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Activation of E–H (E = Sn, Si, S) bonds by cyclooctadieneiridium pyridine-2-carboxylate and related compounds

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Abstract

The complexes [Ir(O_2CArN)(1,5-cod)] (**1**), containing the chelating ligands O_2CArN = pyridine-2-carboxylate (O_2CPic), isoquinoline-1-carboxylate (O_2CIsoq), quinoline-2-carboxylate (O_2CQuin) and pyrazine-2-carboxylate ($O_2CPyraz$) are readily prepared in good yield from [Ir_2(μ-OMe)$_2$(1,5-cod)$_2$] and $NArCO_2H$. The ^{1}H-NMR spectra of these compounds show temperature-dependent changes that are interpreted in terms of an interaction with the solvent. With Ph_3SnH, Ph_3SiH and C_6F_5SH complexes **1** react to give [Ir(O_2CArN)(H)($SnPh_3$)(1,5-cod)] (**2**), [Ir(O_2CArN)(H)($SiPh_3$)(1,5-cod)] (**3**) and [Ir(O_2CArN)(H)(SC_6F_5)(1,5-cod)] (**4**), the reaction with Ph_3SiH being reversible.

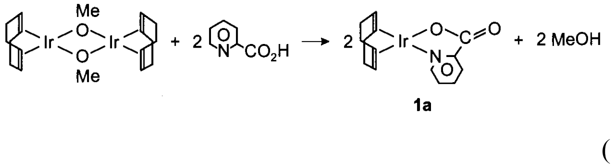
Keywords: Iridium; Hydride; Silicon; Sulfur; Tin; Oxidative addition

1. Introduction

The activation of E–H (E = e.g. C, Si) bonds by complexation to a transition metal is the focus of much research directed toward the useful derivatisation of ‘inert’ hydrocarbons and the development of catalysts for a wide range of processes [1–15]. Iridium has proved to be particularly effective in the activation of C–H and other bonds, a finding which has led to the increasing current interest in low-valent, coordinatively unsaturated Ir complexes and their precursors [16–23]. The types of ligand that can be used in such chemistry are limited by the fact that an aromatic C–H bond is generally activated in preference to an alkane C–H, with the result that potentially valuable complexes such as [Ir(Cl)(PPh_3)$_3$] [24] undergo intramolecular oxidative addition. Clearly a combination of ligands is required that will optimise the electron density on iridium for the desired reaction while avoiding unwanted competing reactions. The ease with which R_3EH will bind to a metal (to form H–M–ER_3) increases in the order E = C < Si < Sn (R = e.g. Ph). A knowledge of the factors that influence the ability of a metal to bind R_3SiH and R_3SnH can be used in the design of complexes that perform the more elusive function of selective alkane C–H activation. In this connection the present study examines the reactivity of complexes of iridium containing 1,5-cyclooctadiene and pyridine-2-carboxylate and related ligands.

2. Results and discussion

The complex [Ir_2(μ-OMe)$_2$(1,5-cod)$_2$] [25], which is readily prepared from chloroiridic acid via [$Ir_2H_2Cl_2$(μ-Cl)$_2$(1,5-cod)$_2$], is a useful precursor for a variety of compounds. It reacts readily with pyridine-2-carboxylic and related acids to give red or dark purple crystalline products (**1a** = pyridine-2-carboxylate, **1b** = isoquinoline-1-carboxylate, **1c** = quinoline-2-carboxylate, **1d** = pyrazine-2-carboxylate) in good yield (Eq. (1)).



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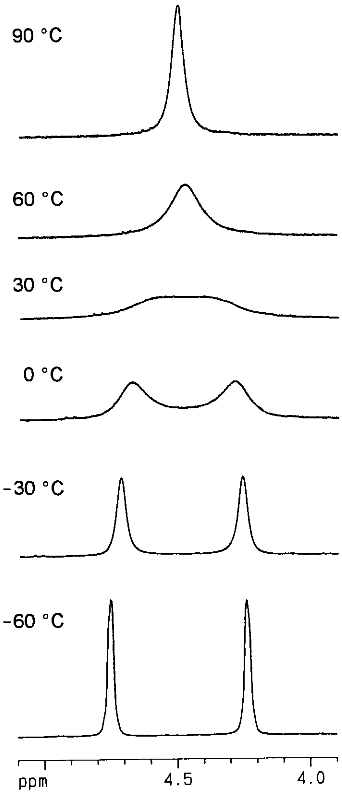


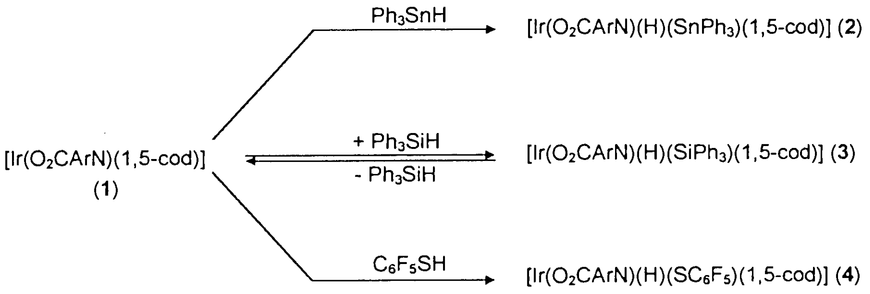
Fig. 1. ^{1}H-NMR signals recorded from the alkene protons of **1c** in toluene at various temperatures.

The ^{1}H-NMR spectra recorded from solutions of **1** in chloroform or toluene show temperature-dependent changes that indicate fluxional behaviour. For complexes **1a** and **1b** these changes only begin to become noticeable at 90°C, but for **1c** (quinolinecarboxylate) and **1d** (pyrazinecarboxylate) broadening of the cyclooctadiene ^{1}H signals occurs at temperatures well below 0°C (Fig. 1). The extent of the broadening (at a given temperature) is solvent-dependent, suggesting that the origin of the fluxionality is an interaction with the solvent, as described by Heitner and Lippard [26] for [Rh(X–Y)(1,5-cod)] (X–Y is a chelating monothiodiketonate), to give a transient, stereochemically nonrigid, five-coordinate species. In the presence of 0.025 M acetontrile at 27°C **1b** (0.012 M in chloroform) gives very broad alkene ^{1}H signals that coalesce on raising the temperature to 68°C, ca. 100°C lower than the estimated coalescence temperature in the absence of CH_3CN. For complex **1c** in toluene a value of 58.8 ± 0.5 kJ mol^{-1} was found for the free energy of activation ($\Delta G_c^{\ddagger}$) at the coalescence temperature ($T_c = 303$ K), calculated using the Eyring equation, with an expression for the rate constant described by Bishop et al. [27].

The fact that **1c** and **d** are fluxional at much lower temperatures than **1a** and **1b** can be rationalised for **1c** in terms of steric properties and for **1d** in terms of electronic properties. For **1d** the low nucleophilicity of the pyrazine will cause the iridium to have a lower electron density than in **1a**–**c**, favouring an interaction with the solvent. In the complexes **1a**–**c** the nucleophilicities of the NAr groups are very similar (see below) and electronic effects are likely to be less important than steric effects in determining the properties of **1c**. In **1c** steric repulsion between the quinoline C_6 ring and the diene may prevent the molecule from taking up the optimum geometry for a nominally square planar complex, reducing the effective nucleophilicity of the quinoline and increasing the electrophilicity of the metal.

Complexes **1** undergo reactions with Ph_3SnH, Ph_3SiH and C_6F_5SH (Scheme 1) to give oxidative addition products in moderate to good yield as crystals or microcrystalline powders, varying in colour from very pale yellow to orange. In the case of **1a** and **b** (reaction with Ph_3SiH to give **3a** and **b**) and **1d** (reaction with Ph_3SiH to give **3d** and with C_6F_5SH to give **4d**) products were slightly impure, while with C_6F_5SH, **1c** gave a mixture from which the desired product could not be isolated. No reaction is observed between **1** and Ph_3CH.

The most likely coordination geometry for complexes **2**–**4** is one with nitrogen positioned *trans* to hydride



Scheme 1. O_2CArN = pyridine-2-carboxylate (a); isoquinoline-1-carboxylate (b); quinoline-2-carboxylate (c); pyrazine-2-carboxylate (d).

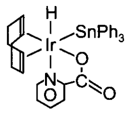


Fig. 2. Coordination geometry proposed for **2a**.

Table 1
Spectral data

Complex	ν(Ir–H) [a]	δ(^{1}H) [b]	δ(^{29}Si) [c], δ(^{119}Sn)
[Ir(O_2CPic)(H)($SnPh_3$)(1,5-cod)] (**2a**)	2191	−16.34 [d]	−146.26
[Ir(O_2CIsoq)(H)($SnPh_3$)(1,5-cod)] (**2b**)	2178	−16.14 [e]	−142.15
[Ir(O_2CQuin)(H)($SnPh_3$)(1,5-cod)] (**2c**)	2230	−15.26 [f]	−152.63
[Ir(O_2CPyraz)(H)($SnPh_3$)(1,5-cod)] (**2d**)	2217	−17.02 [g]	−137.95
[Ir(O_2CPic)(H)($SiPh_3$)(1,5-cod)] (**3a**)	2249	−16.68	−8.23
[Ir(O_2CIsoq)(H)($SiPh_3$)(1,5-cod)] (**3b**)	2254	−16.37	−7.50
[Ir(O_2CQuin)(H)($SiPh_3$)(1,5-cod)] (**3c**)	2257	−15.33	−8.98
[Ir(O_2CPyraz)(H)($SiPh_3$)(1,5-cod)] (**3d**)	2251	−17.21	−7.87
[Ir(O_2CPic)(H)(SC_6F_5)(1,5-cod)] (**4a**)	2238	−15.40	
[Ir(O_2CIsoq)(H)(SC_6F_5)(1,5-cod)] (**4b**)	2212	−14.85	
[Ir(O_2CPyraz)(H)(SC_6F_5)(1,5-cod)] (**4d**)	2245	−15.84	

[a] Nujol mull.

[b] ~0.02 M in $CDCl_3$ at 27°C, TMS internal reference. A signal at −13.86 ppm was recorded from a solution containing **1c** and C_6F_5SH (equivalent to complex **4c**, not shown).

[c] ~0.02 M in $CDCl_3$ at 27°C, TMS internal reference, $SnMe_4$ external reference.

[d] $^2J(^{119}\text{Sn}–^1\text{H}_{cis}) \sim {}^2J(^{117}\text{Sn}–^1\text{H}_{cis}) = 41.6$ Hz (absolute magnitude).

[e] $^2J(\text{Sn–H}_{cis}) = 40.3$ Hz.

[f] $^2J(\text{Sn–H}_{cis}) = 43.3$ Hz.

[g] $^2J(\text{Sn–H}_{cis}) = 40.6$ Hz.

(shown in Fig. 2 for complex **2a**). Chemical shifts reported for hydrides in a variety of iridium(III) complexes [21,28–32] show H *trans* to N in the range δ −14.90 to −18.35 and H *trans* to O in the range −19.2 to −26.25 ppm: δH for **2**–**4** varies from −14.85 to −17.21 ppm (Table 1). The presence of a chiral centre at Ir causes all the cyclooctadiene protons in each of these complexes to have different chemical environments.

Solutions of the Ph_3SiH adducts (**3**), show evidence of dissociation, an effect that can be reversed by the addition of Ph_3SiH. The stabilised solutions (with excess Ph_3SiH) are yellow; the unstabilised solutions are red or brown. From the ^{1}H spectrum the extent of dissociation can readily be measured. In solutions of concentration 0.005 M this is found to be: **3a**, 80% (i.e. only 20% remains as **3a**, 80% is **1a**); **3b**, 86; **3c**, 14; **3d**, 60%. These values are accurate to ±3%. The higher stability of **3c** (quinolinecarboxylate) is likely to arise from the enhanced electrophilicity of Ir caused by steric strain (see above).

The dissociation data can be related to the pK_a values of the parent bases pyridine (5.25), isoquinoline (5.42), quinoline (4.90) and pyrazine (0.65) [33] and thence to the electron density on iridium in complexes **3**. If for this purpose **3c** is discounted (on the basis of an anomalous contribution from steric factors), then the affinity of Ir for Ph_3SiH, which increases in the order **3b** (isoquinolinecarboxylate) < **3a** (pyridinecarboxylate) < **3d** (pyrazinecarboxylate), correlates with a reduction in the electron density on iridium as the base ArN becomes less nucleophilic. A similar relationship has been found for complexes of rhodium [34]. The spectral data provide no clear trends that can be matched with the properties of the ligands O_2CArN.

From the limited range of compounds studied two features emerge that merit further investigation. (i) The relationship between the electron density on the metal and the ability of the metal to bind R_3EH. While such a result is by no means new, the combination of ligands (1,5-cod, NArCO_2) underlying it offers new options. (ii) The presence in the Ir(I) precursor of steric strain (proposed in the case of **1c**) that reduces the effective nucleophilicity of the aromatic base (quinoline) appears to enhance the binding process.

3. Experimental

Complexes [$Ir_2H_2Cl_2$(μ-Cl)$_2$(1,5-cod)$_2$] and [Ir_2(μ-OMe)$_2$(1,5-cod)$_2$] were prepared using published methods [25]. THF was distilled from sodium/benzophenone, dichloromethane was distilled from P_2O_5, diethyl ether was distilled from CaH_2 and hexane was dried over CaH_2. All other materials were of the highest available purity and were used without further treatment. All operations were carried out under an inert atmosphere (N_2 or Ar). Infrared spectra were recorded using a Bruker Vector 22 spectrometer; NMR spectra were recorded using a Bruker DRX 400 spectrometer (^{1}H, 400.32; ^{29}Si, 79.46; ^{119}Sn, 149.09 MHz).

3.1. Preparation of [Ir(O_2CPic)(1,5-cod)] (1a)

[Ir_2(μ-OMe)$_2$(1,5-cod)$_2$] (0.100 g, 0.30 mmol Ir) in THF (1.5 ml) was treated with pyridine-2-carboxylic acid (0.039 g, 0.32 mmol) in THF (1.5 ml) (both solutions obtained by warming) at room temperature (r.t.) The colour quickly changed to red. The mixture was concentrated to 1.5 ml in a stream of nitrogen and allowed to stand at r.t. for 2 h to give red crystals which were washed with Et_2O and dried under vacuum. Yield

0.090 g, 71%. Found: C, 39.93; H, 3.79; N, 3.13. $C_{14}H_{16}IrNO_2$ requires C, 39.80; H, 3.82; N, 3.32%. ^{1}H-NMR ($CDCl_3$, 27°C) δ 8.21 (d 1H), 8.08 (dd 1H), 7.92 (d 1H), 7.58 (dd 1H), 4.62 (s broad, 2H), 3.67 (s broad, 2H), 2.35 (mult. broad, 4H) 1.85–1.70 (mults. 4H) ppm.

3.2. Preparation of [Ir(O$_2$CIsoq)(1,5-cod)] (**1b**)

[$Ir_2(\mu\text{-}OMe)_2$(1,5-cod)$_2$] (0.050 g, 0.15 mmol Ir) in THF (1 ml) was treated with isoquinoline-1-carboxylic acid (0.028 g, 0.16 mmol) in THF (1 ml) (both solutions obtained by warming) at r.t. The colour quickly changed to dark red. The mixture was concentrated to 1 ml in a stream of nitrogen and allowed to stand at r.t. for 2 h to give black crystals which were washed with Et_2O and dried under vacuum. Yield 0.053 g, 74%. Found: C, 45.46; H, 3.66; N, 3.12. $C_{18}H_{18}IrNO_2$ requires C, 45.75; H, 3.84; N, 2.96%. ^{1}H-NMR ($CDCl_3$, 27°C) δ 10.05 (d 1H), 7.89–7.86 (mults. 3H), 7.82 (dd 1H), 7.76 (d 1H), 4.64 (s broad, 2H), 3.75 (s broad, 2H), 2.37 (mult. 4H), 1.87–1.73 (mult. 4H) ppm.

3.3. Preparation of [Ir(O$_2$CQuin)(1,5-cod)] (**1c**)

[$Ir_2(\mu\text{-}OMe)_2$(1,5-cod)$_2$] (0.060 g, 0.18 mmol Ir) in THF (1 ml) was treated with quinoline-2-carboxylic acid (0.033 g, 0.19 mmol) in THF (1 ml) (both warmed to dissolve) at r.t. The colour quickly changed to dark red. The mixture was concentrated to 1 ml in a stream of nitrogen and allowed to stand at r.t. to give a purple microcrystalline powder which was washed with Et_2O and dried under vacuum. Yield 0.057 g, 67%. Found: C, 45.48; H, 3.75; N, 2.85. $C_{18}H_{18}IrNO_2$ requires C, 45.75; H, 3.84; N, 2.96%. ^{1}H-NMR ($CDCl_3$, 27°C) δ 8.52 (d 1H), 8.37 (d 1H), 7.96 (dd 1H), 7.80 (ddd 1H), 7.70 (ddd 1H) 7.49 (d 1H), 4.57 (s broad, 4H), 2.34 (s broad, 4H), 1.8–1.6 (mults. broad, 4H) ppm

3.4. Preparation of [Ir(O$_2$CPyraz)(1,5-cod)] (**1d**)

[$Ir_2(\mu\text{-}OMe)_2$(1,5-cod)$_2$] (0.050 g, 0.15 mmol Ir) in THF (1 ml) was treated with pyrazine-2-carboxylic acid (0.020 g, 0.16 mmol) in THF (1 ml) (both solutions obtained by warming) at r.t. The colour quickly changed to very dark red. The mixture was concentrated to 1 ml in a stream of nitrogen and allowed to stand at r.t. for 2 h to give a purple microcrystalline powder which was washed with Et_2O and dried under vacuum. Yield 0.040 g, 63%. Found: C, 37.31; H, 3.67; N, 6.43. $C_{13}H_{15}IrN_2O_2$ requires C, 36.87; H, 3.57; N, 6.61%. ^{1}H-NMR ($CDCl_3$, 27°C) δ 9.44 (d 1H), 8.96 (d 1H), 7.85 (dd 1H), 4.24 (s broad, 4H), 2.35 (mult. broad, 4H), 1.84 (mult. 4H) ppm.

3.5. Preparation of [Ir(O$_2$CPic)(H)(SnPh$_3$)(1,5-cod)] (**2a**)

A solution of **1a** (0.020 g, 0.047 mmol) in CH_2Cl_2 (0.5 ml) at r.t. was treated with Ph_3SnH l (0.025 g, 0.07 mmol). A change of colour to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand at r.t. for 2 h to give a pale yellow microcrystalline powder. The powder was washed with Et_2O and dried under vacuum. Yield 0.024 g, 66%. Found: C, 49.57; H, 4.04; N, 1.86. $C_{32}H_{32}IrNO_2Sn$ requires C, 49.69; H, 4.17; N, 1.81%. IR (nujol mull) ν(Ir–H) 2191 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 8.64 (d 1H), 7.67 (dd 1H), 7.54 (ddd 1H), 7.40 (mult. 6H), 7.21–7.14 (mults. 9H), 7.08 (ddd 1H), 5.13 (mult. 1H), 4.82 (mult. 1H), 4.68 (mult. 1H), 3.58 (mult. 1H), 2.77 (mult. 1H), 2.67 (mult. 1H), 2.59–2.47 (mults. 2H), 2.53 (mult. 2H), 2.42 (mult. 1H), 2.17–1.93 (mults. 3H), −16.64 (s 1H; J(Sn–H) 41.6 Hz) ppm.

3.6. Preparation of [Ir(O$_2$CIsoq)(H)(SnPh$_3$)(1,5-cod)] (**2b**)

A solution of **1b** (0.020 g, 0.042 mmol) in CH_2Cl_2 (1 ml) at r.t. was treated with Ph_3SnH (0.025 g, 0.07 mmol). A colour change to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand at r.t. for 2 h to give yellow crystals. The crystals were washed with Et_2O and dried under vacuum. Yield 0.028 g, 80%. Found: C, 51.77; H, 3.85; N, 1.88. $C_{36}H_{34}IrNO_2Sn$ requires C, 52.50; H, 4.16; N, 1.70%. IR (nujol mull) ν(Ir–H) 2178 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 9.76 (d 1H), 8.60 (d 1H), 7.71–7.60 (mults. 3H), 7.43–7.30 (mults. 7H), 7.07–6.98 (mults. 9H), 5.25 (mult. 1H), 4.82 (mult. 1H), 4.69 (mult. 1H), 3.62 (mult. 1H), 2.81 (mult. 1H), 2.72 (mult. 1H), 2.57 (mult. 2H), 2.45 (mult. 1H), 2.20–1.95 (mults. 3H), −16.14 (s 1H; J(Sn–H) 40.3 Hz) ppm.

3.7. Preparation of [Ir(O$_2$CQuin)(H)(SnPh$_3$)(1,5-cod)] (**2c**)

A solution of **1c** (0.010 g, 0.021 mmol) in CH_2Cl (0.5 ml) at r.t. was treated with Ph_3SnH (0.015 g, 0.04 mmol). A colour change to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand at r.t. for 2 h to give an orange microcrystalline powder. The powder was washed with Et_2O and dried under vacuum. Yield 0.013 g, 74%. Found: C, 52.42; H, 4.02; N, 1.91. $C_{36}H_{34}IrNO_2Sn$ requires C, 52.50; H, 4.16; N, 1.70%. IR (nujol mull) ν(Ir–H) 2230 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 9.16 (d 1H), 7.98 (d 1H), 7.84 (mult. 2H), 7.77 (dd 1H), 7.65 (dd 1H), 7.24 (mult. 6H), 7.16–7.04 (mults. 9H), 5.08 (mult. 1H), 4.97 (mult. 1H), 4.84 (mult. 1H), 3.58 (mult. 1H), 2.90 (mult. 1H), 2.65 (mult. 2H), 2.51 (mult. 2H), 2.14 (mult. 2H), 1.91 (mult. 1H), −15.26 (s 1H; *J*(Sn–H) 43.3 Hz) ppm.

3.8. Preparation of [Ir(O_2CPyraz)(H)($SnPh_3$)(1,5-cod)] (**2d**)

A solution of **1d** (0.010 g, 0.024 mmol) in CH_2Cl_2 (0.5 ml) at r.t. was treated with Ph_3SnH (0.015 g, 0.04 mmol). A colour change to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand at r.t. for 2 h to give an orange microcrystalline powder. The powder was washed with Et_2O and dried under vacuum. Yield 0.009 g, 49%. Found: C, 47.95; H, 4.03; N, 3.62. $C_{31}H_{31}IrN_2O_2Sn$ requires C, 48.07; H, 4.03; N, 3.62%. IR (nujol mull) ν(Ir–H) 2217 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 8.69 (d 1H), 8.55 (dd 1H), 8.26 (d 1H), 7.40 (mult. 6H), 7.27–7.18 (mults. 9H), 5.18 (mult. 1H), 4.91 (mult. 1H), 4.77 (mult. 1H), 3.66 (mult. 1H), 2.86–2.26 (mults. 2H), 2.55 (mult. 2H), 2.43 (mult. 2H), 2.20–2.08 (mults. 2H), 2.01 (mult. 1H), −17.02 (s 1H; *J*(Sn–H) 40.6 Hz) ppm.

3.9. Preparation of [Ir(O_2CQuin)(H)($SiPh_3$)(1,5-cod)] (**3c**)

A solution of **1c** (0.010 g, 0.021 mmol) and Ph_3SiH (0.012 g, 0.46 mmol) in CH_2Cl_2 (0.5 ml) at r.t. was treated with hexane, concentrated until crystals began to form and allowed to stand for 2 h. The product was obtained as a yellow–orange crystalline powder which was washed with Et_2O and dried under vacuum. Yield 0.012 g, 77%. Found: C, 58.71; H, 4.74; N, 1.97. $C_{36}H_{34}IrNO_2Si$ requires C, 58.99; H, 4.76; N, 1.91%. IR (nujol mull) ν(Ir–H) 2257 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 9.17 (d 1H), 8.04 (d 1H), 7.81 (dd. 1H), 7.63 (dd 1H), 7.58 (d 1H), 7.38 (mult. 1H), 7.33 (mult. 6H), 7.10 (mult. 3H), 7.04 (mult. 6H), 5.28 (mult. 1H), 4.38 (mult. 1H), 4.34 (mult. 1H), 3.84 (mult. 1H), 3.10 (mult. 1H), 2.88 (mult. 1H), 2.72 (mult. 1H), 2.62 (mult. 1H), 2.43 (mult. 1H), 2.11 (mult. 1H), 2.06–1.94 (mults. 2H), −15.33 (s 1H) ppm.

3.10. Preparation of [Ir(O_2CPic)(H)(SC_6F_5)(1,5-cod)] (**4a**)

A solution of **1a** (0.020 g, 0.047 mmol) in CH_2Cl_2 (0.5 ml) at r.t. was treated with C_6F_5SH (0.015 g, 0.07 mmol). A change of colour to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand for 2 h. The product was obtained as pale yellow crystals which were washed with Et_2O and dried under vacuum. Yield 0.020 g, 68%. Found: C, 38.62; H, 2.60; N, 2.38, $C_{20}H_{17}F_5IrNO_2S$ requires C, 38.58; H, 2.75; N, 2.25%. IR (nujol mull) ν(Ir–H) 2238 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 8.60 (d 1H), 8.06 (dd 1H), 7.94 (ddd 1H), 7.42 (ddd 1H), 5.15 (mult. 1H), 4.89 (mult. 1H), 4.69 (mult. 1H), 3.71 (mult. 1H), 2.98 (mult. 1H), 2.68–2.56 (mults. 3H), 2.53 (mult. 1H), 2.37 (mult. 1H), 2.10 (mult. 1H), 1.91 (mult. 1H), −15.40 (s 1H) ppm.

3.11. Preparation of [Ir(O_2Isoq)(H)(SC_6F_5)(1,5-cod)] (**4b**)

A solution of **1b** (0.020 g, 0.042 mmol) in CH_2Cl_2 (0.5 ml) at r.t. was treated with C_6F_5SH (0.015 g, 0.07 mmol). A change of colour to yellow was observed. Hexane was added and the mixture was concentrated and allowed to stand for 2 h. The product was obtained as yellow crystals which were washed with Et_2O and dried under vacuum. Yield 0.022 g, 77%. Found: C, 42.62; H, 2.70; N, 2.14. $C_{24}H_{19}F_5IrNO_2S$ requires C, 42.85; H, 2.85; N, 2.08%. IR (nujol mull) ν(Ir–H) 2212 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 27°C) δ 9.98 (d 1H), 8.54 (d 1H), 7.90–7.80 (mults. 3H), 7.70 (d 1H), 5.19 (mult. 1H), 4.82 (mult. 2H), 3.77 (mult. 1H), 3.04 (mult. 1H), 2.73–2.60 (mults. 3H), 2.55 (mult. 1H), 2.38 (mult. 1H), 2.13 (mult. 1H), 1.94 (mult. 1H), −14.85 (s 1H) ppm.

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