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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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# $O_2$ Activation by Metal–Ligand Cooperation with $Ir^I$ PNP Pincer Complexes

Moran Feller,*[,†] Eyal Ben-Ari,[†] Yael Diskin-Posner,[‡] Raanan Carmieli,[‡] Lev Weiner,[‡] and David Milstein*[,†]

Departments of [†]Organic Chemistry and [‡]Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

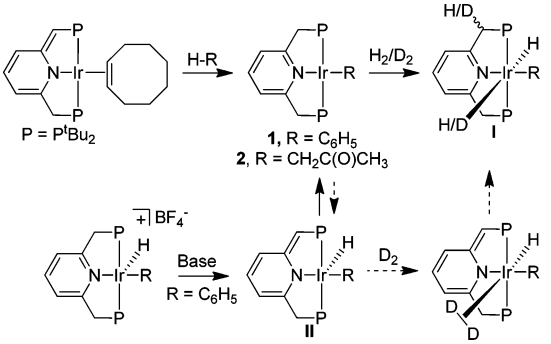
Supporting Information

**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

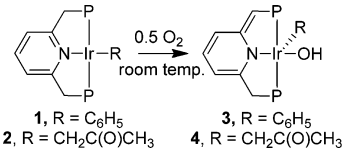
**Received:** February 12, 2015
**Published:** April 1, 2015





DOI: 10.1021/jacs.5b01585
J. Am. Chem. Soc. 2015, 137, 4634–4637

**Scheme 2. $O_2$ Activation by Complexes 1 and 2**



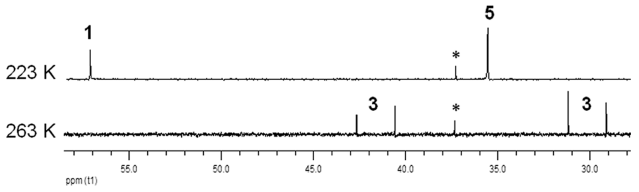




**Figure 1.** Variable-temperature $^{31}P\{^1H\}$ NMR of the reaction of [(PNP)Ir($C_6H_5$)] (**1**) with $O_2$ to give [(PNP)Ir($C_6H_5$)($O_2$)] (**5**) and [(PNP*)Ir($C_6H_5$)(OH)] (**3**). The signal marked with an asterisk is from an unidentified impurity.

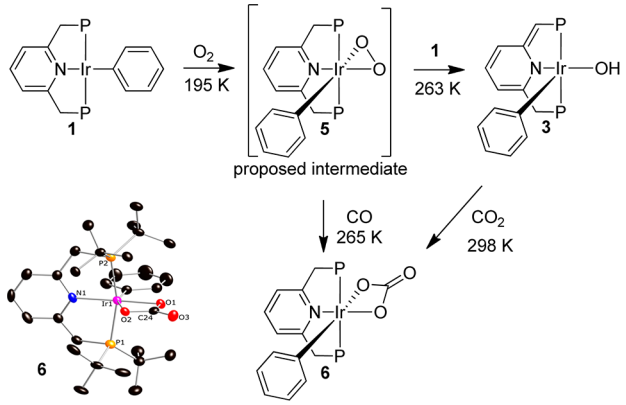
$^{13}$CQDEPT spectra. The hydroxo ligand gives rise to a broad signal at −3.5 ppm. NOESY correlation between an *ortho* proton of the phenyl ligand and a CH−P proton support an apical position for the phenyl ligand in **3**, as expected on the basis of *trans* influence considerations.

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**.

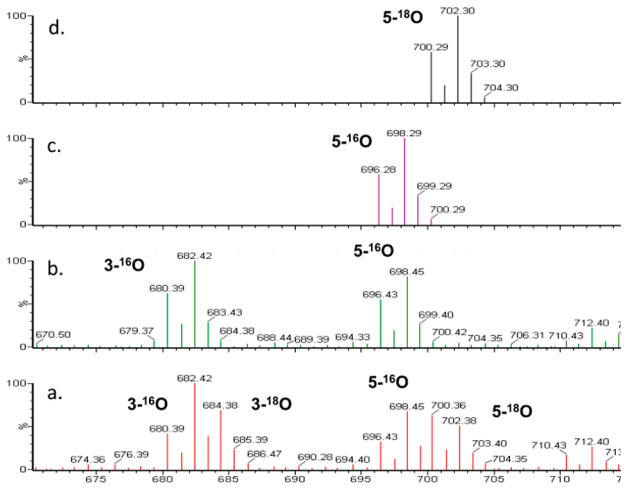


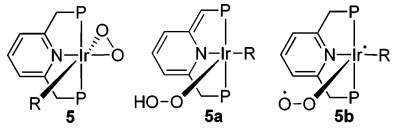

**Figure 2.** ESI-MS spectrum of the reaction mixture of **1** with (a) $^{18}O_2$ and (b) $^{16}O_2$ just after the addition. (c) and (d) are simulated isotopic patterns of **5** with $^{16}O_2$ and $^{18}O_2$, respectively.

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


DOI: 10.1021/jacs.5b01585
J. Am. Chem. Soc. 2015, 137, 4634−4637

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



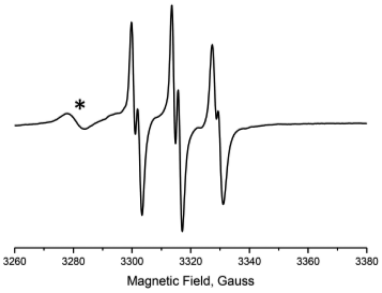




**Figure 3.** EPR spectrum of a toluene solution of **1**, PBN (10 equiv), and $O_2$ (0.5 equiv). The signal marked with an asterisk was observed for **1** with $O_2$ (see SI).

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 ($\eta^2$-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.

## ■ AUTHOR INFORMATION

### Corresponding Author

*moran.feller@weizmann.ac.il; david.milstein@weizmann.ac.il

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported by the European Research Council under the FP7 framework (ERC No. 246837) and by the Israel Science Foundation. We thank Prof. Karen I. Goldberg and Dr. Margaret L. Scheuermann for helpful discussions.

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DOI: 10.1021/jacs.5b01585
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(35) This crossover experiment is not necessarily conclusive since $O_2$ binding by **5** may be reversible. Although reversibility was not observed directly, the fact that **5**, in the absence of **1**, yields **3** at 263 K (although together with several unidentified complexes) may support this assumption.
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DOI: 10.1021/jacs.5b01585
*J. Am. Chem. Soc.* 2015, 137, 4634−4637