Reactions of iridium hydride pincer complexes with dioxygen: new dioxygen complexes and reversible O_2 binding†

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Received (in Berkeley, CA, USA) 18th February 2008, Accepted 10th June 2008
First published as an Advance Article on the web 4th August 2008
DOI: 10.1039/b802739k

The reaction of molecular oxygen with iridium pincer hydride complexes, (^{tBu}PCP)Ir(H)(X) [^{tBu}PCP = κ^3-$C_6H_3(CH_2P^tBu_2)_2$, X = Ph, H, CCPh], results in O_2 induced reductive elimination and formation of the novel dioxygen complexes (^{tBu}PCP)Ir$(O_2)_n$ [n = 1 (7), 2 (6)].

Organometallic reactivity is utilized in a range of organic transformations, but homogeneous organometallic oxidation chemistry remains relatively under-developed.[1] Molecular oxygen is the most attractive terminal oxidant for chemical processes in terms of cost, atom economy, and the potential for few byproducts.[1] Recent studies have described elegant palladium catalysts for the aerobic oxidation of alcohols and other substrates, and have implicated mechanisms where O_2 serves to re-oxidize the palladium and does not interact directly with the substrates.[1a] Oxidation of Pd^0 species by O_2 to form Pd^{II} peroxo complexes and insertion of O_2 into Pd^{II}–H bonds have been proposed as oxygen activation steps in these transformations. Both types of reactions have been observed in model Pd systems.[1a,2] Understanding the various modes of reactivity of oxygen with organometallic complexes will be key to developing effective homogeneous catalysis with this oxidant.

Reported here are reactions of O_2 with the iridium pincer hydride complexes (^{tBu}PCP)Ir(H)(X) [X = Cl (**1**),[3a] Ph (**2**),[3b] H (**3**),[3c] OH (**4**)[3d] and CCPh (**5**)[3e]] [^{tBu}PCP = κ^3-$C_6H_3(CH_2P^tBu_2)_2$]. Our long-term goal is to couple O_2-reactivity with the ability of such iridium pincer complexes to catalytically activate C–H bonds in saturated hydrocarbons.[4] The chemistry described here involves loss of H–X and reversible binding of O_2 to form mono- and bis-dioxygen complexes. Reactions of iridium compounds with O_2 to form Ir(O_2) species are well known, originating with Vaska's complex.[5] The products reported here, however, include an unsaturated iridium peroxide[6] and the first late-transition metal bis-dioxygen complex.

The hydride-chloride complex, (^{tBu}PCP)Ir(H)(Cl) (**1**), is unreactive with 1 atm of O_2 (research grade, <0.5 ppm H_2O) in benzene-d_6 over 12 h at 343 K. This is surprising given the unsaturated nature of complex **1**. In contrast, the phenyl-hydride complex **2** reacts rapidly with 1 atm O_2 in benzene solution at 298 K to give two species, **6** and **7**, in addition to small amounts of unidentified products (^{1}H NMR: δ 10.7 (s), 15.8 (s)). Clean separation of **6** or **7** from these impurities has not been achieved, in part because they slowly decompose in solution. Isolated **7**, however, can be stored in the solid state for several months. Both **6** and **7** have ^{1}H and $^{31}P\{^1H\}$ NMR spectra that indicate C_{2v} symmetry, with equivalent phosphorus nuclei, methylene protons and ^{t}Bu groups.[7]

The ratio of **6** to **7** depends on the concentration of oxygen in solution. Under 5 atm O_2 at 25 °C, **1** is converted completely to **6**, and X-ray quality crystals of **6** were grown from pentane under these conditions.†‡ Structure solution was accomplished using a disorder model for the twinned crystals in which molecules stack in one direction along the $\bar{4}$ axis in some

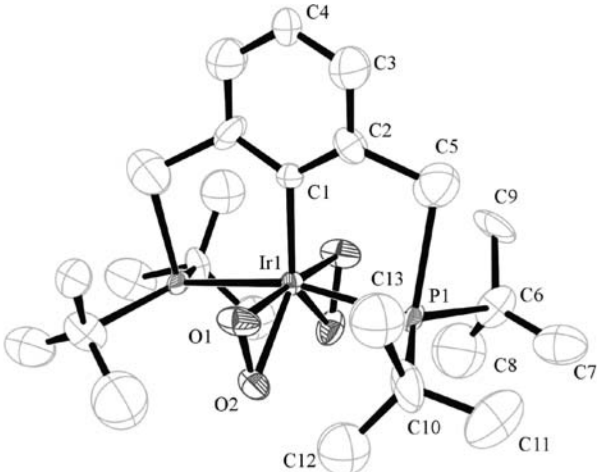

Fig. 1 Molecular structure of (^{tBu}PCP)Ir(η^2-O_2)$_2$ (**6**), with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Ir(1)–O(1) 2.008(10); Ir(1)–O(2) 2.040(9); O(1)–O(2) 1.54(3); Ir(1)–C(1) 2.023(12); Ir(1)–P(1) 2.380(4); O(1)–Ir(1)–C(1) 87.3(8); O(1)–Ir(1)–O(2) 44.7(9); O(2)–O(1)–Ir(1) 68.7(7); O(1)–O(2)–Ir(1) 66.6(7).

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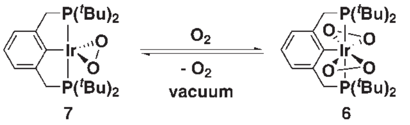
† Electronic supplementary information (ESI) available: Full experimental details and crystallographic data for **6**. CCDC reference number 678650. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b802739k

domains of the $I\bar{4}$ crystals but in the opposite direction in other domains. The connectivity is established, but due to the disorder, the bond lengths are not well defined. The structure of the (pincer)iridium-bis(dioxygen) complex, ($^{t\mathrm{Bu}}$PCP)Ir(η^2-O_2)$_2$ (**6**) is shown in Fig. 1. A similar "trigonal bipyramidal" structure has been reported for an Ir^{III} peroxo ethylene complex.[8] While the refined O–O distance of 1.54(3) Å is comparable to that in iridium peroxo complexes,[5f,9] its limited accuracy prevents any conclusion as to whether **6** is best described as an Ir^{V}-bis(peroxo) complex, an Ir^{III}-bis(superoxo) complex or some combination.

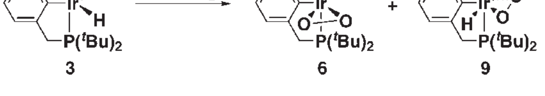
Under vacuum, colorless **6** cleanly forms the bright green **7**, which is assigned as the 5-coordinate mono-peroxo Ir^{III} complex ($^{t\mathrm{Bu}}$PCP)Ir(η^2-O_2) (eqn (1)). Treatment of **7** with O_2 gives **6** by ^{1}H and ^{31}P{^{1}H} NMR, establishing the reversible equilibrium ($K_{eq} \approx 10$ atm^{-1}) in eqn (1).



(1)

The IR spectrum of **7** in a KBr pellet has a band at 893.5 cm^{-1} tentatively assigned as ν(O–O); it is absent in the ^{18}O-labeled complex.[10] Attempts to obtain resonance Raman spectra of **6** have been unsuccessful due to its limited optical absorbance and nominal stability. Characteristic of late-metal peroxo complexes,[11] **7** reacts with SO_2 to give the sulfato complex, ($^{t\mathrm{Bu}}$PCP)Ir(κ^2-SO_4) (**8**), which has been characterized by IR, ^{1}H, and ^{31}P{^{1}H} NMR spectroscopies.[7]

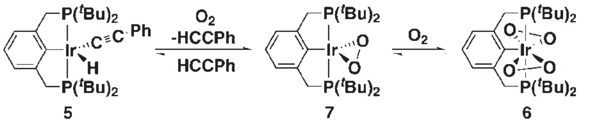
The dihydride complex ($^{t\mathrm{Bu}}$PCP)Ir(H)$_2$ (**3**) reacts with 5 atm O_2 to give a mixture of **6** and a new species **9** in a ratio ~2 : 1 (eqn (2)). Trace amounts of **7** and ($^{t\mathrm{Bu}}$PCP)Ir(H)(OH) (**4**) were also observed. Over time the amount of **9**, **7**, and **4** decreased and ultimately **6** was the sole product observed by ^{1}H and ^{31}P NMR. Complex **4** was identified by comparison with NMR spectra of an authentic sample, particularly the hydride signal at −31.0 ppm.[3d] Independently synthesized **4** was converted by 5 atm of O_2 to cleanly give **6** in *ca.* 30 minutes. Monitoring the reaction of **3** with 1 atm O_2 by ^{1}H NMR showed the appearance and growth of a peak for water, which gradually shifted under the *tert*-butyl signals.



(2)

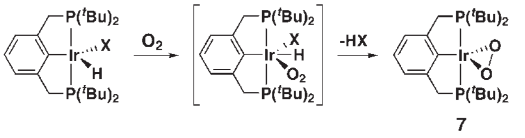
Complex **9** is tentatively assigned as the *trans*-dihydride peroxo complex *trans*-($^{t\mathrm{Bu}}$PCP)Ir(H)$_2$(O_2) based on a hydride signal at −6.8 ppm in the ^{1}H NMR which integrates to two protons relative to the methylene protons of the ligand. This complex appears to be analogous to *trans*-dihydride species ($^{i\mathrm{Pr}}$PCP)Ir(CO)(H)$_2$[12a] [($^{t\mathrm{Bu}}$PNP)Ir(CO)(H)$_2$]PF$_6$,[12b] and ($^{t\mathrm{Bu}}$PNP)Ir(Ph)(H)$_2$[12c] all of which have hydride signals between −6 and −10 ppm.

The acetylide ($^{t\mathrm{Bu}}$PCP)Ir(H)(CCPh) (**5**) also reacted with 5 atm O_2 to very rapidly form **6**. Remarkably, removal of the O_2 by freeze–pump–thaw degassing yielded not only **7**, but also regenerated **5** (22%) (eqn (3)). This reaction indicates that not only can **6** convert to **7** under vacuum, but that the dioxygen ligand of **7** can also apparently be displaced.



(3)

The most likely pathway for the reactions of ($^{t\mathrm{Bu}}$PCP)Ir(H)(X) with oxygen to yield **7** is O_2-induced reductive elimination of HX from ($^{t\mathrm{Bu}}$PCP)Ir(H)(X). O_2-promoted reductive elimination of C–O and C–N bonds from Ni^{II} has been reported.[13] Notably, the dihydride and acetylide complexes, **3** and **5**, do not readily reductively eliminate at 298 K in the absence of O_2,[3e,14] ruling out pre-equilibrium loss of HX followed by O_2 binding to Ir^{I}. The tentative identification of **9** as a dihydride-peroxo complex, in essence an O_2-adduct of **3**, indicates that O_2 coordination may be involved (eqn (4)), although a *cis* isomer would appear more likely to lead to reductive elimination. In an attempt to observe a similar adduct with an iridium hydrocarbyl complex, ($^{t\mathrm{Bu}}$PCP)Ir(H)(tolyl) (**2a**) was reacted with 5 atm of O_2 at 253 K in toluene, but the sole product was **6**, similar to the 298 K reaction between **2** and O_2. The hydrido-chloride complex **1** is inert, presumably because loss of HCl from the metal center is unfavorable.[15] The displacement of O_2 from **7** by HCCPh would be expected to proceed by a similar associative mechanism.

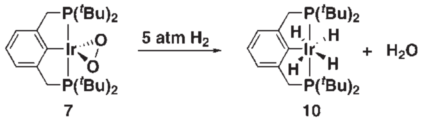


(4)

Thus, in contrast to recent reports of O_2 insertion into metal–hydride bonds,[2,16] the primary reaction observed for the Ir(III) hydrocarbyl hydride species with O_2 is C–H reductive elimination and the eventual formation of an iridium bis(dioxygen) complex without generation of oxygenated organic products. In the reaction of **2** with O_2, neither hydroxyphenyl nor hydrido-phenoxy complexes were observed by ^{1}H NMR spectroscopy, and no phenol was seen by GC. However, the formation of some Ir^{III} hydrido hydroxide **4** in the reaction of **3** with O_2 indicates that oxygen insertion may be possible in this system.

The peroxo complexes themselves are not especially reactive. For instance, they are inert to ethylene and cyclohexene. Complex **6** is a slow catalyst for the oxidation of PPh_3 to $OPPh_3$ by O_2, giving 3.4 turnovers over three days under 5 atm of O_2 in C_6D_6 (by ^{1}H NMR and GC/MS). Surprisingly, the mono-peroxo complex **7** does not oxidize PPh_3, perhaps due to the instability of an intermediate oxo complex. Treatment of isolated **7** with 5 atm H_2 gives the tetrahydride **10** (eqn (5)), which can also be readily formed by addition of H_2 to **3**.

Similarly, **7** + D_2 yields ($^{t\mathrm{Bu}}$PCP)Ir(D)$_4$ (**10**-d_4) and D_2O (by ^{2}H NMR).



(5)

In summary, a number of iridium pincer hydride compounds ($^{t\mathrm{Bu}}$PCP)Ir(H)(X) were found to react with O_2 to give iridium complexes with one or two bound dioxygen molecules, ($^{t\mathrm{Bu}}$PCP)Ir(O_2)$_n$, n = 1 (**7**), or 2 (**6**). Dioxygen in most cases appears to promote reductive elimination of HX rather than inserting into an Ir–H or Ir–C bond. Yet the peroxo complex **7** reacts with hydrogen to form water and the tetrahydride complex **10**. This type of reaction could be a potential alternative to more traditional hydrogen scavengers such as *t*-butylethylene. Studies are continuing in order to more fully develop the organometallic chemistry of O_2 and understand the basic pathways for reactions of O_2 with organometallic compounds.

Support from the NSF Center for Enabling New Technologies through Catalysis (CENTC), Grant No.'s 0650456 & 0434568, is gratefully acknowledged. We thank J. R. Frisch and L. Que, Jr. for their efforts to obtain Raman spectra of **6** and **7**, and A. S. Goldman and M. Kanzelberger for helpful discussions.

Notes and references

‡ Caution should always be taken when working with organic solvents under pressures of O_2.

1 (*a*) S. S. Stahl, *Angew. Chem., Int. Ed.*, 2004, **43**, 3400; (*b*) R. Sheldon and J. K. Kochi, *Metal Catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (*c*) *Dioxygen Activation and Homogeneous Catalytic Oxidation*, ed. L. I. Simándi, Elsevier, New York, 1991; (*d*) B. R. Dible and M. S. Sigman, *J. Am. Chem. Soc.*, 2003, **125**, 872; (*e*) S. S. Stahl, *Science*, 2005, **309**, 1824.

2 (*a*) M. C. Denney, N. A. Smythe, K. L. Cetto, R. A. Kemp and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 2508; (*b*) M. M. Konnick and S. S. Stahl, *J. Am. Chem. Soc.*, 2008, **130**, 5733.

3 (*a*) C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020; (*b*) I. Göttker-Schnetmann, P. S. White and M. Brookhart, *Organometallics*, 2004, **23**, 1766; (*c*) M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer and C. M. Jensen, *J. Am. Chem. Soc.*, 1997, **119**, 840; (*d*) D. Morales-Morales, D. W. Lee, Z. Wang and C. M. Jensen, *Organometallics*, 2001, **20**, 1144; (*e*) R. Ghosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2007, **129**, 853.

4 (*a*) M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083; (*b*) F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, 1999, **121**, 4086.

5 (*a*) L. Vaska, *Science*, 1963, **140**, 809; (*b*) D. M. Roundhill, G. H. Allen, R. A. Bechtold and W. B. Beaulieu, *Inorg. Chim. Acta*, 1981, **54**, L99; (*c*) S. Gopinathan, K. Joseph and C. Gopinathan, *Polyhedron*, 1985, **4**, 955; (*d*) H. J. Lawson and J. D. Atwood, *J. Am. Chem. Soc.*, 1989, **111**, 6223; (*e*) C. Bianchini, A. Meli, M. Peruzzini and F. Vizza, *J. Am. Chem. Soc.*, 1990, **112**, 6726; (*f*) P. Barbaro, C. Bianchini, F. Laschi, S. Midollini, S. Moneti, G. Scapacci and P. Zanello, *Inorg. Chem.*, 1994, **33**, 1622.

6 (*a*) Only one 5-coordinate iridium peroxo complex has been reported, in the supporting information of B. DeBoef, S. J. Pastine and D. Sames, *J. Am. Chem. Soc.*, 2004, **126**, 6556; (*b*) For examples of unsaturated Rh(O_2) complexes, see J. M. Praetorius, D. P. Allen, R. Wang, J. D. Webb, F. Grein, P. Kennepohl and C. M. Crudden, *J. Am. Chem. Soc.*, 2008, **130**, 3724 and references therein.

7 See ESI for full experimental and structural details†.

8 B. de Bruin, T. P. J. Peters, J. B. M. Wilting, S. Thewissen, J. M. M. Smits and A. W. Gal, *Eur. J. Inorg. Chem.*, 2002, **10**, 2671.

9 (*a*) M. J. Nolte, E. Singleton and M. Laing, *J. Am. Chem. Soc.*, 1975, **97**, 6396; (*b*) A. Mezzetti, V. Novelli, A. Del Zotto and P. Rigo, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **43**, 425; (*c*) J.-C. Wang, L.-Y. Chou and W.-Y. Hsien, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 879; (*d*) H. Lebel, C. Ladjel, F. Bélanger-Gariépy and F. Schaper, *J. Organomet. Chem.*, 2008, **693**, 2645.

10 The calculated $\nu(^{18}O–^{18}O)$ of 842 cm^{-1} [from $\nu = (1/2\pi)(k_{ab}/\mu_{ab})^{1/2}$], overlaps with ligand stretches and the IR spectrum of a mixed labeled, $^{16/18}O_2$, sample of **7** was broad and inconclusive[7].

11 J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235.

12 (*a*) B. Rybtchinski, Y. Ben-David and D. Milstein, *Organometallics*, 1997, **16**, 3786; (*b*) S. M. Kloek, D. M. Heinekey and K. I. Goldberg, *Organometallics*, 2006, **25**, 3007; (*c*) E. Ben-Ari, G. Leitus, L. J. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2006, **128**, 15390.

13 (*a*) R. Han and G. L. Hillhouse, *J. Am. Chem. Soc.*, 1997, **119**, 8135; (*b*) B. L. Lin, C. R. Clough and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2002, **124**, 2890.

14 K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord and A. S. Goldman, *J. Am. Chem. Soc.*, 2002, **124**, 11404.

15 There was no evidence for an O_2 adduct of **1** by NMR under 2.6 atm O_2 at 200 K in toluene-d_8. In addition, no initial reaction was observed in a benzene solution of **1** and O_2 (5 atm) in the presence of N^{i}Pr$_2$Et, which should trap any HCl. Multiple, unidentifiable products were present after a couple of days, but neither **6** nor **7** was observed.

16 (*a*) T. T. Wenzel, *Stud. Surf. Sci. Catal.*, 1991, **66**, 545; (*b*) D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, 1999, **121**, 11900; (*c*) A. Bakac, *J. Photochem. Photobiol., A*, 2000, **132**, 87; (*d*) S. Thyagarajan, C. C. Incarvito, A. L. Rheingold and K. H. Theopold, *Chem. Commun.*, 2001, 2198.