

**Reactions of iridium hydride pincer complexes with dioxygen:
new peroxy complexes and reversible O₂ binding**

Supporting Information

D. Bridget Williams, Werner Kaminsky, James M. Mayer,* Karen I. Goldberg*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington, 98195-1700

General Experimental	S2
Synthesis and Characterization of Complexes	S2
[^t BuPCP]Ir(H)(OH) (4)	S2
[^t BuPCP]Ir(O ₂) ₂ (6)	S2
[^t BuPCP]Ir(O ₂) (7).....	S3
[^t BuPCP]Ir(k ² -SO ₄) (8)	S3
(^tBuPCP)Ir(H)₂ (3) + O₂	S3
[<i>trans</i> -(^t BuPCP)Ir(H) ₂ (O ₂)] (9)	S3
(^t BuPCP)Ir(H) ₂ (3) + 1 atm O ₂	S4
(^t BuPCP)Ir(H) ₂ (3) + 5 atm O ₂	S4
(^t BuPCP)Ir(H) ₂ (3) + 10 atm O ₂	S5
(^tBuPCP)Ir(H)(CCPh) + O₂	S5
Oxidation of PPh₃	S5
X-ray determination of 6	S6
Table S1: Crystal and Structure Refinement Data	S8
IR Data	S9
UV-Vis Data	S9

General Experimental

Unless otherwise noted, all reactions were carried out in an argon drybox, using standard Schlenk techniques or under vacuum. Research grade dioxygen (< 0.5 ppm H₂O) was obtained from Airgas. C₆D₆ was dried over sodium metal/benzophenone. All other reagents were used as received from commercial suppliers. GC/MS data were acquired on a Hewlett Packard 5971A gas chromatograph – mass spectrometer equipped with a J&W DB5ms column (25m x 0.2mm with a 0.33mm phase thickness). NMR spectra were carried out using Bruker AV300, DPX200 and DRX499 spectrometers. ¹H NMR spectra are referenced to residual solvent signals and shifts are reported in parts per million (ppm) downfield of tetramethylsilane. ³¹P NMR spectra are referenced to an external H₃PO₄ standard set to 0 ppm. IR spectra were measured as KBr pellets on a Bruker Optics Tensor27 FT-IR spectrometer. C₆H₃(CH₂P^{*t*}Bu₂)₂ (^{*t*}BuPCP),¹ (^{*t*}BuPCP)Ir(H)(Cl)¹ (**1**), (^{*t*}BuPCP)Ir(H)(Ph)² (**2**), (^{*t*}BuPCP)Ir(H)₂² (**3**) and (^{*t*}BuPCP)Ir(H)(CCPh)³ (**5**) were prepared according to reported procedures.

Synthesis and Characterization of Complexes

[(^{*t*}BuPCP)Ir(H)(OH)] (**4**) A modification of the literature procedure⁴ was used starting from complex **2** (0.0056 g, 8.3 μmol), which was weighed into a medium walled NMR tube fitted with a Teflon seal and dissolved in C₆D₆ (0.25 mL). Water (3 μL) was added via syringe to the reaction tube resulting in a light orange solution. Yield: 90.2% by ¹H NMR as referenced to a capillary standard of 4% hexamethyldisilane in CD₂Cl₂. Spectral data (¹H NMR and ³¹P{¹H} NMR) matched those reported.⁴

[(^{*t*}BuPCP)Ir(O₂)₂] (**6**) Complex **2** (0.0083 g, 12 μmol) was loaded into a medium walled NMR tube fitted with a Teflon seal. C₆D₆ (0.38 mL) was vacuum transferred into the tube, then placed under 5 atmospheres of oxygen pressure, using a high pressure

¹ Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

² Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766-1776.

³ Ghosh, R.; Zhang, X.; Achord, P.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2006**, accepted.

⁴ Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144-1147.

manifold, and shaken. Yield: 98% by ^1H NMR as referenced to a capillary standard of 4% hexamethyldisilane in CD_2Cl_2 . ^1H NMR (C_6D_6 , 300 MHz) δ 7.09 (t, 1H, $J_{\text{H-H}} = 7.0$ Hz, aromatic); 6.94 (d, 2H, $J_{\text{H-H}} = 6.0$ Hz, aromatic); 3.27 (s, 4H, CH_2); 1.18 (vt, 36H, apparent $J_{\text{P-H}} = 6.6$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121 MHz) δ 29.4.

$[(^t\text{BuPCP})\text{Ir}(\text{O}_2)]$ (7) The solvent and oxygen atmosphere were removed from an NMR sample of **6** (35 mM, 10.5 mmol) under reduced pressure. The sample was kept under dynamic vacuum for two hours resulting in the formation of **7** as green solid. The crude yield is 90% (5.8 mg, 9.5 μmol) as determined by mass. ^1H NMR (C_6D_6 , 300 MHz) δ 7.09 (d, 2H, $J_{\text{H-H}} = 7.0$ Hz, aromatic), 6.89 (t, 1H, $J_{\text{H-H}} = 7.5$ Hz, Ar), 3.52 (vt, 4H, apparent $J_{\text{P-H}} = 3.6$ Hz, CH_2), 1.33 (vt, 36H, apparent $J_{\text{P-H}} = 6.6$ Hz, $\text{C}(\text{CH}_3)_3$), 10.7 and 15.8 (unidentified singlet resonances that are not associated with complex **7**, integration varies between samples). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121 MHz) δ 46.7. IR (KBr pellet) **7**: 893 cm^{-1} ($\nu_{\text{O-O}}$). The calculated stretch at 842 cm^{-1} for $^{18}\text{O}-^{18}\text{O}$ overlaps with a ligand stretch and no distinguishable stretch was observed for $^{16/18}\text{O}-^{16/18}\text{O}$ as the spectrum was broad. UV-Vis of **7**: 613 nm, $\epsilon = 565\text{ M}^{-1}\text{cm}^{-1}$.

$[(^t\text{BuPCP})\text{Ir}(\text{k}^2\text{-SO}_4)]$ (8) Complex **7** (0.004 g, 6.18 μmol) was weighed into an NMR tube fitted with a Teflon seal and C_6D_6 was added by vacuum transfer. One atmosphere of SO_2 was added to the tube. The solution changed to red-brown color and the product precipitated out of solution. ^1H NMR (C_6D_6 , 300 MHz), ArH (obscured by residual solvent peak); δ 3.29 (vt, 4H, apparent $J_{\text{P-H}} = 3.0$ Hz, CH_2); 1.25 (vt, 36H, apparent $J_{\text{P-H}} = 6.6$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121 MHz) δ 72.5. IR (KBr pellet) 1101, 1121 and 1157 cm^{-1} (ν_3 stretching mode).⁵

$[\text{trans-}(^t\text{BuPCP})\text{Ir}(\text{H})_2(\text{O}_2)]$ (9) Observed in the reaction between a benzene solution of **3** and 5 atmospheres of O_2 . Yield: 33 % by ^1H NMR as referenced to a capillary standard of 4% hexamethyldisilane in CD_2Cl_2 . ^1H NMR (C_6D_6 , 300 MHz), ArH (obscured by

⁵ Kazuo Nakamoto *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1997; pp 79-82.

other aromatic signals); δ 2.96 (vt, 4H, apparent $J_{\text{P-H}} = 3.0$ Hz, CH_2); $\text{C}(\text{CH}_3)_3$ (obscured by ^tBu signals of other compounds); -6.79 (vt, 2H, apparent $J_{\text{P-H}} = 8.3$ Hz, IrH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121 MHz) δ 72.5.

$(^t\text{BuPCP})\text{Ir}(\text{H})_2$ (**3**) + 1 atm O_2

A C_6D_6 (0.25 ml) solution of **3** (30.8 mg, 52.4 μmol) in a medium walled NMR tube fitted with a Teflon seal and a capillary standard of hexamethyldisilane (HMDS) in CD_2Cl_2 was placed under 1 atm O_2 . The reaction was immediately monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. Approximately five minutes after adding O_2 , **6**, **7**, *trans*- $(^t\text{BuPCP})\text{Ir}(\text{H})_2(\text{O}_2)$ (**9**) and **4** were observed in a 4:2:1:1 ratio (accounting for ca. 98% of the initial amount of iridium). Trace amounts of the singlet resonances at 10.7 and 15.8 ppm (ca. 2%). Over the course of the reaction the products amounts varied as the NMR tube was shaken prior to each scan. After 10 minutes **7** has reached a steady amount (15%) and after 20 minutes **9** has reached ca. 5%. The amount of **6** increases over 60 minutes to 45%. Additionally two unassigned singlets at 10.7 and 15.8 ppm were observed by ^1H NMR, for which there are no apparent corresponding resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The amount of this unknown species increases over the course of the reaction to ca. 37% with integration of the resonances to 1H each. The amount of **4** varied over the course of the reaction with 45% present after 20 minutes and 20% after 40 minutes.

$(^t\text{BuPCP})\text{Ir}(\text{H})_2$ (**3**) + 5 atm O_2

A benzene solution of **3** (0.0034g, 5.8 μmol) in a medium walled NMR tube fitted with a Teflon seal was placed under 5 atm O_2 . The reaction was immediately monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. Five minutes after the addition of O_2 , **6**, **7** and **4** were observed in a 1:8:8 ratio (ca. 90% of the initial amount of iridium) as well as, a small amount of *trans*- $(^t\text{BuPCP})\text{Ir}(\text{H})_2(\text{O}_2)$ (**9**) (6%). After a period of 40 minutes, **9** (63%) was the major product and significant decomposition was observed by the appearance of broad signals composed of multiple resonances in the methylene and *tert*-butyl regions of the ^1H NMR spectrum. Additionally two unassigned singlets at 10.7 and 15.8 ppm were observed by ^1H NMR, for which there are no apparent corresponding resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum. The amount of this unknown species increases over the course of the reaction to ca. 36% with integration of the resonances to 1H each.

(^tBuPCP)Ir(H)₂ (2**) + 10 atm O₂**

A C₆D₆ (0.3 ml) solution of **3** (7.8 mg, 13.3 μmol) in a medium walled NMR tube fitted with a Teflon seal and a capillary standard of hexamethyldisilane (HMDS) in CD₂Cl₂ was placed under 10 atm O₂. The reaction was immediately monitored by ¹H and ³¹P{¹H} NMR. Ten minutes after the addition of O₂, **6**, **7** and **4** were observed in a 1:17.5:22.5 ratio (ca. 82.5% of the initial amount of iridium) as well as, a trace amount of **9** (< 0.5%). After a period of 55 minutes, **6** (62%) was the major product and significant decomposition was observed by the appearance of broad signals composed of multiple resonances in the methylene and *tert*-butyl regions of the ¹H NMR spectrum. Additionally two unassigned singlets at 10.7 and 15.8 ppm were observed by ¹H NMR, for which there are no apparent corresponding resonances in the ³¹P{¹H} NMR spectrum. The amount of this unknown species increases over the course of the reaction to ca. 16% with integration of the resonances to 1H each.

(^tBuPCP)Ir(H)(CCPh) (5**) + 5 atm O₂**

A C₆D₆ (0.35 ml) solution of **5** (6.9 mg, 10.0 μmol) in a medium walled NMR tube fitted with a Teflon seal and a capillary standard of hexamethyldisilane (HMDS) in CD₂Cl₂ was placed under 5 atm O₂. The reaction was promptly monitored by ¹H NMR and formation of **6** (76%) was observed immediately after the addition of O₂, as well as free HCCPh (δ 2.7) (27%). The O₂ was then removed from the solution by multiple freeze-pump-thaw cycles over a 40 minute period, after which complex **7** was observed (79%) and **5** (22%).

Oxidation of PPh₃

Complex **7** (0.003g, 4.8 μmol) and PPh₃ (0.0043g, 16.4 μmol) were weighed into a medium walled NMR tube fitted with a Teflon seal. No oxidation of PPh₃ was observed after 16 hours by ³¹P{¹H} NMR. The reaction was then placed under 5 atmospheres of oxygen pressure, resulting in the formation **6**. After 90 minutes, a ratio of 6:1 PPh₃ to

OPPh₃ was observed by ³¹P{¹H} NMR. Complete conversion was observed after three days and was verified by GC/MS (m/z = 277). PPh₃ was not oxidized in the absence of iridium complex under the same conditions.

X-ray determination of (^tBuPCP)Ir(O₂)₂ (**6**)

X-ray quality crystals of **6** were grown by dissolving **2** (0.005 g, 7.5 μmol) in 0.4 ml of pentane. The solution was filtered through glasswool into a medium walled NMR tube fitted with a Teflon seal. The tube was pressurized to five atmospheres of oxygen and left at 298K for 12 hours after which tan needles were observed.

A suitable crystal for structure determination was selected by methods of polarized light microscopy.⁶ The clear tan-orange specimen, size 0.48 x 0.24 x 0.17 mm³ was found to possess flawless extinction and was mounted on a glass capillary with oil. Data was collected at 130K with Ω and ϕ scans with a Nonius-Bruker Kappa CCD spectrometer using Mo-radiation. After merging with the software package hkl-SCALEPACK,⁷ the R_{int} = 0.0368 indicated that the data was excellent. Indexing and unit cell refinement indicated a tetragonal I lattice. The space group was found to be I $\bar{4}$.

Solution by direct methods (SIR97)⁸ produced a largely incomplete heavy atom phasing model showing motives of the proposed structure. Despite the perfect extinction seen under the microscope, the structure was heavily disordered and possibly micro-twinned.

It appears that the molecules built domain like structures, with the phenyl pointing towards the iridium of the next molecule in a head to tail fashion along the c-axis in one half of the domains, and in the other half of the domains opposite to c, quasi inverted and rotated by 90 degrees. Thus, the disorder, confirmed from test-solving the structure in space group P1, is not due to movements on the molecule, but due to the projection of different molecules in different orientations onto each other when looking through the bulk of the crystal. This leaves an extremely densely populated electron density where the t-butyls of the molecule and the projected ones interweave. Iridium is the common atom

⁶ Kaminsky, W.; Claborn, K.; Kahr, B. *Chem. Rev. Soc.* **2004**, *33*, 514-525.

⁷ Otwinowski, Z.; Minor, W. *Methods in Enzymology* **1996**, *276*, 307-326.

⁸ Altomare, A.; Cascarano, G.; Giacovazzo, C.; Burla, M.C.; Polidori, G.; Camalli, M. (1994) *J. Appl. Cryst.* *27*, 435-442.

in all orientations. The disorder of the t-butyls required restraints on the thermal probability ellipsoids. Starting from an optimized geometry of similar compounds, the t-butyls were first forced into that geometry. In succeeding refinement cycles the bond distance restraints were removed one by one until a stable refinement resulted. The structure is non-centrosymmetric, visible in a tilt of the methylene C5 out of the plane of the phenyl group, which is followed by a small but significant distortion of the whole molecule. No bonds are restrained, however, instead of restraining the thermal parameters strongly, most instabilities were removed when employing the DELU - restraint provided by the refinement program SHELXL97⁹. Here it is assumed that starting with the heaviest atom, Ir, the thermal parameters cannot be totally different along bonds. This way, much more stability of the refinement was achieved with the benefit of fewer restraints with the ISOR restraint that forces thermal parameters to become more spherical. A substantial lowering of the R1 value resulted from applying a tetragonal (90 degree rotation) twinning to the refinement in addition to the observed superposition disorder. The crystal data and structure refinement data can be found in Table S1. X-ray crystallographic information in CIF-format is available free of charge via the Internet at <http://pubs.acs.org>.

⁹ Sheldrick, G.M. (1997) SHELXL97 University of Göttingen, Germany.

Table S1. Crystal data and structure refinement for (^tBuPCP)Ir(O₂)₂ (**6**)

chem. formula	C ₂₄ H ₄₃ Ir O ₄ P ₂
Fw	649.72
crystal system	Tetragonal
space group	$\bar{I}4$
T (K)	130(2)
λ (Å)	0.71073
a (Å)	11.8620(4)
b (Å)	11.8620(4)
c (Å)	9.3140(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	1310.55(8)
Z	2
ρ_{calcd} (Mg/m ³)	1.646
F(000)	652
cryst size (mm)	0.48 × 0.24 × 0.17
θ range (deg)	2.78 ≤ θ ≤ 28.26
index ranges	-15 ≤ h ≤ 15, -10 ≤ k ≤ 10, -12 ≤ l ≤ 10
No. of data/restraints/parameters	1337/97/145
goodness of fit on F ²	1.065
R1 ^a (I > 2 σ (I))	0.0270
wR2 ^b (all data)	0.0662

^a $R1 = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|)$.

^b $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^2)^2]^{1/2}$

IR Data

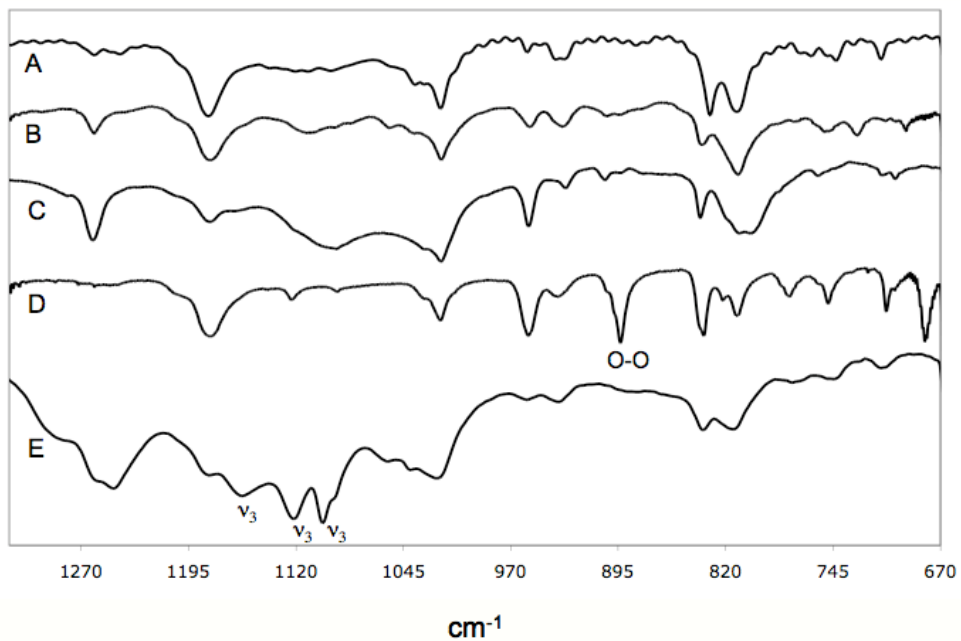


Figure S1. IR spectra of (*t*^{Bu}PCP)Ir(H)(Cl) (A), (*t*^{Bu}PCP)Ir(¹⁸O₂) (B), (*t*^{Bu}PCP)Ir(^{16/18}O₂) (C), (*t*^{Bu}PCP)Ir(¹⁶O₂) (D) and (*t*^{Bu}PCP)Ir(SO₄) (E) taken as KBr pellets.

UV-Vis Data

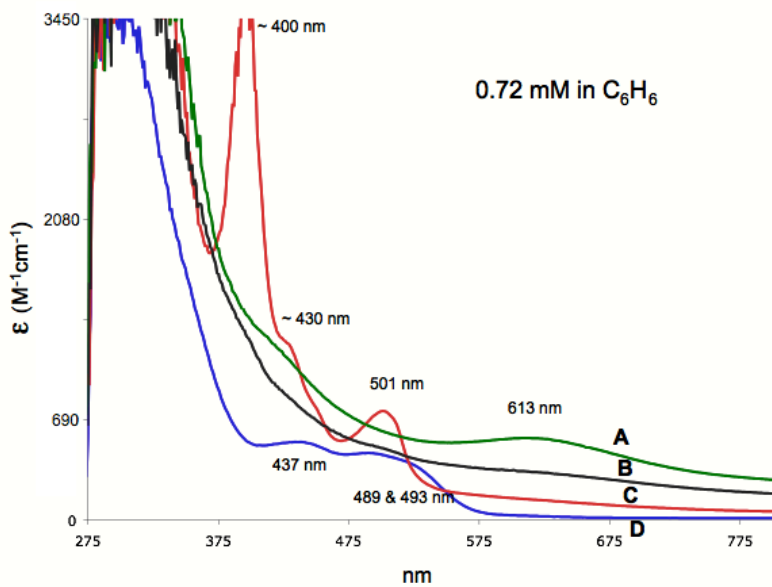


Figure S2. UV-Vis spectra of (*t*^{Bu}PCP)Ir(O₂) (A), (*t*^{Bu}PCP)Ir(O₂)₂ (B), (*t*^{Bu}PCP)Ir(H)(Ph) (C) and (*t*^{Bu}PCP)Ir(H)(Cl) (D).