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ARTICLE

Tuning the Tetraarylcyclopentadienones from iron tricarbonyl complexes: effects in Transfer Hydrogenation and solubility

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The nature of the ligands coordinated to the metal in cyclopentadienone iron tricarbonyl (CIC) complexes is important for the activation or H transfer steps of Transfer Hydrogenation (TH) catalysis. Previous reports showed an existing correlation between the electron-donating or -withdrawing nature of substituents appended to phenyl groups at 3,4 positions of tetraarylcyclopentadienones and the catalytic efficiency of the related CICs. Here we extend these studies to phenyl groups at positions 2,5. Our results show that careful selection of the substituent groups apended to the different aryl groups of tetraarylcyclopentadienone improves the solubility of CIC complexes on protic solvents, or rescues the catalytic efficienty for TH reactions on complexes carrying electron-withdrawing groups in their arene.

Introduction

Transfer hydrogenation (TH) is an alternative catalytic method to direct hydrogenation or the use of stoichiometric reducing reagents for the reduction of carbonyl, imines, and other unsaturated compounds.[1-4] TH uses transition metal catalysts that follow outer-sphere mechanisms to transfer H atoms from donors (normally solvents like alcohols) to the substrates, and is of considerable importance for some types of chemical industry (*i.e.* pharmaceutical, petrochemical, etc.). Most industrial catalysts for TH use metals from the second and third transition rows like Ru, Rh, Os or Ir,[2] so they are expensive to produce and rise environmental and toxicity concerns. Fe-based catalysts for TH are also known,[5-10] and sometimes outperform those from more traditional metals in catalytic efficiency and enantioselectivity.[11] This is interesting for industry, as the use of Fe catalysts can be cost-effective (Fe is the fourth most abundant element in Earth's crust), and help to reduce environmental and toxic negative effects (Fe is the most abundant biometal in most organisms).[12-14]

In this context, cyclopentadienone iron tricarbonyl (CIC) complexes are interesting due to their cheap and accessible synthesis,[10,15] good stability and easy handling. With a structure analogue to the Shvo's Ru catalyst (Fig. 1)[16,17] these complexes are effective catalysts of TH reactions for the reduction of aldehyde, ketones, and imines, or the oxidation of alcohols and amines.[10,15,18,19] But they can also catalyse other reactions like dehydration of primary amides, formation of C-N bonds, hydrosilylation of carbonyl groups, alkylation of indoles, alpha-alkylation of methylketones through hydrogen borrowing, *N*-ethylation and *N*-methylation of amines.[20-28] CICs are precatalysts, and can get activated following different methods like the de-coordination of CO ligands,[10] or Hieber base reactions.[29] After activation, the arene can undergo reversible dearomatization and rearomatization, establishing a Fe^{II}/Fe^{0} cycle that is part of the catalytic mechanism for TH. Moreover, both cyclopentadienone arenes and iron metal centers participate in accepting the H_2 from the donor solvent, and transferring it to the substrate (or *vice versa* in case of oxidation reactions).

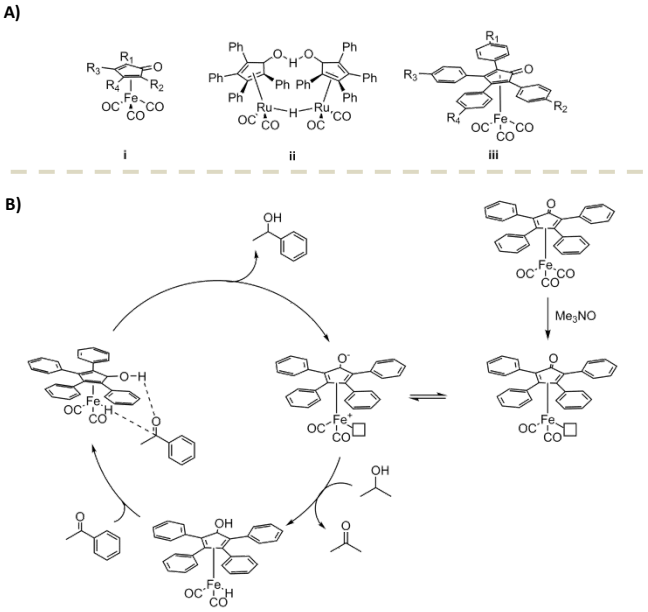

Figure 1. (**A**) cyclopentadienone iron tricarbonyl (CIC) complexes (**i**); the Shvo's catalyst (**ii**); (2,3,4,5-tetraphenylcyclopentadienone) iron tricarbonyl complexes used in this work (**iii**). (**B**) Catalytic cycle for Transfer Hydrogenation using CIC complexes.

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Ligands coordinated to Fe in CICs are important during the activation (CO) or H transfer (cyclopentadienone) steps of TH. Therefore, different studies explored how to improve the catalytic properties of these complexes by careful tuning of such ligands. Modification of the CO groups has proven to be difficult, as strong field ligands seem required to maintain the catalytic activity of CICs. Still, exchange of CO ligands with different nitrile groups (CNR), permitted to maintain the CIC's activity and removed the need of strong bases for their activation.[30,31] Alteration of cyclopentadienone rings was more feasible,[10,15] and multiple publications have reported the effect of different changes in the structure of those arenes over the catalytic efficiency of CICs. As such, the cyclopentadienone has been modified by adding or fusing to it additional aromatic or aliphatic rings,[32] but also aromatic or heterocyclic amines[17,33] or aliphatic chains,[34] both neutral or containing charged groups (to improve the solubility of the complex).[35,36] Cyclopentadienones have also been transformed into non-symmetric arenes to form chiral complexes capable of catalysing asymmetric transfer hydrogenation (ATH) reactions. Early examples of ATH performed with CICs achieved mostly low enantioselectivity,[37-39] but recent examples improved greatly the enantiomeric control of the catalysts.[40]

Remarkably, it has been shown that the catalytic performance of CICs is linked to the electronic density of their arenes. Complexes with electron-rich cyclopentadienones were more efficient catalysts for the reduction of ketones, and reductive aminations or alkylations.[41-43] Recent reports expanded on these studies by placing electron-donor or -withdrawing groups of similar size at *para* positions of phenyl rings in 3 and 4 positions of 2,3,4,5-tetraphenylcyclopentadienone ligands. This showed that a decrease of the electron density on the cyclopentadienone due to substitutions with electron-withdrawing groups reduced catalytic efficiency significantly. Conversely, catalysts bearing electron-donating groups exhibited higher conversion rates and faster initial reaction velocities. Previous studies also probed the importance of electron-donor or -withdrawing groups in phenyl rings in positions 2,5 of the arene of CICs for their ability to catalyse C-N bond formation reactions between amines and alcohols via hydrogen borrowing. However, results obtained seemed to be more dependent on the nature of the substrates employed than in the electron-density of the cyclopentadienone.[21] Moreover, the effect of similar substitutions in phenyl rings in positions 2,5 of the cyclopentadienone over their efficiency in the catalytic reduction of ketones via TH has not been studied (although some studies explored the effect of exchanging those phenyl rings with different aliphatic chains).[34]

This work expands previous explorations on the importance of the electronic properties of the arenes on the catalytic performance of the CICs by placing electron-donor or -withdrawing groups of similar size also on phenyl rings placed in positions 2,5 of the cyclopentadienone. For this, we synthesized and characterized a library of twelve (2,3,4,5-tetraphenylcyclopentadienone) iron tricarbonyl complexes (Fig. 2B) by combining multiple substituents at *para* positions of phenyl rings at all four positions of the arenes. The influence of those substituents on both the catalytic efficiency for the reduction of ketones via TH, and the solubility of the complexes was studied. As such, we identified catalysts combining high catalytic performance and improved solubility in protic solvents. Moreover, our experiments showed that the negative effects of electron-withdrawing substituents on the catalytic efficiency of the complexes can be modulated by combining those groups with electron-donor groups within the same arene.

Results and discussion

Synthesis and characterization of the library of complexes

A library of twelve (2,3,4,5-tetraphenylcyclopentadienone) iron tricarbonyl complexes bearing electron-donor or -withdrawing groups of similar size at *para* positions of all the phenyl rings around the arene was synthesized. Both cyclopentadienone ligands and their related complexes were synthesized using a microwave reactor (to reduce reaction times).[44] Initially, Friedel-Crafts acylations were used to obtain substituted benzyl phenyl ketones from aromatic precursors.[45] C-H oxidation of those compounds yielded substituted benzil intermediates[46] that were used to produce the desired cyclopentadienones via double aldol condensations with substituted diphenylacetones.[46] It is worth noting that ligands carrying fluorinated groups were always obtained in low yields.

Further reaction of the arenes with iron pentacarbonyl following methods previously described[47] led to the corresponding iron tricarbonyl complexes (**0 - 12**). Different substituents were used to modify phenyl rings at 2,5 (*e.g.* -H, -CF_3 or -OH) or 3,4 positions (e.g. -Br, -F, -CH_3 or -OCH_3), and our synthetic strategy allowed us to generate catalysts both homo-substituted (bearing identical substituents on both of those phenyl rings) and hetero-substituted (incorporating different substituents on each of the phenyl rings; see **1**,**4**,**6** and **10**) at 2,3 positions. Substituents used includes both electron-withdrawing (*e.g.* -Br, -F or -CF_3) and electron-donor groups (*e.g.* -CH_3, -CH_3O or -OH) with different strengths, and polarities (aiming to enhance solubility of the complexes in protic solvents).

Across the library, the yields of the complexes isolated does not show a clear dependence on the electronic nature of their aryl substituents (see Fig. 2). For example, complexes **0** and **1**, which are unsubstituted at the 2,5-positions and carry -H or -Br/-OH substitutions at the 3,4-postions, were obtained in relatively low yields (23% and 21% respectively). Instead, it was possible to isolate analogues with both electron-withdrawing CF_3 or electron-donating OH groups at 2,5-positions (complexes **5-6** and **9-10**) with increased yields. Similarly, changing H groups at 3,4-positions for electron-withdrawing or electron-donating substituents can lead both to increases (*i.e.*, complexes **2**,**3** or **8**) or decreases (*i.e.*, complexes **7**,**11** or **12**) in the isolation yields obtained, that are not related to the electronic properties of the new groups introduced. Nevertheless, electron-withdrawing fluorinated substituents seemed to decrease the stability of the

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complexes (*e.g.*, **4**-**8**), and they seemed to get easily degraded once in solution, when compared to other series of complexes. Nevertheless, most CICs in the library could be purified easily via silica-gel column chromatography using gradients of various eluents. Additionally, all intermediates, cyclopentadienone ligands and tricarbonyl iron complexes were fully characterized by IR spectroscopy, multinuclear NMR (^{1}H, ^{13}C, ^{19}F, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC), and high-resolution mass spectrometry (ESI-MS and MALDI-TOF). ^{13}C NMR shows clearly signals corresponding to the three carbonyl groups at around 200 ppm, while the ketone carbon atom of the cyclopentadienone ligand appears at approximately 170 ppm in all cases (see ESI for further details). Equally, the ν(CO) stretching bands are clearly visible at around 2000 cm^{-1} in the IR spectra of all compounds (see ESI for further details). Finally, compounds **2**, **3**, **6**, **7**, and **9** were characterized structurally in the solid state by X-ray diffraction (see ESI Tables S1 and S2). The atomic connectivity for this class of compounds is well established by previous studies.[§]

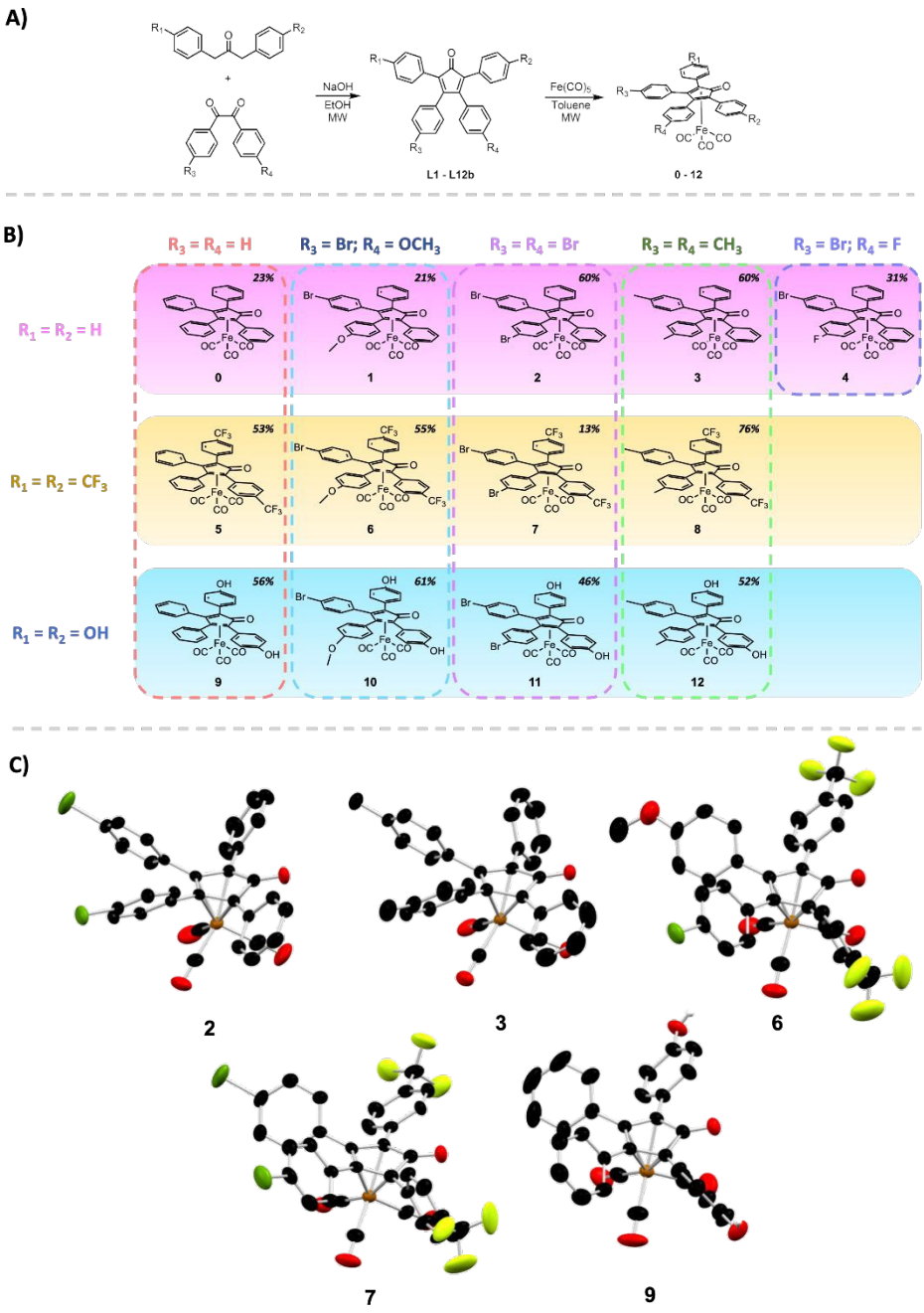

Figure 2. General scheme of the synthesis of cyclopentadienone ligands and iron tricarbonyl complexes (**A**); Cyclopentadienone iron tricarbonyl complexes generated, divided according to the substituents in R_1/R_2 (rows), and to the substituents in R_3/R_4 (columns) (**B**); molecular structure of complexes **2**, **3**, **6**, **7**, **9**, according to X-ray diffraction. Displacement ellipsoids are drawn at 50% probability level, most of hydrogen atoms and solvent molecules are omitted for clarity (**C**).

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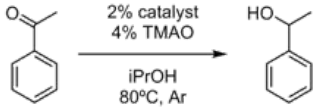
Catalytic activity of the different complexes in the library

The catalytic properties of **0**-**12** were evaluated by exploring their ability to facilitate the reduction of acetophenone via TH. Initially, reduction reactions were performed under standard conditions previously reported (*e.g.*, 2% catalysts, 4% Trimethylamine N-oxide in isopropanol, Ar atmosphere, 80°C; Table 1), and conversions monitored via ^{1}H-NMR by following the changes in the peak of the methyl group of the acetophenone after reduction (see SI Fig. S117). Looking at the total conversion of acetophenone after 16 h (end-point), our results confirm previous reports, as the electronic properties of the substituents seem to be one of the dominant factors dictating the catalytic performance of the CICs (Table 1). In general, complexes carrying electron-withdrawing substituents in their arenes (*e.g.* -Br, -F and -CF_3) suffer a decrease in their catalytic efficiency during TH reactions. Instead, CICs carrying electron donating groups (*e.g.,* -CH_3, -OCH_3 and -OH) improve their catalytic properties when compared with analogues just carrying -H (although exceptions can be found).

Still, the positioning within the cyclopentadienone arene of the phenyl rings that are substituted with those groups is also important. When the different substituents are placed in phenyls in positions 3,4 (in our case -OCH_3, -CH_3, -H, -Br or -F groups) the correlation between catalytic efficiency and Fig S118-S119). If catalysts carry the same substituents in both of those phenyl rings, their efficiency follows the trend -CH_3>-H>-Br (although the -OH series follows marginally the trend -H>-CH_3>-Br). Catalysts carrying electron donating -CH_3 groups (**3** and **8**) are the most active, and those with electron withdrawing -Br (**2**, **7** and **11**) the least. Nevertheless, when substituents with different electronic properties were combined in the same cyclopentadienone arenes we observed behaviours that could be considered as intermediate between those with single ligands. As such, catalysts carrying both -Br and -F electron withdrawing groups in their structure showed low catalytic

Table 1. Transfer hydrogenation of acetophenone. Reaction conditions: acetophenone (1 equiv.), 2 mol% catalyst, 4 mol% TMAO in 1 mL dry iPrOH (80°C, Ar atmosphere).



Entry	Conversion 16 h (%)	Conversion 24 h (%)	$TOF_{1/2}$ (h^{-1})
BLK*	-	-	-
0	93	93	12.8
1	95	95	14.4
2	76	73	4.2
3	97	-	-
4	46	60	7
5	76	-	-
6	51	40	(N/R)
7	41	-	-
8	85	-	-
9	88	83	7.5
10	78	80	7.8
11	52	58	3.5
12	73	76	7.1

*Reaction conditions BLK: acetophenone (0.25 mmol, 1 equiv.), 4 mol% Trimethylamine N-oxide (TMAO) in 1 mL dry isopropanol (iPrOH); 80°C, 16 h, Ar atmosphere. Reaction conditions 16 h end-point: acetophenone (0.25 mmol, 1 equiv.), 4 mol% Trimethylamine N-oxide (TMAO) in 1 mL dry isopropanol (iPrOH) 2 mol% catalysts (**0**-**12**); 80°C, 16 h, Ar atmosphere. Reaction conditions kinetics and $TOF_{1/2}$: acetophenone (0.5 mmol, 1 equiv.), 4 mol% Trimethylamine N-oxide (TMAO) in 2 mL dry isopropanol (iPrOH) 2 mol% catalysts; 80°C, Ar atmosphere; aliquots of the reaction were taken at 30 min, 1, 2, 4, 8 and 24 h. Conversions were calculated by ^{1}H-NMR. Averaged results of duplicates of duplicates.

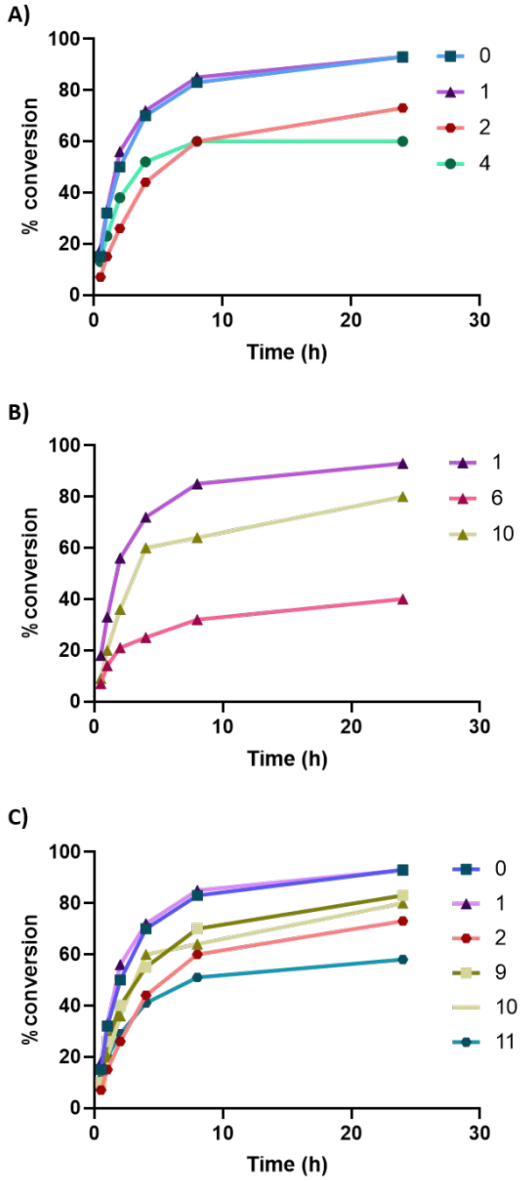


Figure 3. Conversion (%) vs time (h) for the transfer dehydrogenation of acetophenone using catalysts with -H in 2,5 positions and different electron-donating or withdrawing groups in 3,4 positions (**A**); with -OMe/-Br groups in 3,4 positions and different electron-donating or withdrawing groups in 2,5 positions (**B**); and -H or -OH in 2,5 positions and different electron-donating or withdrawing groups in 3,4 positions (**C**). Reaction conditions: acetophenone (0.5 mmol, 1 equiv.), 2 mol% catalyst, 4 mol% TMAO in 2 mL dry iPrOH (80°C, 24 h, Ar atmosphere). An aliquot of the reaction was taken at 30 min, 1, 2, 4, 8 and 24 h. Plotted points are averages of at least two runs. Conversions were determined by ^{1}H-NMR.

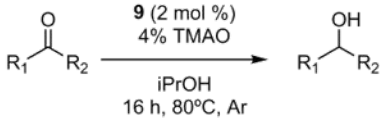
efficiency (**4**). Yet, when -Br and -OCH_3 groups were combined in the same arene (**1**, **6** and **10**), the methoxy group seemed to compensate electronically the presence of the -Br group, and the catalysts recover their catalytic activity to be similar or close to that of -H analogues (**0**, **5** and **9**).

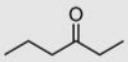
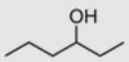
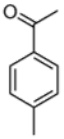
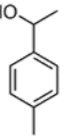
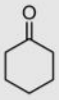
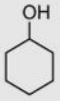
Kinetic analysis of the catalysis reactions confirmed these results, and suggested possible exhaustion of the catalysts after 16 h (as no great changes in conversions were observed between 16 and 24 h). Observed $TOF_{1/2}$ showed similar trends (-OCH_3/Br>-$(CH_3)_2$≈-$(H)_2$>-F/Br>-$(Br)_2$) to those observed previously with our end-point analysis (after 16h). Still, while in the -H series Hammett plots used to analyse the initial rates of the reduction of acetophenone showed linear relationship between the logarithm of the initial reaction rates (relative to CICs with -H groups in phenyls in positions 3,4 of the cyclopentadienone) and Hammett's substituent constants, this was not the case for CIC complexes in the -OH series (Figure S120).[48]

On the contrary, catalytic properties seems to be only partially correlated with the electronic properties of the substituents when they are located in phenyl rings found in positions 2,5 of the arene (-OH, -H or -CF_3 groups). In this case, the efficiency of CICs for the reduction of acetophenone via TH follows the trend -H>-OH>-CF_3. This was confirmed by conversions after 16 h of reaction, and kinetic studies (see Table 1, Fig. 3, and ESI Fig S118-S119). Catalysts with non-substituted phenyl rings (**0-3**) showed always the highest conversion rates and $TOF_{1/2}$ (around 13-14 h^{-1} for **0** or **1**), while those carrying electron-donating -OH groups (**9-12**) achieved also good conversions at 16 h but halved $TOF_{1/2}$ (around 7-8 h^{-1} for **9**, **10** or **12**). Complexes **5-8** featuring electron-withdrawing CF_3 groups were the poorest catalysts, showing the lowest conversions at 16 h and poor stability that complicated the kinetic data of their catalytic properties. Moreover, Hammett plots did not show a linear relationship between the logarithm of the initial reaction rates (relative to CICs with -H in phenyls in positions 2,5 of the arene) and Hammett's substituent constants, as -OH substituted **10** had initial reaction rates lower than expected (Figure S120).[48] Hammett plots obtained for the -OH series with modifications in 3,4 positions were also similar. Therefore, it seems feasible that factors other than the electronic properties of the substituents (maybe steric hindrance or interactions of substituents with the substrate) are of greater importance for the catalytic properties of CICs when phenyl rings in position 2 and 5 are modified with certain chemical groups.

Overall, these experiments show that the modification of 2,3,4,5-tetraphenylcyclopentadienone arenes with electron-withdrawing groups has a negative effect over the catalytic performance of CICs, independently of the position of the arene where the substituents are introduced. Nevertheless, those negative effects can be compensated through strategic pairing in the cyclopentadienone of electron-withdrawing and electron-donor groups. We showcased this by generating CICs carrying simultaneously a single -Br and -OMe substituent in equivalent positions (3,4 phenyl rings), which maintained their catalytic efficiency when compared with analogue complexes carrying only -H or electron-donating substituents.

Table 2. Transfer hydrogenation of different substrates with **9**. Reaction conditions: substrate (1 equiv., 0.25 mmol), 2 mol% **9**, 4 mol% TMAO in 1 mL dry iPrOH (80°C, Ar atmosphere, 16 h).



Entry	Substrate	Product	Conversion (%)
1			93
2			67
3			80

We also show that although the addition of electron-donating groups to the cyclopentadienone increases the catalytic efficiency of CICs, this positive effect is of lesser entity than the reduction caused by electron-withdrawing groups. Moreover, the overall effect observed also depends on the position within the arene where the new substituents are located. In particular, electron-donating groups introduced close to the carbonyl group of the arene seem to affect the properties of CICs not only by modifying the electron density of the arene, but also in otherways that remain unknown as yet. The similar size of all the substituents used in our library suggests that the changes observed in the catalytic efficiency are not linked to steric effects. Equally, the distance between the substituents and the carbonyl group of the cyclopentadienone (separated by a phenyl ring) discards possible interactions between the -OH and the different keto/enol tautomeric forms of the C=O from the same molecule (which can affect H transfer during the TH reaction). Still, we cannot rule out a possible interaction between the -OH substituent and the substrate, or other interactions that could slow down the H transfer. Moreover, kinetic data could be altered by air insertion during sampling (especially for most unstable catalysts), even if an overpressure of argon was used during the process to avoid it. However, further experiments are needed to explore those possibilities.

Finally, the capacity of the catalysts from the -OH series to reduce other types of substrates through transfer hydrogenation reaction was confirmed (Table 2 and Fig. S121-S123). For this, three new substrates including aliphatic, cycloaliphatic and aromatic ketones, were reduced with **9** under standard conditions. The catalyst was able to reduce aliphatic and cycloaliphatic ketones effectively (with yields over 80% in 16 h reaction), while the conversion of the aromatic ketone selected was lower (below 70%). Still, this was expected, as the

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Table 3. Qualitative solubility of **0-3** and **9-12** in mixed aqueous media. Each complex was examined in DMSO/H_2O (1:1) and iPrOH/H_2O (1:1) at room temperature, 40°C and 80°C. Solubility was monitored during 4 h at each condition. Entries are marked in green when a clear homogeneous phase was observed, and in red when solid remained visible under the corresponding conditions.

Entry	rt	40°C	80°C	Mixture
0	✗	✗	✗	DMSO/H_2O
	✗	✗	✗	iPrOH/H_2O
1	✗	✗	✗	DMSO/H_2O
	✗	✗	✗	iPrOH/H_2O
2	✗	✗	✗	DMSO/H_2O
	✗	✗	✗	iPrOH/H_2O
3	✗	✗	✗	DMSO/H_2O
	✗	✗	✗	iPrOH/H_2O
9	✓	✓	✓	DMSO/H_2O
	✓	✓	✓	iPrOH/H_2O
10	✓	✓	✓	DMSO/H_2O
	✓	✓	✓	iPrOH/H_2O
11	✗	✗	✗	DMSO/H_2O
	✓	✓	✓	iPrOH/H_2O
12	✓	✓	✓	DMSO/H_2O
	✓	✓	✓	iPrOH/H_2O

aromatic substrate selected (*para*-methylacetophenone) was deactivated for the reaction due to the presence of a methyl group in *para* position to the ketone.

Improved solubility and catalytic activity at low temperature in water mixtures

CICs carrying -OH groups in phenyls at 2 and 5 positions (**9-12**) showed improved solubility on isopropanol throughout experiments to study their catalytic activity, when compared with those carrying -H or -CF_3 groups. Further tests confirmed this, and indicated that modification of the arene with -OH groups increased substantially the solubility of the complexes in protic solvents and aqueous mixtures independently of the temperature (Table 3).

Remarkably, -OH functionalized catalysts also showed marginal improved catalytic efficiency for the reduction of acetophenone in isopropanol at lower temperatures than normally used. This was independently of the other substituents present in the arene. As such, -OH complexes carrying -H or -Br groups in phenyl groups in 3 and 4 positions (**9** and **11**, respectively) reduced 10% more acetophenone in isopropanol at 40°C than -H analogues (**0** and **2**, respectively). This is interesting, if we consider that the same -H analogues showed between 10 and 20% better conversions at 80°C (Fig. S124). Performing the same reaction in 1:1 isopropanol:water mixtures allowed faster activation of the complexes via Hieber-base reactions.[20] This amplified the reduction of acetophenone achieved by all catalysts at 80°C. But also increased greatly the difference in

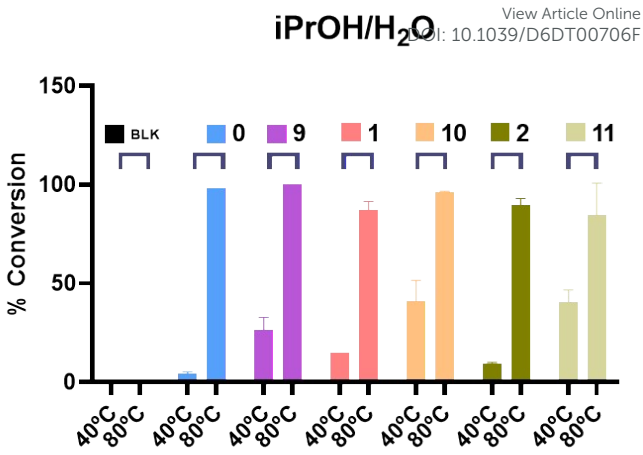

Figure 4. Conversion of the reduction of acetophenone via TH achieved by complexes **0**, **1**, **2**, **9**, **10**, and **11** at 40°C or 80°C (24 h) in a 1:1 isopropanol:water mixture. Plotted points are averages of at least two runs. Conversions were determined by ^{1}H-NMR.

catalytic efficiency between -OH (**9**, **10** and **11**) and -H (**0**, **1**, and **2**) analogues when the reaction was performed at 40°C (Fig. 4). The improved catalytic activity of -OH carrying CICs at 40°C might stem from a better availability of active species in solution (as shown in the ^{1}H NMR spectra of **0** and **9** in 1:1 isopropanol:D_2O mixtures, Fig. S125), as precipitation or aggregation of more hydrophobic -H analogues could be a problem at lower temperatures and water mixtures. Overall, the capacity to act at milder conditions (e.g. lower temperatures and aqueous solutions) of -OH functionalized complexes can help to generate catalysts that reduce energy costs, and decrease losses in volatile organic solvents.

Conclusions

We have shown that positioning of electron-donating and withdrawing modifications in cyclopentadienone arenes it is important for the catalytic properties of CIC complexes. Our results confirm a direct correlation between the ability of (2,3,4,5-tetraphenylcyclopentadienone) iron tricarbonyl complexes to catalyse TH reactions and the absolute electron-donating nature of the substituents in *para* positions on their phenyls rings if they are located far from the ketone group (*e.g.* those found in 3,4 positions of the cyclopentadienone). However, electron-donation is only one of the aspects affecting the catalytic properties of CICs when substituents are located in phenyl rings close to the carbonyl group of the arene (*e.g.* 2,5 positions), and further work is needed to fully understand the other factors and their relative importance.

Furthermore, our work also demonstrates that it is possible to optimize properties like catalytic activity or solubility in protic solvents (even simultaneously) of the CIC complexes by careful tuning of the substituents carried by their cyclopentadienone ligands. As such, pairing electron-withdrawing with electron-donating groups within the same cycloplentadienone arene can compensate for the decreased electron density and deactivation for TH reactions promoted by electron-

withdrawing substituents. Equally, the addition of -OH groups to aryl ring at 2,5 positions improves the solubility of the complexes, and enhances their catalytic performance at low temperature and aqueous mixtures.

Overall, these findings help to establish new and meaningful design principles that can direct the development of new CIC-based catalysts for TH with improved utility in milder industrial contexts.

Conflicts of interest

"There are no conflicts to declare".

Data availability

The data supporting this article has been included in the Supplementary Information document. Crystallographic data has been deposited at the CCDC under deposition numbers 2536500 and 2536504.

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Notes and references

§ The most representative bond distances and angles for these compounds are listed in Tables S1 and S2 in the Supplementary Information document. In addition, the complete crystallographic structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2536500 and 2536504.

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