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Communications

A Rare η^3 Binding Mode of Aryloxides in Iridium, Rhodium, and Ruthenium Complexes

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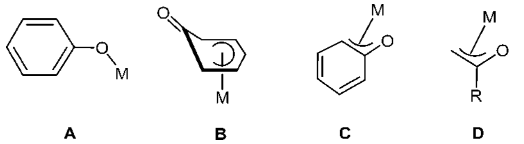
Summary: A rare η^3 binding mode of aryloxides was obtained in the reaction of BINOL and $[Cp^*IrCl_2]_2$. Interconversions between and η^1 and η^3 modes of aryloxides were observed by VT NMR spectroscopy, and the activation barrier was measured. The preference of this binding mode as a function of phenols was discussed.

Aryloxides are widely used as ligands to stabilize both early and late transition metals. Aryloxide complexes are also key intermediates in metal-catalyzed C−O bond formation reactions of phenols.[1] Almost invariably, the aryloxide functionality is O-bound (A, Chart 1), although the η^5 binding mode (B, Chart 1) is occasionally adopted.[2] Moreover, as special biphenols, enantiopure BINOLs have been extensively used in metal-catalyzed asymmetric catalysis to entail highly efficient and enantioselective C−C coupling, olefin metathesis, and heteroatom transfer reactions.[3] Interestingly, Gagne and co-workers reported a rare O,C binding mode of a BINOLate which is in equilibrium with the classic O,O′ fashion (Scheme 1).[4] In this equilibrium, a BINOLate complex in η^1(O):η^3(C,C,O) mode was proposed as an intermediate (Scheme 1).[4] However, to the best of our knowledge, no complexes of aryloxides in the η^3(C,C,O) binding mode (C, Chart 1) have been isolated and characterized, although the relevant η^3-enolate (η^3-oxaallyl, D) complexes are known.[5] We now report the synthesis, structures, and solution dynamics of rare BINOLate complexes of iridium, rhodium, and ruthenium, where the BINOLate consists of interconvertible η^1- and η^3-naphthanolate units. The BINOLate ligand behaves as a six-electron donor, and this coordination mode will likely provide new opportunities for catalyst design.

Chart 1. Binding Modes of Aryloxides and Enolates



The surprising scarcity of iridium BINOLate complexes inspired us to carry out further investigations.[6] Stirring a suspension of (*R*)-BINOL, $[Cp^*IrCl_2]_2$, and Cs_2CO_3 in CH_2Cl_2 quickly led to the formation of **1a**, and it was isolated in 92% yield (Scheme 2). The isostructural rhodium(III) (**1c**) and the ruthenium η^6-(*p*-cymene) complexes **2** could also be obtained in high yields (Scheme 2). All these complexes have been fully characterized by NMR spectroscopy and elemental analysis.

The identities of complexes **1a**,**c** were further confirmed by X-ray crystallography (Figure 1).[7] The BINOLate ligand in **1a** consists of a classic η^1-naphthanolate and an unusual η^3(*C*,*C*,*O*)-naphthanolate moiety. In comparison with the corresponding bond lengths in typical iridium η^3-allyl complexes, the Ir(1)−C(11) (2.254(7) Å) and Ir(1)−C(12) (2.204(7) Å) bonds in the η^3-aryloxide entity are slightly longer.[8]The Ir(1)−O(2) bond (2.187(5) Å) is significantly longer than the Ir(1)−O(1) bond (2.045(5) Å), while the C(12)−O(2) distance (1.306(9) Å) is slightly shorter than that of C(1)−O(1) (1.332(8) Å)

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(7) The asymmetric unit of **1a**,**c** contains two independent molecules with slightly different bond lengths and angles, and only one of them is discussed here. See the Supporting Information for details.

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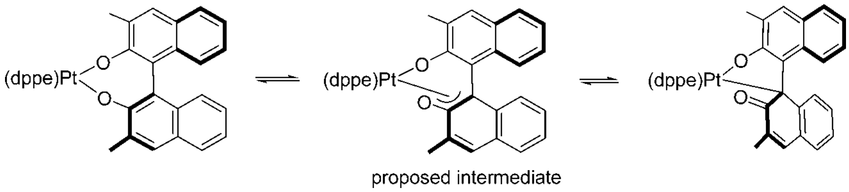
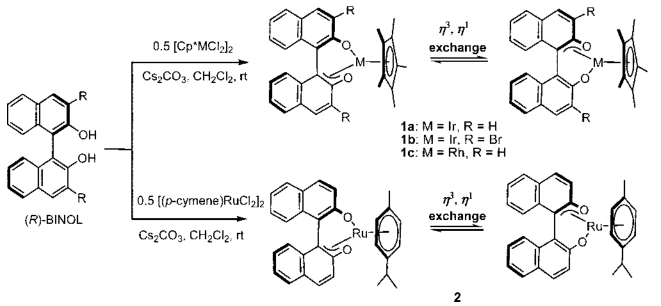
Scheme 1. η^3-BINOLate Complex Proposed as an Intermediate[4]



Scheme 2. Synthesis of η^3-Naphthanolate Complexes



(Figure 1 and the Supporting Information). To accommodate this η^3-aryloxide binding mode, C(11) is essentially sp^3-hybridized, which disrupts the aromaticity of the C(11)-containing ring. The Rh$-\eta^3$-aryloxide interaction seems weaker in **1c**, as evidenced by the longer Rh$-$C(11) bond (2.290(3) Å). This rare η^3 binding mode of aryloxides is reminiscent of that known for benzyl and arylamide complexes.[9] It is also reminiscent of Ru-BINAP complexes in which the naphthyl backbone interacts with the metal.[10] Moreover, only one example of arylthiolates in this binding mode has been reported (for uranium complexes).[11]

^{1}H and ^{13}C NMR spectra (CD_2Cl_2) of complex **1a** at room temperature all point to a C_2-symmetrical structure, as evidenced by 10 aromatic resonance signals in the ^{13}C NMR spectrum. Among these 10 aromatic ^{13}C signals, 2 quaternary ones (δ 156.5 and 103.8) are noticeably broadened, suggesting that complex **1a** is fluxional on the NMR time scale. The inconsistency between the solid state (C_1 symmetrical) and the solution (C_2 symmetrical) structures can be reconciled by the reversible η^1 to η^3 slippages of the two naphthanolate units proposed in Scheme 2. This process results in a degenerate intramolecular substitution reaction, since the two structures involved in this dynamic process are chemically identical (Scheme 2). This exchange process likely proceed via a dissociative mechanism, where the η^3-aryloxide slips to the η^1 form to give a 16-electron intermediate, followed by the slippage of the original η^1-aryloxide to the η^3 mode. Decoalescence of the 10 aromatic carbon signals to 20 sharp ones was observed at -78 °C in the ^{13}C NMR spectrum (CD_2Cl_2). In particular, the broad peak at δ 156.5 at 35 °C transformed to δ 172.7 (C(1)) and 142.3 (C(12)) at -78 °C and the other broad peak at δ 103.8 transformed to δ 117.7 (C(10)0 and 88.7 (C(11)). DFT calculations of the ^{13}C NMR spectrum of **1a** were then carried out at the BL3YP level to further support the above assignment, and there is reasonably good agreement between experimental and theoretical data.[12] Similarly, fluxionality on the NMR time scale was also observed for rhodium complex **1c**, and most aromatic ^{13}C signals (100 MHz, CD_2Cl_2) are still broadened ($W_{1/2} \approx 14$ Hz) even at -90 °C so that no ^{103}Rh$-^{13}$C coupling could be detected for C(11) or C(12).

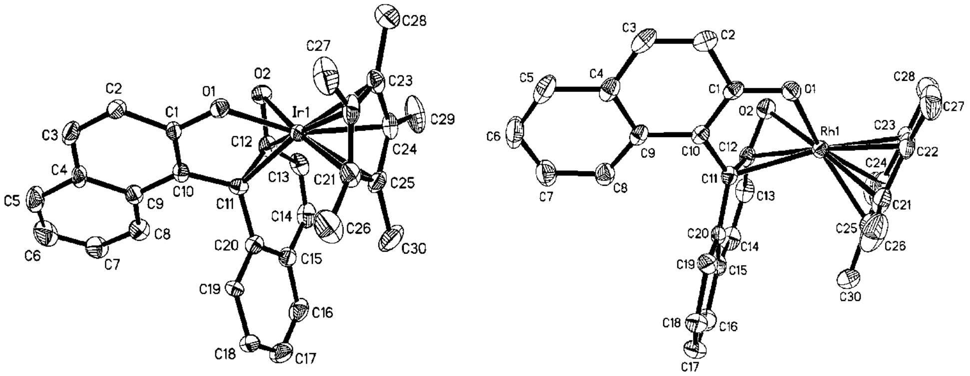
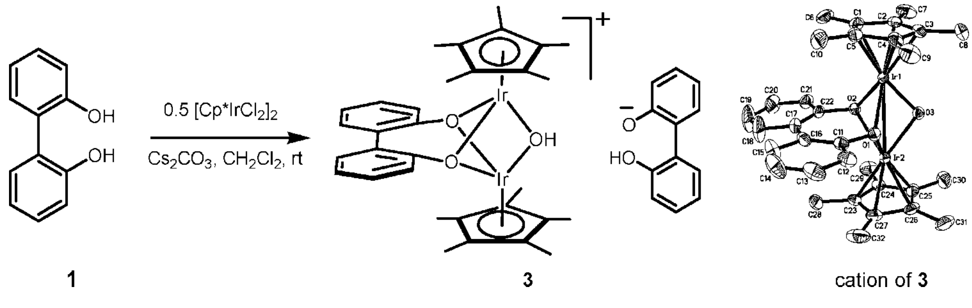


Figure 1. Molecular structures of **1a** (left) and **1c** (right) shown with thermal ellipsoids at the 50% probability level. Selected lengths (Å) and angles (deg) are as follows. **1a**: Ir(1)$-$O(1), 2.045(5); Ir(1)$-$O(2), 2.187(5); Ir(1)$-$C(11), 2.254(7); Ir(1)$-$C(12), 2.204(7); C(11)$-$C(12), 1.473(10); C(10)$-$C(11)$-$C(12), 117.6(6); C(11)$-$C(12)$-$O(2), 117.3(6). **1c**: Rh(1)$-$O(1), 2.0404(17); Rh(1)$-$O(2), 2.1840(18); Rh(1)$-$C(11), 2.290(3); Rh(1)$-$C(12), 2.211(3); C(11)$-$C(12), 1.447(4); C(10)$-$C(11)$-$C(12), 118.6(2); C(11)$-$C(12)$-$O(2), 119.0(2).

Scheme 3. Synthesis of Iridium Biphenolate Complexes

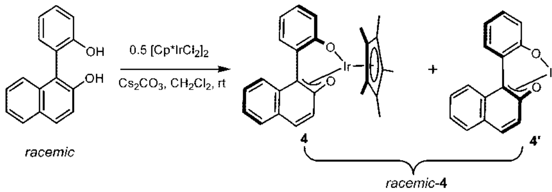


1 **3** cation of **3**

Activation parameters of this dynamic exchange process were estimated for complex **1b** by VT ^{1}H NMR spectroscopy. Lineshape analysis of the two aromatic singlet signals gave $\Delta H^{\ddagger} = 10.6$ kcal/mol and $\Delta S^{\ddagger} = 3.2$ eu (see the Supporting Information). This small value of $\Delta S^{\ddagger}$ is consistent with an intramolecular exchange process.

We then replaced the BINOL starting material to investigate if other biphenols can undergo similar reactions. Interestingly, the reaction of 2,2′-biphenol and $[Cp^*IrCl_2]_2$ under the same conditions afforded the dimeric complex **3** (Scheme 3). X-ray crystallography revealed that each iridium center is supported by a η^5-Cp* ring, two μ-aryloxides, and a μ-hydroxide (see the Supporting Information). Two characteristic broad OH signals appear at δ 10.06 and 15.05 in the ^{1}H NMR spectrum (CD_2Cl_2, −80 °C). The ESI-MS spectrum of **3** shows peak clusters with *m*/*e* values and isotopic patterns corresponding to $[Ir_2Cp^*_2(\text{biphenolate})(OH)]^+$. These results indicate that the 2,2′-biphenolate ligand here prefers to adopt the bridging η^1-aryloxide binding mode.

To further understand the selectivity and preference of this η^3-aryloxide binding mode, racemic 1-(2-hydroxyphenyl)naphthalen-2-ol was allowed to react with $[Cp^*IrCl_2]_2$ under the same conditions (eq 1). Complex (±)-**4** was isolated and characterized by NMR spectroscopy and elemental analysis. Spectroscopic similarities between **4** and **1a**,**c** were noted. In the ^{13}C NMR spectrum, two characteristic high- (δ 92.5) and low-field (δ 174.3) signals were observed *at room temperature* and are directly comparable to those of **1a**,**c** or **2** *at low temperature*, supporting the presence of an η^3-aryloxide group. In sharp contrast to complexes **1a**−**c** and **2**, no fluxionality was observed on the basis of ^{1}H and ^{13}C NMR spectroscopy (−90 to +39 °C, CD_2Cl_2). We reason that an aryloxide with elongated aromaticity (naphthanolate here) prefers to adopt the η^3 binding mode, since this leads to only partial disruption of the aromaticity. Thus, η^3 to η^1 slippage of the naphthanolate in **4** is unfavorable, leading to a static structure of **4**. The preference for the η^3-aryloxide formation in an aryloxide that has extended conjugation is in line with the observations by Hartwig and co-workers in their studies of palladium(II) η^3-benzyl complexes, where η^3-naphthylmethyl complexes are both more thermodynamically stable and more kinetically reactive than the corresponding η^3-benzyl complexes.[13] This has also been proposed to rationalize the regioselectivity of palladium-catalyzed arylhalogenation reactions of alkenes.[14]



(1)

In summary, a series of metal complexes featuring a rare η^3 binding mode of aryloxides have been synthesized and characterized. Dynamic exchange of reversible and degenerate $\eta^1-\eta^3$ exchange of naphthanolate moieties has been observed, and the activation parameters have been measured. This binding mode might contribute to the capability of aryloxide ligands to stabilize otherwise reactive species. Studies are underway to apply these BINOLate complexes to catalytic asymmetric organic transformations.

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Note Added after ASAP Publication. The version of this paper published on November 5, 2008, was missing an author name. The version published on November 11, 2008 contains the correct information.

Supporting Information Available: Text, tables, figures, and CIF files giving details of the synthesis of all metal complexes, NMR spectra, and X-ray data for complexes **1a**,**c** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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