogenation of acetophenone (**S1**).[a]

Entry	Cat.	Conv. [%]	TON	TOF [h^{-1}]
1	**1a**	13	130	7.5
2	**1b**	62	620	35.9

[a] c_0 (**S1**) = 1.429 M, substrate/**1b**/Me_3NO = 100:0.1:0.2, P_{H2} = 30 bar, T = 70 °C, 17 h, solvent = 5:2 *i*PrOH/H_2O.

Such a remarkable difference in terms of activity, induced us to evaluate the kinetics of acetophenone hydrogenation in the presence of pre-catalysts **1a** and **1b** (activated with Me_3NO). The conversions were calculated from the hydrogen uptake, measured with a computer-controlled Parr autoclave system. As can be seen in Figure 4, in the initial part of the two experiments (t < 23 min) the in situ formed complexes ***act*-1a** and ***act*-1b** (see Figure 1 A) showed similar activity, with pseudo-first order kinetic profiles (see Table 4 for the kinetic parameters). However, after about 23 min the two catalysts started behaving very differently: while the **1b**-derived catalyst went on following pseudo-first order kinetics (Figure 4, blue diamonds ♦), the ***act*-1a**-catalyzed reaction slowed down (Figure 6, red squares ■) and then proceeded until completion at reduced rate.

These findings seem to suggest that the "classical" **1a**-derived catalyst undergoes quite fast decomposition,[27] so that most of it is transformed into a less active or inactive species before the hydrogenation of **S1** is complete. On the contrary, the catalyst derived from the new [bis(hexamethylene)cyclopentadienone]iron complex **1b** seems to be more robust and not to undergo substantial decomposition before the hydrogenation is finished. The lower stability of catalyst ***act*-1a/2a** compared to ***act*-1b/2b** would also explain the lower TON, TOF and conversion obtained with the former at 0.1 mol% catalytic loading (Table 3).

Table 4. Kinetic parameters of the hydrogenation of acetophenone (**S1**) in the presence of pre-catalysts **1a** and **1b**.[a,b]

Entry	Pre-cat.	k_{app} [min^{-1}][c]	$t_{1/2}$ [min]	k [L mol^{-1} min^{-1}][c]
1	**1a**	0.042	16.3	8.5
2	**1b**	0.034	20.5	6.8

[a] **S1**/pre-cat./Me_3NO = 100:1:2; solvent: 5:2 *i*PrOH/H_2O; c_0 (**S1**) = 0.501 M; P_{H2} = 30 bar; T = 70 °C; $c_{cat.}$ = 5 mM; [b] Kinetic parameters calculated on the following time/conversion intervals: 1-23 min (corresponding to 1-63% conversion) for **1a**, 3-57 min (corresponding to 1-83% conversion) for **1b**; [c] $k_{app} = k \cdot c_{cat}$.

The proposed mechanism for the hydrogenation of acetophenone, shown in Scheme 4 (Cycle A), is the commonly accepted one for Knölker-Casey catalysts:[15c, 28] after the activation of pre-catalyst **1b** by decoordination of one CO ligand, the active species ***act*-1b** splits H_2 generating the (hydroxycyclopentadienyl)iron complex **2b**. The latter reacts with the substrate through a concerted pericyclic transition state (**II**), forming complex ***act*-1b** together with the reaction product.

Casey and Guan reported that the isolated (hydroxycyclopentadienyl)iron complex **2a** is also able to catalyze the transfer hydrogenation of acetophenone (**S1**) with *i*PrOH.[15a]

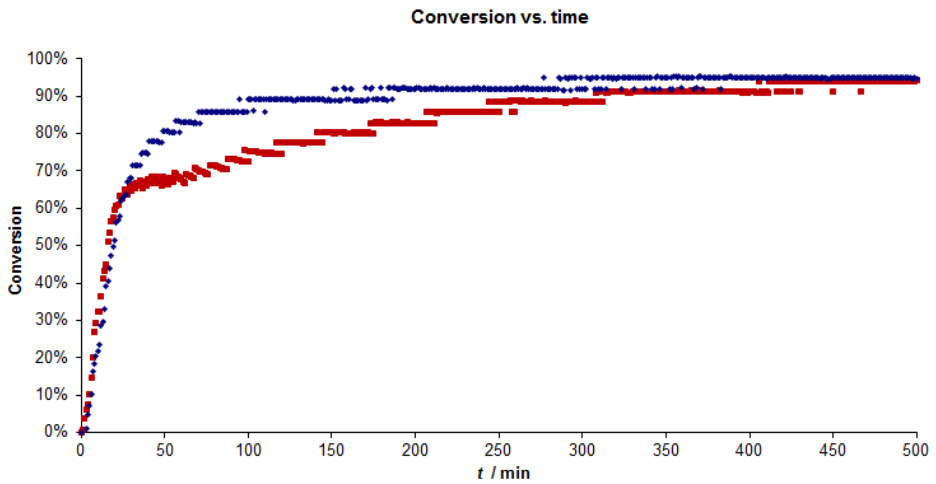
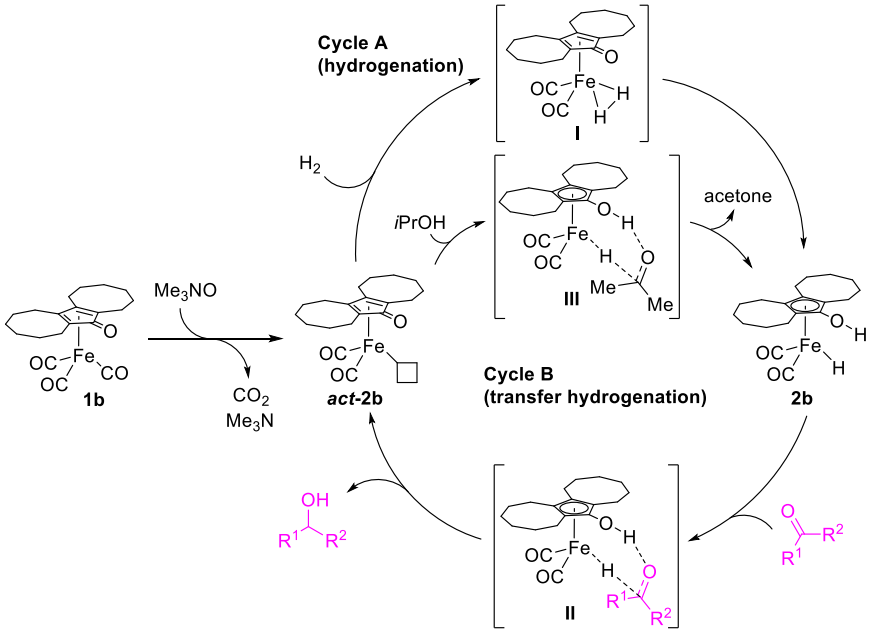


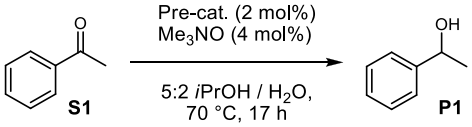
Figure 4. Kinetics of acetophenone (**S1**) hydrogenation promoted by pre-catalyst **1a** (■) and **1b** (♦) activated with Me_3NO. Reaction conditions: **S1**/Pre-cat./Me_3NO = 100:1:2; solvent: 5:2 *i*PrOH/H_2O; c_0 (**S1**) = 0.501 M; P_{H2} = 30 bar; T = 70 °C; $c_{cat.}$ = 5 mM.



Scheme 4. Proposed mechanism for ketone hydrogenation (Cycle A) and transfer hydrogenation (Cycle B) promoted by complex **1b** activated with Me_3NO.

We thus tested the (cyclopentadienone)iron complex **1a** and our new [bis(hexamethylene)cyclopentadienone]iron complex **1b**, activated in situ with Me_3NO, in this reaction (Table 5). Just as observed in hydrogenation, pre-catalyst **1b** was found more active than the "Knölker complex" **1a**: while only moderate conversion was obtained in the presence of the latter complex (Table 5, entry 1), use of pre-catalyst **1b** allowed to obtain almost full conversion (Table 5, entry 2). This finding is in agreement with the hypothesis that mechanism and active catalytic species are similar to those of the hydrogenation: as shown in Scheme 4 (Cycle B), first the active complex ***act*-1b** dehydrogenates *i*PrOH (through the pericyclic transition state III) forming the hydride **2b**, then the latter reduces the substrate (through transition state II).

Table 5. Transfer hydrogenation of acetophenone (**S1**) with *i*PrOH in the presence of pre-catalysts **1a** and **1b**.[a]



Entry	Pre-cat.	Conv. [%]
1	**1a**	34
2	**1b**	90

[a] **S1**/Pre-cat./Me_3NO = 100:2:4, c_0 (substrate) = 0.7 M, T = 70 °C, 17 h, solvent: 5:2 *i*PrOH/H_2O.

Conclusions

In this paper we have reported the first efficient synthesis and full characterization of the [bis(hexamethylene)cyclopentadienone]iron complex **1b**. The latter compound has been obtained in preparatively useful yield (56%) by reaction of cyclooctyne with $Fe(CO)_5$. The yield obtained is remarkable for this kind of intermolecular cyclative carbonylation/complex-ation, which usually gives good results only with a few, properly substituted alkynes.[12a,23,24] The observed reactivity of cyclooctyne – the smallest cyclic alkyne – is probably due to ring strain, as suggested by the lack of reactivity of its unstrained higher homolog cyclododecyne. Complex **1b** has been tested as pre-catalyst in the hydrogenation of ketones, in which, after activation with Me_3NO, it displayed a catalytic activity superior (in terms of TON and TOF) to that of the well-known complex **1a**. The same trend was observed also in the transfer hydrogenation of acetophenone, in which **1b** allowed to obtain a higher conversion compared to **1a**. Further exploration of the pre-catalyst's scope showed that **1b** can promote also the hydrogenation of aldehydes and trifluoroacetate esters. Kinetic studies on the hydrogenation of acetophenone in the presence of complexes **1a** and **1b** suggest that this difference is due to the higher stability of the **1b**-derived catalyst compared to the "Knölker-Casey catalyst" generated in situ from **1a**.

Experimental Section

General Remarks. All reactions were performed in flame-dried glassware with magnetic stirring under an inert atmosphere

(nitrogen or argon), unless otherwise stated. The solvents for the reactions were distilled from the following drying agents and transferred under nitrogen: CH_2Cl_2 (CaH_2), THF (Na), toluene (Na). 2-Propanol (over molecular sieves in bottles with crown caps) was purchased from Sigma–Aldrich and stored under nitrogen. The reactions were monitored by analytical thin layer chromatography (TLC) with silica gel 60 F254 precoated glass plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp. Flash column chromatography was performed with silica gel (60 Å, particle size 40–64 μm) as the stationary phase by following the procedure of Still and co-workers.[29]

The ^{1}H NMR spectra were recorded with a spectrometer operating at 400.13 MHz. The ^{1}H chemical shifts (δ) are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$ δ = 7.26 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, m = multiplet, br = broad signal. The ^{13}C NMR spectra were recorded with a 400 MHz spectrometer operating at 100.56 MHz with complete proton decoupling. The ^{13}C chemical shifts are reported in ppm (δ) relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$ δ = 77.16 ppm). ^{19}F NMR spectra were recorded with a 300 MHz spectrometer operating at 282 MHz. ^{19}F NMR chemical shifts are reported in ppm (δ) relative to $CFCl_3$ with α,α,α-trifluorotoluene (δ = -63.72 ppm) as internal standard. Positive values indicate downfield shifts, and the coupling constant values are given in Hz. The infrared spectra were recorded with a standard FTIR spectrometer. The hydrogenation experiments with UV irradiation were carried out in a glass autoclave (total capacity 20 mL, maximum pressure 25 bar) which was put in a photochemical reactor (Rayonet RPR-100, Southern New England UV Company, USA). The UV lamps used have the specification F8T5BLB, 8 W, 352 nm (Sanyo Denki, Japan). The other hydrogenation experiments were run in a 450 mL Parr autoclave equipped with a removable aluminium block that can accommodate up to fifteen magnetically stirred 7 mL-glass vials.

For the synthesis of cyclooctyne **4** and cyclododecyne **6**, see the Supporting Information.

Synthesis of bis(hexamethylene)cyclopentadienone irontricarbonyl (1b). Cyclooctyne **4** (230 μL, 1.85 mmol) and $Fe(CO)_5$ (1.2 mL, 9.25 mmol, 5 equiv) were dissolved in dry toluene (10 mL), under argon, and heated to 90 °C overnight in a sealed glass tube. Evaporation of the solvent gave the crude product, which was then purified by flash chromatography (7:3 hexane/AcOEt). Yellow crystals. Yield: 198 mg (56%). m.p. = 156 °C. ^{1}H NMR (400 MHz $CDCl_3$): *δ* 1.44-1.59 (m, 10H), 1.74-1.92 (m, 8H), 2.40-2.49 (m, 2H), 2.59-2.64 (m, 2H), 2.76-2.78 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): *δ* 23.43, 23.70, 25.77, 26.24, 28.81, 31.29, 85.54, 102.42 171.42, 209.35. FT-IR: *v* = 2924.1, 2856.6, 2050.3, 1978.9, 1950.0, 1620.2, 1585.5, 1456.3, 1354.0, 1278.8, 1203.6, 1118.7, 1097.5, 1031.9, 987.5, 817.8, 736.8, 648.1, 621.1 cm^{-1}.

HRMS (ESI+): m/z 385.1098 [M + H]+; 407.0919 [M + Na]+ (calcd. for C21H24O4Fe: 385,1102; C20H24O4FeNa: 407.0922).

Synthesis of bis(decamethylene)cyclopentadienone irontricarbonyl (1c). Cyclododecyne **6** (167μL, 0.91 mmol) and $Fe(CO)_5$ (613 μL, 4.6 mmol, 5 eq) were dissolved in dry toluene (5 mL), under argon and heated to 110 °C overnight in a sealed glass tube. Evaporation of the solvent gave the crude product, which was then purified by flash chromatography (6:4 hexane/AcOEt). Orange solid. Yield: 12 mg (5%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.37-2.35 (4H, br), 2.10-2.08 (2H, br), 1.94-1.97 (2H, br), 1.78 (2H, br), 1.56-1.30 (27H, m), 1.21-1.19 (3H, br). MS (ESI+): m/z 497.11 $[M + H]^+$; 519.11 $[M + Na]^+$ (calcd. for $C_{28}H_{41}O_4Fe$: 497.24; $C_{28}H_{40}O_4FeNa$: 519.22).

General Procedure for the Hydrogenation Reactions. The pre-catalyst (0.005 mmol, 0.01 equiv) was weighed in the glass vials and then *i*PrOH (0.25 mL) was added to each vial and stirring was started. An aqueous solution of Me_3NO (0.01 mmol, 0.02 equiv, 0.1 mL) was dispensed to each vial. After stirring at room temperature under nitrogen for 10 min, the substrate (0.5 mmol, 1 equiv) was added to the catalyst solutions. Each vial was capped with a Teflon septum pierced by a needle, and transferred into the autoclave, and stirring was started. After purging four times with hydrogen at the selected pressure, heating was started. The reactions were stirred under hydrogen pressure overnight and then analysed for conversion.

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