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O_2 Activation by Metal–Ligand Cooperation with Ir^I PNP Pincer Complexes

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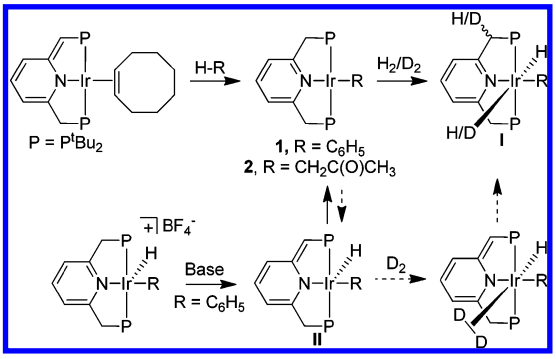
Supporting Information

ABSTRACT: A unique mode of molecular oxygen activation, involving metal–ligand cooperation, is described. Ir pincer complexes [(^{t}BuPNP)Ir(R)] (R = C_6H_5 (**1**), CH_2COCH_3 (**2**)) react with O_2 to form the dearomatized hydroxo complexes [(^{t}BuPNP*)Ir(R)(OH)] (^{t}BuPNP* = deprotonated ^{t}BuPNP ligand), in a process which utilizes both O-atoms. Experimental evidence, including NMR, EPR, and mass analyses, indicates a binuclear mechanism involving an O-atom transfer by a peroxo intermediate.

Although molecular oxygen is the most environmentally benign, abundant, and inexpensive oxidant, it has limited synthetic use due to over-oxidation and lack of selectivity. The use of organometallic catalysts with O_2 for selective oxidation of hydrocarbons is a growing field,[1] pioneered by Hay[2] and Shilov.[3] The active species in the catalytic oxidation are superoxo or hydroperoxo complexes, although these are rarely directly observed. While Fe^{III}–superoxo heme centers are well characterized, few examples of non-heme Fe^{III}–superoxo[4] or other late transition metal–superoxo complexes[5] are reported. Hydroperoxo complexes can be obtained by O_2 insertion into M–H bonds, and several mechanisms were reported, such as radical chain processes with Pt^{IV}–H[6] and Rh^{III}–H,[7] or H-atom abstraction by O_2 with Pd^{II}–H,[8] Ir^{III}–H,[9] and Rh^{III}–H.[10] Complexes of Pd^{II} hydrides react with O_2 also via Pd^0 intermediates by oxidative addition of O_2 followed by protonolysis to give hydroperoxides.[11] Oxidative addition of O_2 by Pt^{II} [12] and Pd^{II},[13] and protonolysis of the corresponding peroxo complexes, are also known. O_2 insertion into metal–alkyl bonds was reported to take place via a radical chain mechanism for Pd–Me^{II} [14] and Pt–Me^{II} [15] complexes. Recently, O_2 insertion into photogenerated dinuclear Pd and Pt methyl intermediates was reported.[16] Here we present a novel mode of O_2 activation by an Ir pincer complex to give a dearomatized hydroxo complex via metal–ligand cooperation (MLC).

In recent years our group has developed a new mode of MLC, involving aromatization/dearomatization of pyridine-based pincer complexes, including ^{R}PNP and PNN (R = ^{t}Bu, ^{i}Pr) pincer ligands, as well as bipyridine- and acridine-based pincer ligands.[17] This new mode of reactivity enables novel activation of H–H,[18] C–H (sp^2 and sp^3),[18a,19] O–H,[20] S–H,[20b,21] N–H,[20b,22] and B–H[23] bonds, and it is a key step in environmentally benign catalysis.[17g] Recently we have also reported on reversible C–C bond formation via MLC between the exocyclic methine carbon of our dearomatized pincer complexes and CO_2,[24] aldehydes,[25] and nitriles.[26] Activation of Csp^2–H and Csp^3–H bonds was demonstrated by the dearomatized pincer complex [(^{t}BuPNP*)Ir(COE)] (^{t}BuPNP* = deprotonated ^{t}BuPNP ligand), which reacts with benzene and acetone to give the aromatic complexes [(^{t}BuPNP)Ir(R)] (R = C_6H_5 (**1**)[18a] and CH_2COCH_3 (**2**),[18b] respectively), with no overall change in the formal metal oxidation state (Scheme 1). Complexes **1** and **2** react with H_2 to give exclusively the *trans* dihydride complexes, and upon reaction with D_2 the *trans* hydride–deuteride complexes [(^{t}BuPNP)Ir(H)(D)(R)] (**I**), with one D-atom incorporated into a benzylic position, are obtained (Scheme 1).[18a,b] DFT calculations suggest that H_2 activation actually takes place by Ir^{III} dearomatized intermediates [(^{t}BuPNP*)Ir(H)(R)] (**II**), which are in equilibrium with the aromatic Ir^I complexes [(^{t}BuPNP)Ir(R)] (**1**, **2**).[18b,27] Although such equilibria were not directly observed, **II** (R = C_6H_5) was observed as the kinetic product of deprotonation of the cationic [(^{t}BuPNP)Ir(H)(C_6H_5)][BF_4] at −78 °C and was trapped by CO to give the dearomatized complex [(^{t}BuPNP*)Ir(CO)(H)(C_6H_5)].[18a]

Scheme 1. Csp^2–H, Csp^3–H, and H_2 Activation with PNP-Ir Complexes via MLC



Significantly, **1** and **2** react rapidly with 0.5 equiv of O_2 at room temperature to give the dearomatized hydroxo complexes [(^{t}BuPNP*)Ir(OH)R] (**3**, R = C_6H_5; **4**, R = $CH_2C(O)CH_3$) (Scheme 2).[28] **3** and **4** exhibit an AB splitting pattern, indicating two non-equivalent P-atoms. The deprotonated "arm" of **3** and **4** gives rise to a doublet signal at 3.76 and 3.60 ppm, respectively, in the ^{1}H NMR spectrum, corresponding to one proton, and a CH doublet signal at 61 ± 1 ppm ($^1J_{PC}$ = 63 ± 1 Hz) in the

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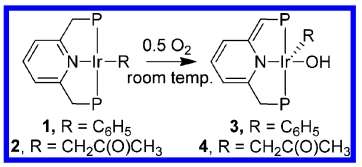
Scheme 2. O_2 Activation by Complexes 1 and 2



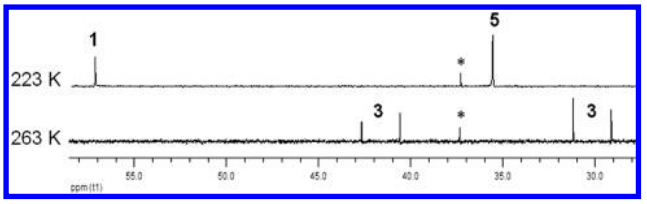


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR of the reaction of [(PNP)Ir(C_6H_5)] (**1**) with O_2 to give [(PNP)Ir(C_6H_5)(O_2)] (**5**) and [(PNP*)Ir(C_6H_5)(OH)] (**3**). The signal marked with an asterisk is from an unidentified impurity.

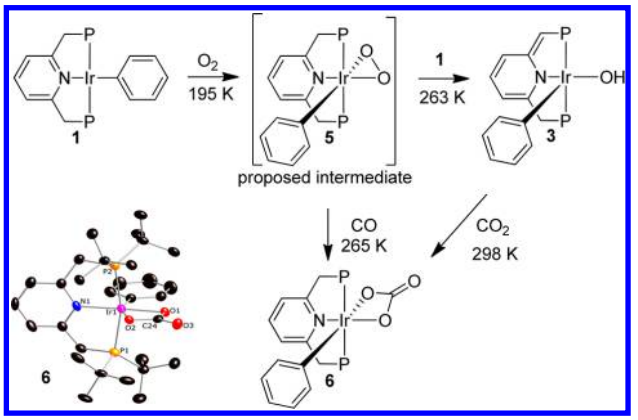
^{13}CQDEPT spectra. The hydroxo ligand gives rise to a broad signal at −3.5 ppm. NOESY correlation between an *ortho* proton of the phenyl ligand and a CH−P proton support an apical position for the phenyl ligand in **3**, as expected on the basis of *trans* influence considerations.

While **3** is stable and could be isolated, **4** is unstable at room temperature, and after 1 h a mixture of unidentified complexes was observed in the $^{31}P\{^1H\}$ NMR. The difference in stability of **3** and **4** is in accordance with the reported reactivity of **1** and **2**. While **1** reacts with CO to give a stable Ir^{III} complex [(^{t}BuPNP*)Ir(CO)(H)(C_6H_5)], **2** reacts with CO to give free acetone and a dearomatized Ir^I carbonyl complex [(^{t}BuPNP*)-Ir(CO)].[18b] In addition, **2** reacts with benzene at 80 °C to give **1**, while heating **1** with C_6D_6 did not result in aryl exchange.

Since **4** is not stable, all experiments regarding the reaction mechanism were conducted with **1**. Complex **3** was rapidly obtained both in the dark and under ambient light. In addition, **3** was also obtained in the presence of phosphines (PEt_3, PPh_3) which were unreactive. When the reaction was repeated in the presence of a radical scavenger (30 equiv of BHT or 10 equiv of PBN; BHT = 3,5-di-*tert*-butyl-4-hydroxytoluene, PBN = *α*-phenyl *N*-*tert*-butylnitrone), no retardation was observed, ruling out a radical chain mechanism for the O_2 activation.

Adding 0.5 equiv of O_2 to **1** at 195 K formed a new complex (**5**), as observed by NMR spectroscopy (Figure 1), in ∼50% yield (by integration). Upon heating the reaction mixture to 263 K, **3** was obtained in 85% yield. Complex **5** exhibits a singlet in the $^{31}P\{^1H\}$ NMR spectrum at 223 K, consistent with chemically equivalent phosphines. The CH_2−P benzylic protons give rise to two broad signals at 3.5 and 3.8 ppm, implying the loss of the C_{2v} symmetry present in **1**. According to the NMR data, we believe that **5** is a peroxo complex (Scheme 3).[29] In support of this assumption, adding CO to **5** at 220 K formed the new carbonate complex **6** upon warming the reaction mixture to 265 K. **6** was fully characterized by NMR and X-ray crystallography (Scheme 3). $^{31}P\{^1H\}$ NMR of **6** reveals a sharp singlet at 9.60 ppm, indicating equivalent phosphines. The CH_2−P benzylic protons give rise to a four-proton AB signal in the ^{1}H NMR, and the carbonate carbon gives rise to a singlet at 166.46 ppm. NOESY correlation between the benzylic CH_2−P protons and an *ortho* proton of the phenyl ligand is consistent with an apical position of the phenyl ligand, as described for **3** and in accordance with the X-ray structure. Examples of CO insertion into the O−O

Scheme 3. Reaction Pathway of Complex 1 with O_2 and Formation of Complex 6 from CO or CO_2, and X-ray Structure of 6 at 50% Probability[a]



[a]H-atoms are omitted for clarity. See SI for a full description of the structure of **6**.

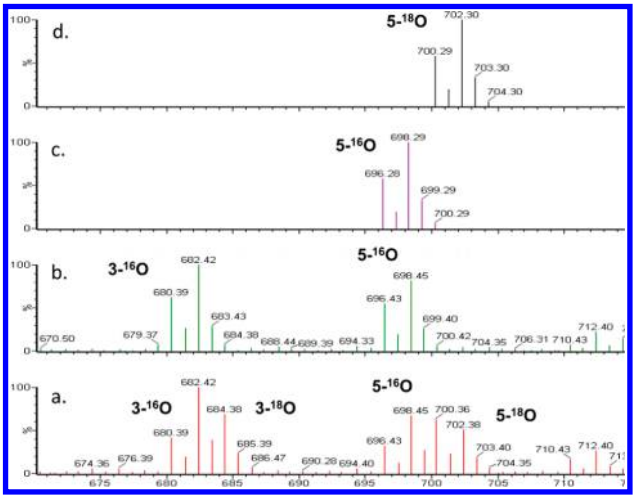


Figure 2. ESI-MS spectrum of the reaction mixture of **1** with (a) $^{18}O_2$ and (b) $^{16}O_2$ just after the addition. (c) and (d) are simulated isotopic patterns of **5** with $^{16}O_2$ and $^{18}O_2$, respectively.

bond of peroxo complexes to yield carbonate complexes such as **6** were reported.[30] **6** was obtained also by reacting **3** with CO_2 (Scheme 3). It is likely that **6** was formed from **3** via CO_2 insertion into the Ir−OH bond, yielding a bicarbonate intermediate, which protonated the exocyclic double bond of the dearomatized ligand to give an aromatic carbonate complex. Similar CO_2 insertions into Ir−OH[31] and Pt−OH[32] bonds to yield carbonate complexes and water were reported recently. The existence of a peroxo intermediate was also confirmed by mass and EPR spectroscopy. Electrospray ionization mass spectrometry (ESI-MS) of **1** just after it was exposed to $^{16}O_2$ or $^{18}O_2$ revealed an isotopic pattern that can be assigned to the proposed intermediate **5** (Figure 2). These isotopic patterns were not observed in analysis of the same reaction mixtures after ca. 30 min. Two other possible intermediates, the dearomatized hydroperoxo (**5a**) and the superoxo (**5b**), share the same mass as **5** and are indistinguishable by ESI-MS (Scheme 4).

An EPR spectrum of the reaction mixture of **1** and O_2 in the presence of the radical trap PBN reveals formation of a spin adduct with g = 2.0067, a_N = 13.50 G, and a_H = 1.90 G, obtained

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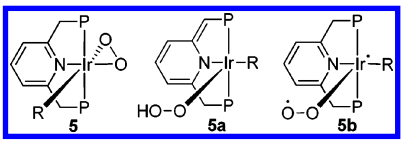
Scheme 4. Possible Isomeric Structures of the Intermediate Detected by ESI-MS



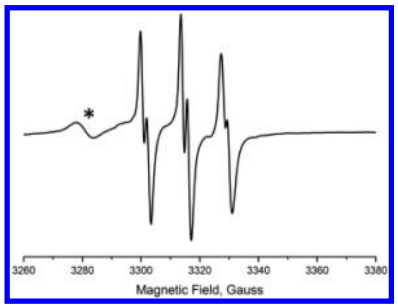


Figure 3. EPR spectrum of a toluene solution of **1**, PBN (10 equiv), and O_2 (0.5 equiv). The signal marked with an asterisk was observed for **1** with O_2 (see SI).

by simulation of experimental EPR spectra, in accordance with the reported values of peroxo PBN adducts (Figure 3).[33,34]

Following the reaction of **1** with O_2 by NMR and EPR, one or more unidentified paramagnetic species were observed. In the ^{1}H NMR, characteristic broad paramagnetic species at 12 and 14 ppm were observed immediately after O_2 addition and disappeared after 30 min. These paramagnetic signals were observed only above 253 K. In accordance, a broad EPR signal appeared at room temperature just after O_2 addition and disappeared after 30 min. Since the reaction of **1** with O_2 to give **3** is immediate, and the paramagnetic species were obtained along with the final complex, it is likely that the paramagnetic species are unstable byproducts. Moreover, the initial yield of **3** (~85%) did not change with time, as shown by ^{1}H and ^{31}P{^{1}H} NMR spectra using internal standards. Reacting **1** with >0.5 equiv of O_2 formed several unidentified complexes (see SI) along with **3** in various yields, depending on the amount of O_2. When **1** was exposed to an excess of O_2 (2 and 6.4 equiv) at 195 K, only **5** was observed by NMR. Heating the reaction mixture with excess of O_2 to 263 K formed **3** and the unidentified complexes.

The observation that mixing **5** and **1** in a 1:1 ratio exclusively forms **3** indicates an intermolecular mechanism, in which a possible intermediate peroxo species (**5**) transfers an O-atom to an unreacted complex (**1**) to give two identical hydroxo complexes (**3**). This is in line with a crossover experiment in which **1-*d***[18a] was reacted with 0.5 equiv of O_2 at 195 K to give the labeled intermediate **5-*d***. Subsequently adding an approximately equimolar solution of **1** at 195 K, and warming the reaction mixture to ambient temperature, yielded a mixture of **3-*d*** and **3**.[35]

A similar mechanism, in which peroxo intermediates are protonated to hydroperoxo intermediates, followed by comproportionation with an unreacted starting complex to give two identical molecules of hydroxo complexes, was reported previously. For example, Bercaw reported oxidation of (tmeda)-$Pt^{II}Me_2$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) by O_2 in methanol to give (tmeda)$Pt^{IV}Me_2$(OMe)(OH).[12a] The proposed mechanism involves the reduction of O_2 in two consecutive two-electron steps, first forming a hydroperoxo complex in the presence of methanol as a proton source. The hydroperoxo oxidizes the unreacted Pt^{II} complex to give 2 equiv of the final product.

Vedernikov also described a bimolecular mechanism for oxygen transfer from a hydroxoperoxo (dpms)Pt^{IV} intermediate to (dpms)Pt^{II}(Me)(OH_n) (n = 1−2, dpms = di(2-pyridyl)-methanesulfonate) to give 2 equiv of (dpms)Pt^{II}(Me)$(OH)_2$ in the pH range of 4−12.[12c,d] Mirica described the formation of hydroperoxide Pd^{IV} intermediates in the presence of proton donors, which further react with the starting complex to give hydroxo Pd^{IV} complexes.[13] Recently Goldberg reported the oxidation of a Pd^0 complex by O_2 to give a Pd^{II} hydroxide dimer; experimental and computational studies support a mechanism involving formation of an (η^2-peroxo)Pd^{II} species, which facilitates C−H bond cleavage, leading to protonation of the peroxo.[36] In the reaction presented herein, the proton source for formation of the hydroxo ligand is a benzylic proton of the PNP ligand, resulting in a dearomatized hydroxo complex.

In summary, we have presented a new mode of O_2 activation, involving metal−ligand cooperation. Complexes [(^{t}BuPNP)Ir-(R)] (R = C_6H_5 (**1**), CH_2COCH_3 (**2**)) readily activate O_2 to yield the hydroxo complexes [(^{t}BuPNP*)Ir(R)(OH)] with ligand dearomatization. Experimental evidence, including NMR, EPR, mass analysis, and CO trapping, indicates a binuclear mechanism involving an O-atom transfer by a peroxo intermediate, while the PNP ligand serves as a proton source, eventually forming a dearomatized hydroxo complex, although the details of the bimolecular process are unclear at this stage. Since aromatization/dearomatization MLC processes of pincer complexes can play key roles in catalysis, we are now exploring the catalytic potential of O_2 activation by MLC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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