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Tetrathiafulvalene–oxazoline ligands in the iridium catalyzed enantioselective hydrogenation of arylimines

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Abstract—Cationic iridium complexes based on enantiomerically pure tetrathiafulvalene–oxazoline ligands have been used in the asymmetric hydrogenation of *N*-(phenylethylidene)aniline. Complete conversions with ee's up to 68% could be reached in the case of the TTF–phosphinooxazoline (TTF–PHOX) ligands.
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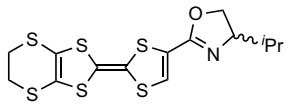
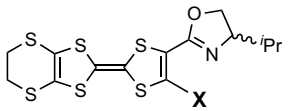
1. Introduction

Catalytic enantioselective hydrogenation of prochiral functionalized alkenes and ketones has been extensively studied.[1] Rhodium[2] and ruthenium[3] catalysts, coordinated by chiral diphosphane ligands, are very efficient in such processes. In most cases, the ee's are excellent (>90%) and the catalytic turnovers are amongst the highest of any asymmetric process. On the other hand, catalytic asymmetric hydrogenation of simple alkenes[4] and imines[5] is less common and has been proven to be much more difficult in terms of activity and stereoselectivity. Nevertheless, the synthesis of enantiomerically pure amines remains a real challenge because they are synthetic intermediates in many biological active compounds. Classical catalysts based on Rh and Ru are often inefficient for this purpose. Buchwald[6] has developed a Ti-catalyst, which has been successfully applied for the hydrogenation of cyclic imines (ee's up to 99%). Finally, iridium complexes were found to be excellent catalysts for the hydrogenation of a large variety of imines.[7] Among the chiral auxiliaries evaluated so far, the ferrocenyl Josiphos $R_2PFerr\text{-}PR'_2$ and derivates[8] represent the most successful diphosphane ligands for the enantioselective hydrogenation of imines, and have even been applied in industrial processes.[9] Phosphine–oxazoline ligands (PHOX) have also been found to be highly effective for the Ir-catalytic enantioselective hydrogenation of imines.[10] Alternatively, ligands possessing an oxazoline ring and a second functional group, such as a phosphinite,[11] a thioether,[12] or an amino-phosphine,[13] have been synthesized and used in the imine Ir-catalyzed hydrogenation.

Recently, some of us have reported on the synthesis of a new class of electroactive ligands containing a methyl or an isopropyl substituted oxazoline linked to an ethylenedithio-tetrathiafulvalene core (EDT-TTF–OX),[14] as well as on their use as precursors for chiral molecular conductors.[15] Functionalized precursors, bearing either phosphino (EDT-TTF–PHOX)[16] or thiomethyl groups (EDT-TTF–SMe–OX),[17] thus providing potential chelating P,N or S,N ligands, have also been prepared (Scheme 1). The compounds containing an ^{i}Pr–oxazoline unit have been evaluated in the asymmetric allylic substitution reaction,[18] with



EDT-TTF-^{i}Pr-OX
1a (±), **1b** (*R*), **1c** (*S*)



X = PPh_2, EDT-TTF-PHOX
2a (±), **2b** (*R*), **2c** (*S*)
X = SMe, EDT-TTF-SMe-OX
3a (*R*), **3b** (*S*)

Scheme 1. TTF–OX, TTF–PHOX and TTF–SMe–OX ligands.

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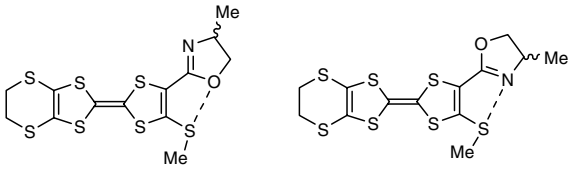
very good selectivities in the case of the TTF–PHOX ligands.

Herein we report on the evaluation of chiral ligands **1**–**3** in the asymmetric hydrogenation of *N*-(phenylethylidene)aniline catalyzed by cationic iridium complexes.

2. Results and discussion

The syntheses of EDT-TTF–^{i}PrOX **1a**–**c**,[14,16] EDT-TTF–PPh_2–^{i}PrOX **2a**–**c**[16,18] and EDT-TTF–SMe–^{i}PrOX **3a**–**b**[17,18] have previously been described. Single crystal X-ray analyses revealed that the twist angle between the TTF and oxazoline moieties is close to 0°, thus leading to an overall planar conformation of the compounds.[14] Moreover, in the case of the EDT-TTF–SMe–Me–OX derivatives, intramolecular $O_{OX}\cdots S_{SMe}$ 1,5-non-bonded interactions, characterized by short S···O distances and linear C–S···O angle, are established, providing a planar conformation of the *s-trans* type (Scheme 2).[17] The *s-cis* conformation, characterized by an intramolecular $N_{OX}\cdots S_{SMe}$ non-bonded interaction was found to be isoenergetic, yet it was not experimentally observed in the neutral donor. The associated energy barrier between the two stable planar conformations was estimated to be at around 7 kcal mol^{-1}.



Scheme 2. S···O and S···N nonbonded interactions in EDT-TTF–SMe–MeOX ligands.

Therefore, the establishment of O···S non-bonded interactions within the EDT-TTF–SMe–OX ligands provides, most likely, additional stabilization for these planar conformations. Thus, if the thioether–oxazolines are expected to act as chelating N,S ligands, the associated energy of the non-bonded interaction has to be overcome by the stabilization provided by the chelation onto the metal centre. In the case of the $Cu^{II}(hfac)_2$ (hfac = hexafluoro-acetylacetonate) fragment, the metal centre was only monocoordinated to the N_{OX} atom, thus still preserving the O···S non-bonded interaction, whereas the Co(II) centre, which has a much more pronounced tendency towards hexacoordination, was N,S chelated.[19] It is worthwhile mentioning this feature in view of the catalytic experiments planned with such auxiliaries. Indeed, an N,S chelation onto an iridium centre will most probably be beneficial to the selectivity of the hydrogenation process. Over the course of our present investigations, we have been able to grow single crystals from the enantiopure EDT-TTF–SMe–^{i}PrOX ligands **3a** and **3b** upon recrystallization in a THF/cyclohexane mixture, and then to determine their solid state structure. Both enantiomers crystallize in the monoclinic non-centrosymmetric space group $P2_1$, with two independent molecules in the asymmetric unit. As in the case of the Me–oxazoline counterparts,[17] the most striking structural feature consists of the occurrence of short intramolecular S···O distances of 2.83–2.84 Å within quasi planar conformations, indicative of the establishment of 1,5 non-bonded interactions (**3b** in Fig. 1).

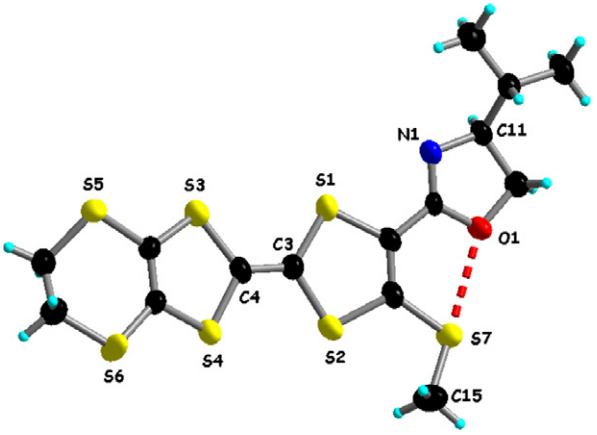
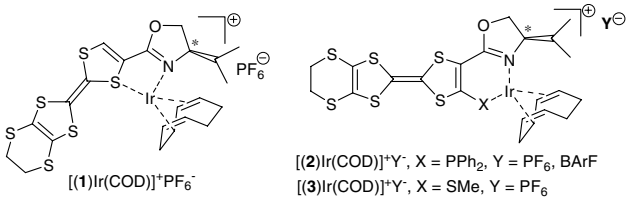


Figure 1. ORTEP view of one of the two independent molecules of (*S*)-EDT-TTF–(SMe)–OX **3b** (thermal ellipsoids set at 50% probability). Selected parameters: distances (Å) C(3)–C(4) 1.353(8), O(1)···S(7) 2.84; angles (°): O(1)···S(7)–C(15) 168.4, folding (°): S(1)···S(2) 6.9, S(3)···S(4) 14.4. Crystal data: monoclinic $P2_1$; $a = 11.1573(12)$ Å, $b = 12.9363(11)$ Å, $c = 13.6472(16)$ Å, $\beta = 101.212(13)°$; cell volume $V = 1932.2(3)$ Å^3; $Z = 4$; $T = 293(2)$; $R_1 = 0.0464$ ('observed' data).

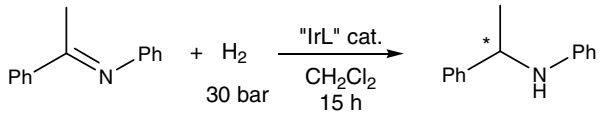
However, in spite of the stabilization provided by these short intramolecular contacts, the N,S auxiliary should very likely coordinate to the iridium(I) centre in a chelating manner, as already described with thioether–oxazoline ligands,[12] although no X-ray structural data on this type of Ir complexes have been reported so far.

Cationic iridium complexes of our TTF-based ligands (Scheme 3) have been conventionally synthesized from the dimeric precursor $[Ir(COD)Cl]_2$. One equivalent of the dimer was reacted with 2.1 equiv of the selected TTF ligand in CH_2Cl_2 for 6 h. Then 1 equiv of $AgPF_6$ was added and, within a period of 15 min stirring, the chloride abstraction occurred, to yield the required cationic catalyst precursor. A filtration over Celite allowed us to remove the AgCl salt. Alternatively, instead of $AgPF_6$, NaBArF ($BArF^-$ = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) can be used, in which case, the resulting NaCl was eliminated simply by washing with water.

The cationic complexes thus obtained were used without any further purification in catalysis, since they were analytically pure according to the ^{1}H and ^{31}P NMR data. The hydrogenation of the imine was performed into an autoclave under 30 bar of H_2 (Scheme 4) and the results are reported in Table 1. The solution containing the imine and the selected iridium precatalyst in dry degassed CH_2Cl_2 was introduced into the autoclave. After pressurization with dihydrogen, the reaction mixture was stirred under



Scheme 3. Cationic iridium complexes.



Scheme 4. Imine hydrogenation.

the conditions reported in Table 1. At the end of the reaction, the crude mixture was analyzed by GC for conversion determination. Then, after filtration through basic alumina to eliminate the catalyst, the mixture was analyzed on a chiral HPLC column for determination of the ee's.

The first series of experiments have been performed with the cationic iridium complexes containing the PF_6^- counterion. With the simple TTF–oxazolines **1**, the conversion was very disappointing (only 4%, entry 1) with also a low ee (9%). Although one can assume that in the catalytic intermediates the iridium(I) centre probably interacts with the appropriate TTF inner S atom, in order to form a chelate, this interaction is certainly very weak and does not provide a good stabilization of the coordination sphere of the metal during the enantiodetermining step of the catalytic cycle. Indeed, it is known that TTF inner sulfur atoms do not possess good coordination abilities,[19,20] and, moreover, simple TTF–oxazolines are poor ligands for the asymmetric allylic substitution.[18,21] Similar results were obtained with TTF–SMe–oxazoline auxiliaries **3** (entry 2), despite the fact that recently, oxazoline thioether ligands proved to be effective in terms of activity for this reaction, yet without any selectivity.[12] Interestingly, we found that the catalyst obtained from the precursor [Ir(**2b**)(COD)]PF_6 was very active (100% conversion after several hours) and quite selective (57% ee, entry 3).[22] In an attempt to increase the selectivity, the temperature was decreased first to 5 °C, then to −10 °C. A temperature decrease was very detrimental to the conversion, which dropped to 20% (entry 4) and then to 13% (entry 5), respectively. Unexpectedly, the ee dropped to 35% at −10 °C versus 57% at room temperature. Conversely, a reaction temperature of 50 °C did not allow any improvement of the selectivity, although the activity was unaltered (entry 6).

A peculiar aspect in the TTF–PHOX auxiliaries series is represented by the sense of the enantioselectivity they induce. Indeed, with our enantiopure ligands, the absolute configuration of the resulting amine is the same as the one of the PHOX ligand, that is, the (*R*)-TTF–PHOX affords the (*R*)-amine. This observation is in sharp contrast with the results obtained in the case of other PHOX ligands, for which opposite absolute configurations are noticed generally between the ligand and the amine.[10] Indeed, if the iridium catalyst contains the (*S*)-PHOX ligand enantiomer, the sense of the selectivity was rationalized by considering the hydrogen transfer to the *Si* face of the imine.[10b,c,k] The latter is usually the *anti*-isomer, although it is known that acyclic imines exist as mixtures of slowly interconverting *anti*- and *syn*-isomers.[23] This rationale is in agreement with the quadrants rule, when taking into account the steric hindrance around the coordinated metal centre, as deduced from single crystal X-ray structures of the starting Ir complexes. Unfortunately, in our case, we were unable to grow single crystals from the iridium complexes. Therefore, in order to explain this difference in selectivity, we can only suggest that the steric hindrance provided by the TTF backbone induces the coordination of the imine with the *Si* face in the case of the (*R*)-TTF–PHOX, thus affording the (*R*)-amine after the hydrogen transfer. In addition, electronic interactions, such as π stacking or C–H···Ph, with the imine phenyl group might be important as well.

Next, we used iridium precatalysts containing the more hindered non-coordinating anion $BArF^-$ in the same hydrogenation conditions. Accordingly, the ee increased

Table 1.

Entry	Ligand or catalytic precursor[a]	Anion	*T* (°C)	Conv.[b] (%)	ee (%) (Config).[c]
1	EDT-TTF–(*R*)-^{i}PrOX	PF_6^-	20	4	9 (*S*)
2	EDT-TTF–SMe–(*R*)-^{i}PrOX	PF_6^-	20	7	nd
3	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	PF_6^-	20	100	57 (*R*)
4	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	PF_6^-	5	20	56 (*R*)
5	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	PF_6^-	−10	13	35 (*R*)
6	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	PF_6^-	50	100	58 (*R*)
7	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	$BArF^-$	20	100	68 (*R*)
8	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	$BArF^-$	5	32	62 (*R*)
9	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	$BArF^-$	−10	22	69 (*R*)
10	EDT-TTF–PPh_2–(*R*)-^{i}PrOX	$BArF^-$	50	100	57 (*R*)
11	[Ir(COD)EDT-TTF–PPh_2–^{i}PrOX]$^{2+}$, PF_6^-, SbF_6^-		20	20 (70[d])	23 (*R*)

[a] Reactions were carried out by using 0.42 mmol of imine in 5 mL of distilled CH_2Cl_2 under 30 bar of hydrogen. S/Ir = 50; *t* = 15 h.
[b] Conversions were determined by GPC.
[c] Enantiomeric excesses were determined by HPLC on a Chiralpak OJ column. Absolute configuration was determined by comparison with those obtained with (*S*)-PHOX ligand.
[d] Conversion after 4 days.

up to 68% always with full conversion (entry 7). A variable temperature study afforded the same trends as in the case of the PF_6 anion, namely a dramatic loss of activity at low temperatures (entries 8 and 9) and basically no influence between room temperature and 50 °C (entry 10). Finally, the hydrogenation reaction was carried out with the cationic Ir(I) complex of the oxidized ligand **2b** (entry 11), prepared upon chemical oxidation of the complex with $NOSbF_6$. This preliminary experiment aimed at emphasizing the influence of the TTF oxidation state on the catalytic process, such as it was demonstrated with ferrocene based redox active ligands.[24] Unlike the case of the asymmetric allylic alkylation, for which no real influence on the activity or selectivity was observed,[18] in the present experiment a dramatic decrease of both activity (20%) and selectivity (20% ee) were observed. Nevertheless, prolonged reaction times allowed us to reach up to 70% yield in amine. However, it should be pointed out that, at this preliminary stage, it is difficult to conclude whether the effect we observed here is due to the electronic modulation provided by the oxidized ligand or to another catalytic species generated in the reaction mixture under the reducing conditions of the hydrogenation process. Additional investigations are needed in order to investigate the different hypotheses.

3. Conclusion

Chiral redox active monodentate EDT-TTF–^{i}Pr–oxazolines (TTF–OX) and bidentate EDT-TTF–SMe–^{i}Pr–oxazolines (TTF–SMe–OX) and EDT-TTF–PPh_2–^{i}Pr–oxazolines (EDT-TTF–PHOX) have been evaluated in the catalytic hydrogenation of *N*-(phenylethylidene)aniline, while associated to cationic iridium(I) complexes. High activities (100% conversion) and good selectivities could be attained with the EDT-TTF–PPh_2–^{i}PrOX ligands and PF_6^- (up to 58% ee) or $BArF^-$ (up to 68% ee) anions. Further studies in our groups will be aimed at the utilization of these TTF–oxazoline based ligands in other catalytic processes, and also at the understanding of the influence of the TTF oxidation state on the catalytic process.

4. Experimental

All the reactions were carried out under an inert gas atmosphere. Solvents were purified by standard techniques: THF was distilled over sodium and benzophenone; acetonitrile was dried over P_2O_5. The triethylamine was distilled over KOH. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ^{1}H, 125.75 MHz for ^{13}C and 202.39 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from the external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet; o, octuplet; m, multiplet; b, broad. ^{31}P chemical shifts are reported with positive values downfield from external 85% H_3PO_4 in D_2O. MALDI-TOF MS spectra were recorded on Bruker Biflex-IIITM apparatus, equipped with a 337 nm N_2 laser. Elemental analyses were performed by the 'Service d'Analyse du CNRS' at Gif/Yvette, France.

4.1. Synthesis of complexes [Ir(COD)(1b)]PF_6 (*R*) and [Ir(COD)(1c)]PF_6 (*S*)

The ligand **1b** (38.4 mg, 94.5 μmol) and the dimer complex bis(η^4-cycloocta-1.5-diene)-di-μ-chlorodiiridium(I) $[Ir(COD)Cl]_2$ (30 mg, 44.2 μmol) were placed under an inert atmosphere, then dissolved in distilled and degassed methylene chloride (2 mL). The dark red solution was stirred for 6 h at room temperature, before addition of 1 equiv of $AgPF_6$ (23 mg, 88.4 μmol) in the dark. After 15 min of stirring, filtration through dry Celite and evaporation in vacuo afforded a dark brown powder (42.9 mg, 57% yield). MS (MALDI-TOF) *m*/*z*: 704.55 $(M-PF_6)^+$; Anal. Calcd for $C_{22}H_{27}F_6IrNOPS_6$: C, 31.05; H, 3.20; N, 1.64; Found: C, 31.85; H, 3.58; N, 1.79.

The same procedure with ligand **1c** afforded the Ir complex (dark powder, 43.6 mg, 58% yield). Anal. Calcd for $C_{22}H_{27}F_6IrNOPS_6$: C, 31.05; H, 3.20; N, 1.64. Found: C, 31.62; H, 3.38; N, 1.85.

4.2. Synthesis of complexes [Ir(COD)(3a)]PF_6 (*R*) and [Ir(COD)(3b)]PF_6 (*S*)

The ligand (*R*)-EDT-TTF–SMe–^{i}PrOX **3a** (42.8 mg, 94.5 μmol) and the dimer complex bis(η^4-cycloocta-1.5-diene)-di-μ-chlorodiiridium(I) $[Ir(COD)Cl]_2$ (30 mg, 44.2 μmol) were placed under an inert atmosphere, then dissolved in distilled and degassed dichloromethane (2 mL). The dark red solution was stirred for 6 h at room temperature, then 1 equiv of $AgPF_6$ (23 mg, 88.4 μmol) was added in the dark. After 15 min of stirring, filtration through dry Celite and evaporation of solvent in vacuo afforded a dark brown powder (52.1 mg, 66% yield). ^{1}H NMR (CD_2Cl_2, δ): 0.66 (d, $^3J = 7.0$ Hz, 3H, CH_3), 0.89 (d, $^3J = 7.0$ Hz, 3H, CH_3), 1.74 (m, 3H, CH_2 (COD) and CH–$(CH_3)_2$), 2.37 (m, 2H, CH_2, COD), 2.40 (s, 3H, SCH_3), 2.46–2.82 (m, 5H, 2CH_2 and 1 CH, COD), 3.22 (m, 1H, CH, COD), 3.31 (m, 4H, S–CH_2–CH_2–S), 4.40 (m, 1H, CH, COD), 4.58 (m, 1H, CH, COD), 4.65–4.76 (m, 2H, N–CH and C$H_{syn/i\text{-}Pr}$H′O), 5.01 (m, 1H, CH$H'_{anti/i\text{-}Pr}$O); ^{31}P NMR (CD_2Cl_2, δ): −144.4 (h, $^1J_{P-F} = 710$ Hz, PF_6); MS (MALDITOF) *m*/*z*: 704.50 $(M-SMe-PF_6)^+$; Anal. Calcd for $C_{23}H_{29}F_6NOPIrS_7$: C, 30.79; H, 3.26; N, 1.56. Found: C, 29.85; H, 3.43; N, 1.27.

The same procedure with the ligand **3b** afforded the Ir complex (dark powder, 53.7 mg, 68% yield). Anal. Calcd for $C_{23}H_{29}F_6NOPIrS_7$: C, 30.79; H, 3.26; N, 1.56. Found: C, 30.06; H, 3.25; N, 1.31.

4.3. Synthesis of complexes [Ir(COD)(2a)]PF_6 (±), [Ir(COD)(2b)]PF_6 (*R*) and [Ir(COD)(2c)]PF_6 (*S*)

The ligand (±)-EDT-TTF–PHOX(^{i}Pr) **2a** (37 mg, 0.063 mmol) and the dimer complex $[Ir(COD)Cl]_2$ (20 mg, 0.03 mmol) were placed under an inert atmosphere, and then dissolved in distilled and degassed dichloromethane (1.4 mL). The dark solution was stirred for 6 h at room temperature, and then 1 equiv of $AgPF_6$ (16 mg, 0.06 mmol) was added in the dark. After stirring for 15 min, filtration through dry Celite and evaporation in

vacuo afforded a black crystalline powder (60.8 mg, 98% yield). ^{1}H NMR (CD_2Cl_2, δ): 0.26 (d, $^3J = 7.0$ Hz, 3H, CH_3), 0.92 (d, $^3J = 7.0$ Hz, 3H, CH_3), 1.61 (m, 2H, CH_2, COD), 2.09 (m, 4H, CH–$(CH_3)_2$, CH_2 and CH, COD), 2.34 (m, 1H, CH, COD), 2.43–2.55 (m, 2H, CH_2, COD), 3.29 (m, 4H, S–CH_2–CH_2–S), 3.88 (m, 1H, CH, COD), 4.17 (m, 1H, N–CH), 4.22 (m, 1H, CH, COD), 4.44 (t, $^3J = {}^2J = 9.5$ Hz, 1H, C$H_{syn/i\text{-}Pr}$H′O), 4.50 (dd, $^2J = 9.5$ Hz, $^3J = 3.3$ Hz, 1H, CH$H'_{anti/i\text{-}Pr}$O), 7.31 (m, 2H, Ph), 7.47–7.71 (m, 4H, Ph), 8.00 (m, 4H, Ph); ^{31}P NMR (CD_2Cl_2, δ): 12.1 (s, PPh_2), −144.5 (h, $^1J_{P-F} = 710$ Hz, PF_6); MS (MALDITOF) m/z: 889.72 $(M-PF_6)^+$; Anal. Calcd for $C_{34}H_{36}F_6NOP_2IrS_6$: C, 39.45; H, 3.51; N, 1.35. Found: C, 38.62; H, 4.06; N, 1.14.

The same procedure with ligand **2b** (black powder, 55.7 mg, 90% yield) and **2c** (black powder, 60.9 mg, 98% yield). [Ir(COD)(**2b**)]PF_6: Anal. Calcd for $C_{34}H_{36}F_6NOP_2IrS_6$: C, 39.45; H, 3.51; N, 1.35. Found: C, 38.75; H, 4.05; N, 1.03. [Ir(COD)(**2c**)]PF_6: Anal. Calcd for $C_{34}H_{36}F_6NOP_2IrS_6$: C, 39.45; H, 3.51; N, 1.35. Found: C, 38.73; H, 4.01; N, 1.01.

4.4. Synthesis of complexes [Ir(COD)(2b)]BArF (*R*) and [Ir(COD)(2c)]BArF (*S*)

The ligand **2b** (16.8 mg, 28.5 μmol) and the dimer complex $[Ir(COD)Cl]_2$ (9.5 mg, 14 μmol) were placed under an inert atmosphere and dissolved in 5 mL dry and degassed dichloromethane. The dark solution was stirred for one night at room temperature. Then, 1 equiv of NaBArF (26 mg, 28 μmol) was added, followed by water (6 mL). The two layers were separated and the aqueous one was extracted with dichloromethane (3×10 mL). The organic layers were combined and dried over $MgSO_4$. Filtration and removal of the solvent provided a black crystalline powder (37.2 mg, 76% yield). ^{1}H NMR (CD_2Cl_2, δ): 0.23 (d, $^3J = 7.0$ Hz, 3H, CH_3), 0.90 (d, $^3J = 7.0$ Hz, 3H, CH_3), 1.72 (m, 2H, CH_2, COD), 1.95–2.16 (m, 3H, CH_2 (COD) and CH–$(CH_3)_2$), 2.43–2.60 (m, 4H, CH_2, COD), 2.85 (m, 1H, CH, COD), 3.29 (m, 4H, S–CH_2–CH_2–S), 3.38 (m, 1H, CH, COD), 4.13 (m, 1H, N–CH), 4.39 (t, $^3J = {}^2J = 9.3$ Hz, 1H, C$H_{syn/i\text{-}Pr}$H′O), 4.51 (dd, $^2J = 9.3$ Hz, $^3J = 3.0$ Hz, 1H, CH$H'_{anti/i\text{-}Pr}$O), 5.01 (m, 1H, CH, COD), 5.16 (m, 1H, CH, COD), 7.25 (m, 2H, Ph), 7.47–7.77 (m, 16H, Ph, BArF), 7.98 (m, 4H, Ph); ^{31}P NMR (CD_2Cl_2, δ): 12.9 (s, PPh_2); MS (MALDITOF) m/z: 889.82 $(M-BArF)^+$; Anal. Calcd for $C_{66}H_{48}F_{24}BNOPIrS_6$: C, 45.21; H, 2.76; N, 0.80. Found: C, 44.55; H, 2.91; N, 0.44.

The same procedure with ligand **2c** (black powder, 55.7 mg, 90% yield). Anal. Calcd for $C_{66}H_{48}F_{24}BNOPIrS_6$: C, 45.21; H, 2.76; N, 0.80. Found: C, 44.65; H, 2.88; N, 0.56.

4.5. Synthesis of the oxidized complexes [Ir(COD)(2a–c)$^{+\cdot}$]-PF_6,SbF_6

The series of complexes [Ir(COD)(**2a**–**c**)]PF_6 (30 mg, 29 μmol) and the oxidizing agent $NOSbF_6$ (7.7 mg, 29 μmol) were weighed in a glove box, placed into a Schlenk tube, and dissolved in dry and degassed acetonitrile (2 mL). The dark solution thus obtained was stirred for 1 h at room temperature. The solvent was then removed upon evaporation, and thus a black powder was obtained (42 mg, 87 % yield). Anal. Calcd for $C_{34}H_{36}F_{12}NOP_2SbIrS_6$: C, 32.13; H, 2.86; N, 1.10. Found: C, 31.35; H, 3.02; N, 1.75.

4.6. General procedure for the hydrogenation of *N*-benzylmethyl-phenylimine (Ir/substrate ratio = 2 mol %)

[{EDT-TTF–PPh_2–^{i}PrOX}Ir(COD)]PF_6 (8.9 mg, 8.6 μmol) was placed under a nitrogen atmosphere and dissolved in freshly distilled and degassed dichloromethane (5 mL). The imine (83 mg, 0.42 mmol) and a magnetic stirring bar were placed in a 50 mL autoclave, which was then purged with nitrogen. The catalyst solution was transferred under nitrogen in the autoclave, which was then pressurized (30 bars) with dihydrogen. The mixture was stirred at the specified temperature for 15 h. Then, the autoclave was depressurized and the solution, of which a sample was taken in order to determine the conversion by GC, was purified through a short silica gel column (eluant: dichloromethane) to afford the amine as a clear yellow oil.

The conversion was evaluated by gas chromatography (GC). When the temperature rises from 120 °C to 230 °C with a 10 °C/min gradient, the retention times are 10.1 min for the amine and 10.4 min for the starting imine.

4.7. X-ray crystallography

Data were collected on a Stoe Imaging Plate System (IPDS) operating with a Mo-Kα X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F^2.[25] Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. All the heavy atoms have been refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC 652986 (**3a**) and CCDC 652987 (**3b**) (CIF files). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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