Formation of 5-Membered Metallacycles at $i\text{PrPCP}Ir$ by C–H, O–H, and C–CO Bond Cleavage

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Keywords: Iridium, Pincer ligand, PCP pincer, Cyclometalation, Metallacycle, C–H activation, O–H activation, Decarbonylation.

Graphical Abstract:

Abstract:

Cyclometalation of the 16 electron $i\text{PrPCP}Ir$ fragment ($i\text{PrPCP} = \kappa^3\text{-2,6-C}_6\text{H}_3(\text{CH}_2\text{P}(i\text{Pr})_2)_2$) by biphenyl, phenanthrene, fluorenone, benzophenone, and 1-naphthol is reported. Biphenyl and phenanthrene are found to undergo facile double C–H activation to form complexes $(i\text{PrPCP})Ir(\kappa^2\text{-2,2'}\text{-C}_{12}\text{H}_8)$ (**1**) and $(i\text{PrPCP})Ir(\kappa^2\text{-2,2'}\text{-C}_{14}\text{H}_8)$ (**2**) which are readily converted to their octahedral CO adducts **1-CO** and **2-CO**, respectively, by exposure to 1 atm of carbon monoxide. Complex **1-CO** is also formed through the decarbonylation of fluorenone by $i\text{PrPCP}Ir$. Reaction of $i\text{PrPCP}Ir$ with benzophenone leads to C–H activation and oxygen coordination yielding the *trans*-(C,H) addition species $(i\text{PrPCP})Ir(\text{H})(\kappa\text{-O,C-OC}_{13}\text{H}_9)$ (**3a**) as the kinetic product. Heating of **3a** induces isomerization to the *trans*-(O,H) orientation product **3b**. Reaction of $i\text{PrPCP}Ir$ with 1-naphthol at room temperature provides the surprisingly labile O–H

addition product ($i^{\text{Pr}}\text{PCP}$)Ir(H)(OC₁₀H₇) (**4**). Heating of **4** effects cyclometalation of 1-naphthol, to form ($i^{\text{Pr}}\text{PCP}$)Ir(κ -O,C-OC₁₀H₆) (**5**) by subsequent C–H activation.

1. Introduction

Cyclometalation reactions are integral to many important organometallic transformations, finding roles in the formation of reaction intermediates as well as in the ligation of transition metal complexes [1,2]. For example, metallacycles have been determined as key intermediates in olefin metathesis reactions [3,4], a number of C–H functionalization reactions [5-9] and alkyne trimerisation [10,11]. The chemistry of iridacycles is quite diverse [12-14]. Complexes containing iridium metallacycles have been used for OLED applications [15], the hydrogenation of imines [16], the conversion of ethanol to butanol [17], and have even shown anti-cancer activity [18]. In particular, the use of metallacyclic iridium pincer complexes has been an area of rapid development in recent decades [19-22].

While already the product of cyclometalation, iridium pincer complexes may undergo further cyclometalation processes in the formation of new species or during catalysis. Pincer iridium species have been shown to form metallacycles by C–H activation of phosphine alkyl substituents in POCOP [23] and PCP [24] systems, by metalation of a second pincer ligand in less sterically demanding systems [25], as well as during the catalytic cleavage of C–O bonds in substituted alkyl aryl ethers [26]. However, while the use of pincer iridium species has been extensively investigated in alkane dehydrogenation and similar reactions [19,22,27], examples of processes or complexes employing metallacycles are limited. Goldman and coworkers have reported the formation of metallacycles by ortho C–H activation in the reaction between $t^{\text{Bu}}\text{PCPIr}$ ($^{\text{R}}\text{PCP} = \kappa^3\text{-2,6-C}_6\text{H}_3(\text{CH}_2\text{PR}_2)_2$) precursors and nitrobenzene or acetophenone [28] (Scheme 1).

Scheme 1. Reactivity of the $t^{\text{Bu}}\text{PCPIr}$ fragment with nitrobenzene [28].

Interestingly, these reactions were found to be *non*-chelation assisted. In fact, the kinetic products were determined to result from para and meta C–H activation by low temperature ($-47\text{ }^{\circ}\text{C}$) NMR experiments. Warming these solutions to $-10\text{ }^{\circ}\text{C}$ leads to ortho C–H activation and oxygen coordination giving a *trans*-(C,H) addition product, and further heating at $135\text{ }^{\circ}\text{C}$ leads to formation of the *trans*-(O,H) isomer. This reactivity was interpreted to indicate that in PCPIr

systems directing groups may actually hinder C–H activation at ortho positions due to steric interaction. Similar 5-membered metallacycle formation, as well as one example of a 4-membered ring, was later observed with $^t\text{BuPCPIr}$ during the dehydrogenation of ketones [29] and during reactions with anisole derivatives, methyl benzoate, and several acetates [24]. Recently, metallacycle formation by C–C activation of biphenylene was also reported [30]. In this system a drastic difference in reactivity was noted between *tert*-butyl and isopropyl substituted PCP ligands. While $^t\text{BuPCPIr}$ reacts with biphenylene to form C–H activation products at room temperature, only providing the C–C activation product after heating at 125 °C for 24 hours, $^i\text{PrPCPIr}$ was found to form the C–C activation product with 95% conversion within 30 minutes at room temperature (Scheme 2). This drastic difference is attributable to the reduced steric congestion of the isopropyl system. Calculations indicate that the preferred transition state geometry for C–C activation involves tilting the biphenylene molecule as close as possible to 60° with respect to the C–Ir–C bond cleavage plane which leads to significant steric interactions when using $^t\text{BuPCPIr}$.

Scheme 2. Reactivity of $^t\text{BuPCPIr}$ and $^i\text{PrPCPIr}$ with biphenylene [30].

In the present work we report the synthesis and characterization of 5-membered metallacycles resulting from the reaction of the $^i\text{PrPCPIr}$ fragment with a variety of substrates. These reactions proceed by C–H, O–H, and C–CO bond cleavage, and may have implications for the use of PCPIr catalysts in the synthesis of useful chemicals such as fluorenes [31] and C–H functionalized aryl-ketones [5]. A comparison to the reactivity of other $^R\text{PCPIr}$ species is also made where possible.

2. Experimental

2.1. General procedures

All manipulations were carried out under argon atmosphere either in a Vacuum Atmospheres glove box, or by modified Schlenk techniques. All NMR spectra were collected on a Bruker AMX 400 MHz spectrometer except low temperature experiments which were done on a Bruker AMX 500 MHz spectrometer. All ^{31}P -NMR spectra were referenced to external H_3PO_4 . Proton NMR spectra were referenced to residual deuterated solvent signal. All aromatic/alkane solvents were dried over sodium/benzophenone, distilled from the resultant

purple solution prior to use, and stored over 3 Å molecular sieves. X-ray structure collection was conducted on a Bruker SMART APEX II CCD platform diffractometer. FTIR spectra were collected on a Shimadzu IR Prestige-21 spectrometer. The ⁱPrPCPH ligand and ⁱPrPCPIrH₄ complex were synthesized by literature methods [32,33].

2.2. Synthetic Procedures

2.2.1. (ⁱPrPCP)Ir(κ²-2,2'-C₁₂H₈), **1**

To a J. Young NMR tube, 10 mg (0.019 mmol) ⁱPrPCPIrH₄ and 4 mg (0.026 mmol) biphenyl were added. This was followed by 6 μL (0.047 mmol) *tert*-butylethylene and 0.5 mL benzene, after which the color immediately turned deep brown-red. After 30 min at room temperature, ≥ 99% conversion to (ⁱPrPCP)Ir(κ²-2,2'-C₁₂H₈) was observed by ³¹P-NMR spectroscopy (later tests gave the same results within 5-10 min). Complete conversion was seen after allowing the sample to rest at room temperature overnight. All volatiles were then removed by vacuum and the solid residue re-dissolved in pentane. Crystals suitable for X-ray diffraction were obtained from this solution at -17 °C in 30-35% yield. ³¹P{¹H} NMR (C₆D₆): δ 39.71 (s). ¹H-NMR (C₆D₆): δ 7.73 (d, *J*_{HH} = 4 Hz, 2H, biphenyl), 7.45 (d, *J*_{HH} = 8 Hz, 2H, meta-PCP), 7.36–7.29 (m, 3H, biphenyl and para-PCP), 7.10 (t, *J*_{HH} = 7 Hz, 2H, biphenyl), 6.90 (t, *J*_{HH} = 7.4 Hz, 2H, biphenyl), 3.30 (t, *J*_{HH} = 4 Hz, 4H, CH₂), 1.99–1.88 (m, 4H, CH), 0.55 (m, 24H, CH₃).

2.2.2. (ⁱPrPCP)Ir(κ²-2,2'-C₁₂H₈)(CO), **1-CO**

(Method A) A J. Young NMR tube containing 0.019 mmol **1** and 0.5 mL benzene was freeze-pump-thaw degassed three times. The contents were then placed under 1 atm carbon monoxide pressure. Mixing the contents led to an immediate color change to very pale yellow. ³¹P-NMR spectroscopy showed complete conversion to the product. All volatiles were removed by vacuum and the solid residue re-dissolved in pentane. Crystals suitable for X-ray diffraction were obtained from this solution at -17 °C in 60-70% yield. ³¹P{¹H} NMR (C₆D₆): δ 24.50 (s). ¹H NMR (C₆D₆): δ 8.55 (d, *J*_{HH} = 7 Hz, 1H, biphenyl), 7.91 (d, *J*_{HH} = 8 Hz, 1H, biphenyl), 7.83 (d, *J*_{HH} = 7.6 Hz, 1H, biphenyl), 7.30–7.17 (m, 6H, biphenyl and meta-PCP), 7.01 (d, *J*_{HH} = 7.2 Hz, 1H, biphenyl), 6.87 (t, *J*_{HH} = 7.2 Hz, 1H, para-PCP), 3.52 (dvt left side AB pattern, *J*_{HP} = 4 Hz, *J*_{HH} = 16 Hz, 2H, CH₂), 3.09 (dvt right side AB pattern, *J*_{HP} = 3.2 Hz, *J*_{HH} = 16 Hz, 2H, CH₂), 1.98 (m, 2H, CH), 1.69 (m, 2H, CH), 0.91 (m, 12H, CH₃), 0.45 (q, *J*_{HP} = 8 Hz, 6H, CH₃), 0.28 (q, *J*_{HP} = 8 Hz, 6H, CH₃). FTIR: (thin film) ν_{CO} = 1977 cm⁻¹.

(Method B) To a J. Young NMR tube, 5 mg (0.009 mmol) ⁱPrPCPIrH₄ and 3 μL *tert*-butylethylene (0.024 mmol) in 0.5 mL benzene-*d*₆ were added. To this, 3.4 mg (0.019 mmol) fluorenone was added and the tube then sealed and mixed. The sealed vessel was then heated in an aluminum heating block at 125 °C. After ~23 h, > 98% conversion to a single product was observed by ³¹P-NMR spectroscopy. This material was found to be spectroscopically identical to that produced by Method A.

2.2.3. (*i*^{Pr}PCP)Ir(κ^2 -2,2'-C₁₄H₈), **2**

To a J. Young NMR tube, 10 mg (0.019 mmol) *i*^{Pr}PCPIrH₄, and 5 mg (0.030 mmol) phenanthrene were added followed by 6 μ L *tert*-butylethylene (0.047 mmol) and 0.5 mL benzene. The color of the solution became a deep red-brown. After either 2.5 h at room temperature, or 10 min at 65 °C, complete conversion to the cyclometallated product was observed. Crystals of the product suitable for X-ray diffraction were obtained in ~40% yield by removing volatiles under vacuum, re-dissolving the solid residue in pentane, and then storing this solution at -17 °C. ³¹P{¹H} NMR (C₆D₁₂): δ 40.1 (s). ¹H NMR (C₆D₁₂): δ 7.39 (s, 2H, phenanthrene), 7.26 (d, *J*_{HH} = 4 Hz, 2H, meta-PCP), 7.19 (d, *J*_{HH} = 8 Hz, 2H, phenanthrene), 7.09 (d, *J*_{HH} = 8 Hz, 2H, phenanthrene), 6.97 (t, *J*_{HH} = 8 Hz, 1H, para-PCP) 6.91 (t, *J*_{HH} = 8 Hz, 2H, phenanthrene), 3.51 (t, *J*_{HP} = 4 Hz, 4H, CH₂), 2.03 (m, 4H, CH), 0.58-0.47 (dqt, *J*_{HP} = 8 Hz, 24H, CH₃). Anal. Calcd: C = 57.85%, H = 6.14%. Found: C = 58.54%, H = 6.18%.

2.2.4. (*i*^{Pr}PCP)Ir(κ^2 -2,2'-C₁₄H₈)(CO), **2-CO**

A J. Young NMR tube containing 0.019 mmol **2** and 0.5 mL benzene was freeze-pump-thaw degassed three times. The contents were then placed under 1 atm carbon monoxide pressure. Mixing the contents led to an immediate color change to very pale yellow. ³¹P-NMR spectroscopy showed complete conversion to the product. All volatiles were removed by vacuum and the solid residue re-dissolved in pentane. Crystals suitable for X-ray diffraction were obtained from this solution at -17 °C in 60-65% yield. ³¹P{¹H} NMR (C₆D₁₂): δ 24.88 (s). ¹H NMR (C₆D₁₂): δ 8.24 (d, *J*_{HH} = 4Hz, 1H, phenanthrene), 7.45-7.36 (multiple overlapping peaks, 4H), 7.20 (t, *J*_{HH} = 8 Hz, 1H, para-PCP), 7.09 (d, *J*_{HH} = 4 Hz, 2H, meta-PCP), 6.98 (q, *J*_{HH} = 8 Hz, 2H, phenanthrene) 6.76 (d, *J*_{HH} = 4 Hz, 1H, phenanthrene), 3.74 (dvt left side AB pattern, *J*_{HH} = 16 Hz, *J*_{HP} = 4 Hz, 2H, CH₂), 3.70 (dvt right side AB pattern, *J*_{HH} = 16 Hz, *J*_{HP} = 2 Hz, 2H, CH₂) 2.27 (m, 2H, CH, other 2H obscured by solvent), 1.04 (m, 12H, CH₃), 0.56 (q, *J*_{HP} = 8Hz, 6H, CH₃), -0.33 (q, *J*_{HP} = 8 Hz, 6H, CH₃). FTIR: (benzene solution) ν_{CO} = 1983 cm⁻¹. Anal. Calcd: C = 57.28%, H = 5.91%. Found: C = 55.80%, H = 5.69%.

2.2.5. (*i*^{Pr}PCP)Ir(H)(κ -O,C-OC₁₃H₉), **3a**

To a J. Young NMR tube, 10 mg (0.019 mmol) *i*^{Pr}PCPIrH₄ and 5 mg (0.027 mmol) benzophenone were added. This was followed by 6 μ L (0.047 mmol) *tert*-butylethylene in 0.5 mL toluene, and the vessel was then sealed and mixed providing a red solution. Within 5-10 min $\geq$ 99% conversion to a single product was observed by ³¹P-NMR spectroscopy. The solvent was then removed by vacuum and the residue redissolved in minimal pentane. Deep red crystals suitable for X-ray diffraction were obtained from this solution by slow evaporation at -14 °C in ~30% yield. These crystals proved very difficult to completely separate from the oil in which they formed. Attempts to wash these crystals resulted in complete dissolution, and an elemental analysis of pure material could not be obtained. ³¹P{¹H} NMR (C₆D₆): δ 44.54 (s). ¹H NMR (C₆D₆): δ 8.03 (t, *J*_{HH} = 8 Hz, 2H, benzophenone), 7.82 (m, 2H, ligated benzophenone partially

obscured by excess benzophenone), 7.3-7.08 (multiple overlapping peaks, 6H, benzophenone and meta-PCP, partially obscured by solvent and excess benzophenone), 7.04 (t, $J_{HH} = 7$ Hz, 1H, benzophenone), 6.95 (t, $J_{HH} = 8$ Hz, 1H, para-PCP), 3.19 (dvt left side AB pattern, $J_{HH} = 16$ Hz, $J_{HP} = 3$ Hz, 2H, CH₂), 3.03 (dvt right side AB pattern, $J_{HH} = 16$ Hz, $J_{HP} = 4$ Hz, 2H, CH₂), 2.00 (m, 2H, CH), 1.68 (m, 2H, CH), 1.31 (q, $J_{HP} = 8$ Hz, 6H, CH₃), 1.21 (q, $J_{HP} = 8$ Hz, 6H, CH₃), 0.67 (overlapping quartets, $J_{HP} = 8$ Hz, 12H, CH₃), -8.43 (t, $J_{HH} = 8$ Hz, Ir-H).

2.2.6. (*i*^{Pr}PCP)Ir(H)(κ -C,O-OC₁₃H₉), **3b**

To a J. Young NMR tube, 10 mg (0.019 mmol) ⁱPrPCPIrH₄ and 5 mg (0.027 mmol) benzophenone were added. This was followed by 6 μ L (0.047 mmol) *tert*-butylethylene in 0.5 mL toluene, and the vessel was then sealed and mixed providing a red solution. The sealed vessel was then heated in an aluminum heating block at 160 °C for 1.5 h, at which time ³¹P-NMR spectroscopy revealed 83% conversion to a new product observed as a singlet at 46.04 ppm. Further heating did not increase the conversion. The volatiles were removed by vacuum and the solid residue redissolved in minimal pentane which was then stored at -14 °C. Deep red crystals suitable for X-ray diffraction were obtained from this solution in 60 to 70% yield based on the NMR conversion. ³¹P{¹H} NMR (C₆D₆): δ 45.97 (s). ¹H NMR (C₆D₆): δ 8.64 (d, $J_{HH} = 8$ Hz, 1H, benzophenone), 7.97 (d, $J_{HH} = 8$ Hz, 1H, benzophenone), 7.75 (vdd, $J_{HH} = 8$ Hz, 2H, benzophenone), 7.38-7.06 (multiple overlapping peaks partially obscured by solvent, 7H, benzophenone and meta-PCP), 6.88 (t, $J_{HH} = 8$ Hz, 1H, para-PCP), 3.33 (dvt left side AB pattern, $J_{HH} = 16$ Hz, $J_{HP} = 3$ Hz, 2H, CH₂), 3.23 (dvt right side AB pattern, $J_{HH} = 16$ Hz, $J_{HP} = 4$ Hz, 2H, CH₂), 1.78 (m, 4H, CH), 1.08 (q, $J_{HP} = 8$ Hz, 6H, CH₃), 0.92 (q, $J_{HP} = 8$ Hz, 6H, CH₃), 0.70 (q, $J_{HP} = 8$ Hz, 6H, CH₃), 0.61 (q, $J_{HP} = 8$ Hz, 6H, CH₃), -24.24 (t, $J_{HP} = 14$ Hz, 1H, Ir-H). Anal. Calcd: C = 55.68%, H = 6.37%. Found: C = 56.20%, H = 6.44%.

2.2.7. (*i*^{Pr}PCP)Ir(H)(OC₁₀H₇), **4**

To a J. Young NMR tube, 11 mg (0.021 mmol) ⁱPrPCPIrH₄ and 4 mg (0.027 mmol) 1-naphthol were added. This was followed by 6 μ L (0.047 mmol) *tert*-butylethylene and 0.5 mL toluene providing a bright red solution. After 30 min at room temperature, ³¹P-NMR spectroscopy showed quantitative conversion to the product. The volatiles were removed by vacuum and ~1 mL pentane was then added followed by dropwise addition of toluene until the solid residue was fully dissolved. Crystals suitable for X-ray diffraction were obtained from this solution at -17 °C in 25-35% yield. ³¹P{¹H} NMR (C₆D₆): δ 56.71 (s). ¹H NMR (C₆D₆): δ 7.81 (d, $J_{HH} = 8$ Hz, 1H, naphthol), 7.5-7.2 (multiple overlapping peak partially obscured by solvent, 5H), 6.95 (bs, 3H), 6.68 (d, $J_{HH} = 8$ Hz, 1H, naphthol), 2.82 (dvt left side AB pattern, $J_{HH} = 17$ Hz, $J_{HP} = 4$ Hz, 2H, CH₂), 2.73 (dvt, right side AB pattern, $J_{HH} = 18$ Hz, $J_{HP} = 4$ Hz, 2H, CH₂), 2.12 (m, 2H, CH), 1.79 (m, 2H, CH), 1.01 (m, 12H, CH₃), 0.83 (q, $J_{HP} = 8$ Hz, 12H, CH₃), -33.84 (very broad hump, Ir-H). Anal Calcd: C = 53.47%, H = 6.43%. Found: C = 53.69%, H = 6.18%.

2.2.8. (*i*^{Pr}PCP)Ir(κ -O,C-OC₁₀H₆)(H₂O)•(OC₁₀H₈), **5-H₂O**. Observation of (*i*^{Pr}PCP)Ir(κ -O,C-OC₁₀H₆), **5**

To a J. Young NMR tube, 11 mg (0.021 mmol) *i*^{Pr}PCPIrH₄ and 4 mg (0.027 mmol) 1-naphthol were added. This was followed by 6 μ L (0.047 mmol) *tert*-butylethylene and 0.5 mL toluene providing a bright red solution. The sealed vessel was then heated in an aluminum heating block at 100 °C for 1 h during which time the solution changed to a darker red-brown color and quantitative conversion to a single product was observed by ³¹P-NMR spectroscopy (41 δ , complex **5**, vide infra). The volatiles were then removed by vacuum and the solid residue redissolved in minimal benzene. Crystals suitable for X-ray diffraction were obtained from this solution by vapor diffusion of pentane over several days followed by storing at -17 °C (circa 6 months). X-ray diffraction revealed this product to result from coordination of adventitious water and co-crystallization with excess substrate. Yield 40-45% based on **5**. An additional 1-2 mg of fine polycrystalline material spectroscopically identical to **5-H₂O** was also obtained. ³¹P{¹H} NMR (C₆D₆): δ 36.4 (s). ¹H NMR (C₆D₆): δ 8.56 (d, *J*_{HH} = 8 Hz, 1H, naphthol), 7.78 (d, *J*_{HH} = 8 Hz, 1H, naphthol), 7.56-7.13 (multiple overlapping peaks partially obscured by solvent, 15H, naphthol and meta-PCP), 6.85 (t, *J*_{HH} = 8 Hz, 1H, para-PCP), 6.32 (d, *J*_{HH} = 4 Hz, 1H, naphthol), 3.24 (dvt left side AB pattern, *J*_{HH} = 16 Hz, *J*_{HP} = 4 Hz, 2H, CH₂), 2.96 (dvt, right side AB pattern, *J*_{HH} = 16 Hz, *J*_{HP} = 4 Hz, 2H, CH₂), 2.19 (bm, 2H, CH), 1.65 (bm, 2H, CH), 0.97 (overlapping quartets, *J*_{HP} = 8 Hz, 12H, CH₃), 0.60 (q, *J*_{HP} = 8 Hz, 6H, CH₃), 0.52 (q, *J*_{HP} = 8 Hz, 6H, CH₃). Anal. Calcd: C = 57.61%, H = 6.16%. Found: C = 57.78%, H = 5.83%.

3. Results and discussion

3.1. Reactions with biphenyl, phenanthrene, and fluorenone

In the presence of an excess of *tert*-butylethylene (TBE), PCP ligated iridium hydrides are known to lose hydrogen (via TBE hydrogenation) and subsequently form alkenyl or aryl hydrides by C(sp²)H activation of TBE or arene solvent [34]. These C-H adducts are in rapid dissociative exchange at ambient temperature, and provide facile access to the reactive PCPIr fragment. When a 37.4 mM benzene or toluene solution of (*i*^{Pr}PCP)IrH₄ containing 1.4 equivalents of biphenyl is treated with 2.5 equivalents of TBE (TBE = *tert*-butylethylene), the solution immediately turns a deep brown color which is red to transmitted light. Within 5-10 minutes, $\geq 99\%$ conversion to a product with a ³¹P-NMR resonance at 39.7 ppm is observed. This shift is consistent with that of the previously reported compound (*i*^{Pr}PCP)Ir(κ^2 -2,2'-C₁₂H₈) (**1**) which was found to be the product of the reaction between (*i*^{Pr}PCP)IrH₄ and biphenylene in the presence of TBE [30]. Indeed, treatment of this product with 1 atm carbon monoxide in arene or alkane solvent led to the quantitative formation of a product with a ³¹P-NMR resonance at 24.5 ppm. Again, this observation is consistent with previous findings during studies with biphenylene. Crystallization of this material from pentane provided crystals which were a unit cell match for the previously reported (*i*^{Pr}PCP)Ir(κ^2 -2,2'-C₁₂H₈)(CO) (**1-CO**). These results indicate that the reaction of the *i*^{Pr}PCPIr fragment with biphenyl involves a *double* C-H

activation with concomitant release of hydrogen (Scheme 3). While metallocfluorene complexes of iridium are known, they have all been synthesized/observed by reaction of 2,2'-dilithiobiphenyl with an iridium halide [35], by C–C activation of biphenylenes [30,36,37], or net C–CO and C–H activation of 2-arylbenzoyl chlorides [38]. To the best of our knowledge, the PCPIr system is the first example of iridium 2,2'-biphenyl complexes formed by double C–H activation, although double C–H activation of biphenyl with (dtbpm)Pt⁰ is known [39]. The analogous reaction with ^tBuPCPIr has recently been observed [30] and complete conversion to the cyclometalated product requires >24 hours at room temperature [40], which is in accord with the increased steric congestion in comparison to ⁱPrPCPIr.

Scheme 3. Reactivity of ⁱPrPCPIr with biphenyl and phenanthrene.

Similar to biphenyl, the (ⁱPrPCP)Ir fragment is observed to form a new product without hydrides when reacted with phenanthrene in benzene or toluene (Scheme 3). This product is associated with the appearance of a singlet at 40.1 ppm in the ³¹P-NMR spectrum. However, in the case of phenanthrene complete conversion requires approximately 2.5 hours at room temperature or heating at 65 °C for 10 minutes. The structure was conclusively determined as the expected product, (ⁱPrPCP)Ir(κ²-2,2'-C₁₄H₈) (**2**), by X-ray diffraction of crystals grown from pentane at –17 °C (Fig. 1). The analogous reaction with ^tBuPCPIr was found to require > 24 hrs to reach completion [40]. Exposure of a benzene solution of this product to 1 atm of carbon monoxide quantitatively yields a product with a ³¹P-NMR resonance at 24.9 ppm with an associated color change to very pale yellow, indicating coordination of CO to iridium. An associated asymmetry above/below the plane of the PCP ligand backbone is clearly manifest in the ¹H NMR spectrum by separation of the pincer arm CH₂ resonance into 2 doublets of virtual triplets representing either side of an AB splitting pattern and 2 protons each. This type of coupling environment is well preceded in octahedral PCPIr complexes with asymmetric auxiliary ligands such as ⁱPrPCPIr(CO)(CH₃)(I) and cis-ⁱPrPCPIr(CO)H₂ [41]. Crystals were

obtained of this product as well which confirmed the formation of an octahedral CO adduct, **2-CO**, with CO in an apical position (Fig. 1).

Fig. 1. X-ray structures of $(i\text{PrPCP})\text{Ir}(\kappa^2\text{-}2,2'\text{-C}_{14}\text{H}_8)$ (**2**) and $(i\text{PrPCP})\text{Ir}(\kappa^2\text{-}2,2'\text{-C}_{14}\text{H}_8)(\text{CO})$ (**2-CO**).

Though the products of biphenyl and phenanthrene cyclometalation should display only negligible differences sterically, it is interesting that the reaction with phenanthrene requires 2.5 hours at room temperature to reach completion while in the case of biphenyl nearly quantitative conversion is observed within <10 minutes. However, this may be less surprising in light of recent findings with biphenylene (*vide supra*). Calculations [30] indicate that the tilting of biphenylene in the preferred transition state geometry for C–C addition results from steric repulsion between the iridium center and the H(C2) and H(C2') hydrogens of biphenylene. For planar biphenyl (or phenanthrene), the interatomic distance between the H(C2) and H(C2') (or H(C4) and H(C5)) hydrogens is even less than that of biphenylene (approx. 2.26 Å vs 3.85 Å) and, accordingly, the calculated C–C activation pathway involves a fully perpendicular approach. As evidenced by the separate rotamers formed from C–H activation of biphenylene with $t\text{BuPCPIr}$, as well as its reluctance to reductively eliminate $\text{C}_{(\text{Ph})}\text{--C}$ bonds [42], rotation of phenyl groups bound to $t\text{BuPCPIr}$ is severely hindered. By extension, in the double C–H activation of biphenyl it is likely that the initial C–H activation occurs with the un-activated Ph ring *syn* to the hydride since rotation from the *anti*-addition product to form **1** would be restricted (Scheme 4). That said, in order to reduce steric interaction between the Ir–H and H(C2') after initial C–H activation, it is likely that the biphenyl molecule would twist. Indeed, free biphenyl is known to adopt a torsional angle of $\sim 45^\circ$ to prevent interaction of the alpha-hydrogens [43]. The fused rings of phenanthrene prevents such a twisting in the formation of **2** and the whole molecule would have to rotate as opposed to one Ph ring, likely resulting in significant steric interaction and the longer reaction time observed. The markedly reduced reaction time of $i\text{PrPCPIr}$ with

respect to ^tBuPCPIr in the cyclometalation of biphenyl and phenanthrene clearly illustrates the appreciably reduced steric congestion around iridium in the isopropyl system.

Scheme 4. Steric interactions in the C–H activation of biphenyl by ⁱPrPCPIr.

The formation of **1-CO** gave rise to the possibility of catalyzing the synthesis of fluorenone from biphenyl and carbon monoxide. In this effort 38 mM toluene solutions of **1-CO** were heated in the presence of excess CO and/or biphenyl at temperatures up to 160 °C. Unfortunately, no release of fluorenone or change to **1-CO** was observed by NMR spectroscopy, which may be due to thermodynamic limitations [44]. Somewhat unsurprisingly, the 18-electron, d⁶, multi-chelate molecule seems to be quite stable. In fact, heating an 18 mM benzene-*d*₆ solution of ⁱPrPCPIr(TBE) at 125 °C with 2 equivalents of fluorenone leads to full conversion to **1-CO** in ~ 24 hours by a net double C–CO cleavage (Scheme 5). Additionally, when a 38 mM toluene solution of ⁱPrPCPIr(TBE) is treated with 1 atm CO, a yellow-orange solution containing several products, one of which is ⁱPrPCPIr(CO), is obtained. Heating this solution at 165 °C for 24 hours in the presence of 5 equivalents of biphenylene still afforded several products as observed by ³¹P and ¹H NMR spectroscopy, with ~5% of these products represented by **1-CO**. Further heating slowly increased conversion to **1-CO**. This indicates that **1-CO** is at least somewhat lower in energy than even the CO adducts which would already be a concern as a thermodynamic sink. By microscopic reversibility arguments, the formation of **1-CO** from ⁱPrPCPIr and fluorenone demonstrates that reduced sterics in the ⁱPrPCPIr system should be sufficient to permit C_(sp2)–C bond reductive elimination. However, in the potential catalytic synthesis of fluorenes the pronounced thermodynamic stability of **1-CO**, and by inference related species, may preclude completion of a catalytic cycle.

Scheme 5. Formation of (ⁱPrPCP)Ir(κ²-2,2'-C₁₂H₈)(CO) (**1-CO**) from ⁱPrPCPIr(TBE) and fluorenone.

3.2. Reaction with benzophenone

We were inspired by the C–CO activation of fluorenone to attempt an analogous reaction not benefited by the formation of a metallacyclic product, namely, the decarbonylation of benzophenone to yield $i\text{PrPCPIr}(\text{CO})(\text{Ph})_2$. Treatment of 38 mM $i\text{PrPCPIrH}_4$ in toluene containing 1.4 equivalents of benzophenone with 2.5 equivalents of TBE at room temperature immediately provides a bright red solution and quantitative conversion to a single product with a ^{31}P -NMR resonance at 44.5 ppm, and associated hydride triplet at -8.4 ppm in the ^1H -NMR spectrum. These shifts are characteristic of a 6-coordinate $\text{PCPIr}(\text{III})$ hydride with hydrogen in an apical position [30,34,41]. Crystals were obtained of this product and X-ray diffraction confirmed the formation of cyclometalated C–H activation product **3a**. Heating a solution of **3a** obtained in this manner at 160°C for 1.5 hours led to 83% conversion to a new product with an associated ^{31}P -NMR signal at 46 ppm and associated hydride triplet at -24.2 ppm in the ^1H -NMR spectrum. No byproducts were observed, and further heating did not increase conversion. This hydride shift is intermediate between the expected ranges of 5 and 6-coordinate PCPIr hydrides which indicates a ligand exchange trans to the hydride, and certainly rules out the desired C–CO activation product. X-ray diffraction of crystals obtained from a pentane solution of the reaction products revealed this new product to be the *trans*-(O,H) isomer **3b** (Scheme 6 and Fig. 2).

Scheme 6. Reactivity of $i\text{PrPCPIr}$ with benzophenone

Fig. 2. X-ray structures of $(i\text{PrPCP})\text{Ir}(\text{H})(\kappa\text{-O,C-OC}_{13}\text{H}_9)$ (**3a**) and $(i\text{PrPCP})\text{Ir}(\text{H})(\kappa\text{-C,O-OC}_{13}\text{H}_9)$ (**3b**).

Although the desired product was not obtained, the observed reactivity is in excellent agreement with the reported behavior of ^tBuPCPIr with aryl and α,β -unsaturated ketones [28,29]. In the reaction between ^tBuPCPIr and acetophenone, C–H activation followed by oxygen coordination quantitatively produces *trans*-(C,H)-^tBuPCPIr(acetylphenyl)(hydride). Heating for 5 hours at 125 °C generates the *cis*-(C,H) isomer in 98% conversion. Since rotation of phenyl groups bound to PCPIr (especially ^tBuPCPIr) [34] is restricted, the mechanism of this isomerization is uncertain. However, sterics would seem to play a role in the thermodynamics as evidenced by the establishment of an apparent equilibrium in the formation of **3b** from **3a**, while related ^tBuPCPIr species are formed essentially quantitatively. As determined from the crystal structure of **3b**, the C3–C2 and C1–O1 bonds are longer, and C2–C1 bond shorter, than those reported for free benzophenone [45]. Though the differences are somewhat small (1.43, 1.26, and 1.45 Å, vs 1.40, 1.23, and 1.48 Å, respectively), they are consistent with the expected lengthening/shortening pattern in the event of resonance between iridium and the benzophenone ligand (Scheme 7) and are comparable to the differences observed between the related ^tBuPCPIr ethyl vinyl ketone adduct [29] and a reported α,β -enone [46] where resonance has been suggested. Based on these data it is likely that proposed resonance form **II** contributes at least somewhat to the molecular structure of **3b**.

Scheme 7. Possible resonance forms of (ⁱPrPCP)Ir(H)(κ -C,O-OC₁₃H₉) (**3b**).

3.3. Reaction with 1-naphthol

The formation of **3a** and **3b** by cyclometalation of benzophenone begged the question of whether this chemistry, and that seen with biphenyl, could be brought together to form 5-membered metallocycles at ⁱPrPCPIr by combined C–H/O–H activation. Towards this end, a 42 mM toluene solution of ⁱPrPCPIrH₄ containing 1.3 equivalents of 1-naphthol was treated with 2.2 equivalents of *tert*-butylethylene. A bright red solution was immediately obtained, and within 30 minutes quantitative conversion to a product with a ³¹P-NMR resonance at 56.7 ppm was observed. The ¹H-NMR spectrum revealed an asymmetric environment as evidenced by the inequivalency of ligand CH₂, CH, and isopropyl group hydrogens above and below the plane of the PCP phenyl ring, similar to that observed with **1-CO**, **2-CO**, **3a**, and **3b**. No associated hydride peak was observed initially which seemed to indicate formation of the cyclometalated product. However, upon closer inspection of the ¹H-NMR spectrum a broad (~ 400 Hz) signal was detected at –31 ppm, indicative of a 5-coordinate product [29,34]. Cooling this solution to 0 °C resulted in downfield shifting and sharpening of the signal to ~150 Hz half-width. Further cooling resulted in re-broadening and downfield shifting of this signal (Fig. 3). Cooling was

continued as low as $-90\text{ }^{\circ}\text{C}$ but no other clear hydride signal was seen to form. These results suggest that the product is undergoing some type of relatively rapid exchange on the NMR time scale. X-ray diffraction of crystals obtained from pentane/toluene at $-17\text{ }^{\circ}\text{C}$ elucidated the structure as the O–H activation product of 1-naphthol (**4**) (Fig. 4 and Scheme 8) though the hydride could not be located and refined from the data obtained.

Fig. 3. Low temperature ^1H -NMR spectra of $(i\text{PrPCP})\text{Ir}(\text{H})(\text{OC}_{10}\text{H}_7)$ (**4**) in toluene (42mM): a) room temperature, b) $0\text{ }^{\circ}\text{C}$, c) $-20\text{ }^{\circ}\text{C}$, d) $-30\text{ }^{\circ}\text{C}$, e) $-40\text{ }^{\circ}\text{C}$, f) $-50\text{ }^{\circ}\text{C}$.

Fig. 4. X-ray structure of $(i\text{PrPCP})\text{Ir}(\text{H})(\text{OC}_{10}\text{H}_7)$ (**4**).

Though the structure of **4** has been unambiguously assigned, it was surprising that only a barely detectable broad hydride signal was seen at room temperature since reported ^1H -NMR spectra of phenolic O–H adducts of $^t\text{BuPCPIr}$ display well defined hydride triplets at room temperature [29]. In order to determine whether this divergence in reactivity was related to the substrate or the ligand an 18 mM toluene solution of $^i\text{PrPCPIr}(\text{TBE})$ was treated with an excess of phenol at room temperature. The solution immediately turned red-orange and within 20 minutes 73% conversion to a product with a ^{31}P -NMR chemical shift of 48.8 ppm was observed, along with an associated hydride triplet ($J_{\text{HP}} = 16$ Hz) at -32.4 ppm. This is in good agreement with expected chemical shift values for $^i\text{PrPCPIr}(\text{H})(\text{OPh})$, supporting 1-naphthol as the cause of the broadness in the spectrum of **4**, not the $^i\text{PrPCP}$ ligand. This hypothesis is supported by two factors. Firstly, 1-naphthol is in general more reactive than phenol, with a heat of formation ~ 10 kcal/mol more positive [47] and O–H bond dissociation energy 5.7 kcal/mol lower [48,49]. Second, even though the naphthyl group is one bond removed from the $^i\text{PrPCPIr}$ active “pocket” in **4**, rotation may be hindered by steric interaction of paddle-like 1-naphthol with the pincer methyl groups, destabilizing the O–H addition product, while the much smaller phenol has greater freedom of rotation and lower overall enthalpy. Alternatively, it may be that adventitious water is coordinating reversibly to the complex at lower temperatures. This possibility would be consistent with the formation of aquo complex **5**· H_2O (vide infra). Another possibility is that there is a weak agostic interaction of the hydrogen on C8 with the iridium center [50]. This possibility would also be consistent with the formation of complex **5** via C–H activation (vide infra).

To assess whether metallacycle formation by combined O–H/C–H activation could proceed, a sample of **4** prepared as described above was heated at 100°C for 1 hour, during which time the solution darkened to a more brown-red color. Gratifyingly, full conversion to a single product with a ^{31}P -NMR resonance at 41 ppm and no detectable hydrides was achieved, ostensibly complex **5** (Scheme 8). Single crystals were obtained by vapor diffusion of pentane into a benzene solution of this product. X-ray diffraction showed that the anticipated cyclometalation had occurred as well as coordination of adventitious water despite the water/air free techniques employed. Excess 1-naphthol was also found to co-crystallize in a 1:1 ratio in the new complex **5**· H_2O (Fig. 5). Upon dissolution of the crystals obtained in benzene- d^6 , the signal observed by ^{31}P -NMR was shifted upfield to 36.4 ppm, likely due to water coordination which occurred during the crystallization. Though the formation of metallacycle **5** likely demonstrates the main hurdle toward catalytic transformations of 1-naphthols, the observed preference for O–H activation followed by C–H activation hints at the possibility of O–H/C–H cross coupling type reaction development with the appropriate ligand/substrate modifications.

Scheme 8. Reactivity of $^i\text{PrPCPIr}(\text{TBE})$ with 1-naphthol.

Appendix A. Supplementary data

CCDC #1448764-1448769 contain the supplementary crystallographic data for complexes **2**, **2-CO**, **3a**, **3b**, **4**, and **5-H₂O**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article, including ¹H-NMR spectra, can be found, in the online version, at <http://dx.doi.org>

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