C–O Activation

Self-Oxidation of a Phenolate Complex to a Bimetallic Stilbene Quinone**

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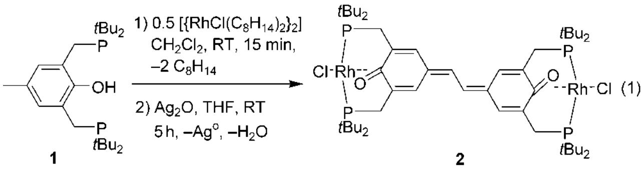
Oxidation chemistry of phenol derivatives is of interest,[1–4] mainly since it affords convenient routes to a variety of basic chemicals.[1] Widely used phenolic food antioxidants, such as 4-methyl-2,6-di-*tert*-butylphenol (butylated hydroxy toluene, BHT) are known to form a diversity of compounds upon oxidation, including colored stilbenequinone systems.[2] Selective oxidative C–C coupling of alkylated phenols to stilbenequinones is rare[3] and this process often requires strong oxidants.[4] To our knowledge, self-oxidation of phenols or phenol derivatives, in the absence of external oxidant, has not been reported. Herein we report an unprecedented oxidative-coupling process in which a phenolate oxygen atom serves as the oxidant, which results in cleavage of the aryl–oxygen bond. This process involves a phenolate metal complex and results in the synthesis and crystallographic characterization of a new bimetallic stilbenequinone complex having two quinonoid C=O bonds η^2-coordinated to the metal centers.[5] The metal oxidation state in the C–O cleaved product is retained. Oxidative coupling of the metal complex, can also be affected by an external oxidant, and, significantly, it is metal selective.

Treatment of the 4-methylphenol bisphosphine ligand **1**[6] with 0.5 equivalents of [{RhCl(cyclooctene)$_2$}$_2$] in CH_2Cl_2 at room temperature for 15 min followed by addition of Ag_2O (2–3 equiv) and continuous stirring for 5 h resulted in the selective formation of the bimetallic stilbenequinone complex **2** [Eq. (1)]. Formation of **2** was indicated by a change of the green reaction mixture to deep blue.



The diamagnetic complex **2** was formed quantitatively as judged by $^{31}P\{^1H\}$ NMR spectroscopy, isolated as a blue solid in 50 % yield, and fully characterized by a combination of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy techniques, UV/Vis spectroscopy, FAB mass spectrometry, and by single-crystal X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum showed a doublet at $\delta = 44.18$ ppm ($^1J_{\mathrm{Rh,P}} = 117.7$ Hz), which indicates that the phosphorus atoms are chemically equivalent and coordinated to a metal center. FAB-MS measurements showed the signal for the molecular ion (m/z 1118.307) and a correct isotope pattern. The UV/Vis spectrum of **2** exhibited one broad charge-transfer band at $\lambda_{\max} = 576$ nm ($\omega_{1/2} = 77$ nm, $\varepsilon = 29 \times 10^3$ in acetone).

Dark blue crystals of complex **2** were obtained upon slow evaporation of a CH_2Cl_2 solution under a nitrogen atmosphere at room temperature. The X-ray structure of **2** reveals the formation of the bimetallic stilbenequinone structure and the rare η^2 coordination mode of the metal centers to the quinonoid C=O double bonds (Figure 1).[17]

The fourteen carbon atoms of the stilbenequinone backbone are located in the same plane with the two metal-coordinated oxygen atoms out of the plane by about 0.3 Å. The relatively short C(14)-C(14A) bond length of 1.404(5) Å may indicate a contribution of other resonance structures.[3] The phosphine groups are mutually *trans* with a significantly distorted P-Rh-P angle of 167.84(2)°. Distorted P-M-P angles are common for pincer complexes.[7] The C–O, Rh–O, and Rh–C bonds of 1.325(3), 2.0562(16), and 2.186(2) Å, respec-

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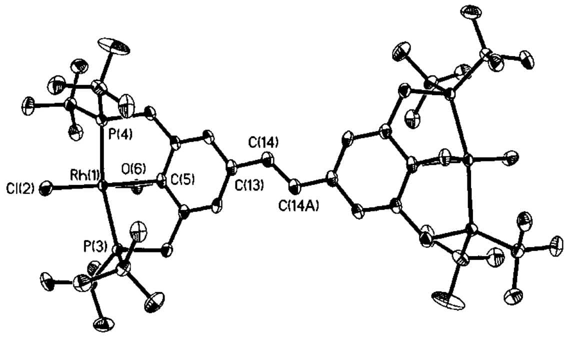
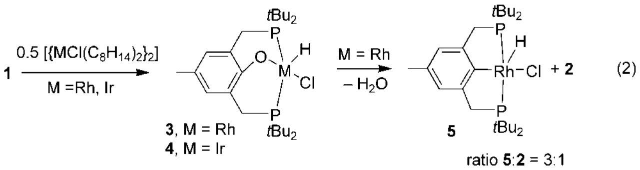


Figure 1. Ortep diagram of complex **2** (thermal ellipsoids set at 50 % probability). Selected bond lengths [Å] and angles [°]: Rh(1)-O(6) 2.0562(16), Rh(1)-C(5) 2.186(2), Rh(1)-Cl(2) 2.3156(8), Rh(1)-P(3) 2.3290(7), Rh(1)-P(4) 2.3457(7), C(5)-O(6) 1.325(3), C(13)-C(14) 1.395(3), C(14)-C(14A) 1.404(5); P(3)-Rh(1)-P(4) 167.84(2).

tively, compare well with those observed for a monomeric Ir^I phenoxonium cation.[8] Other coordination modes in quinonoid systems are much more common.[9–12]

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy measurements of a sample of the reaction mixture before addition of the oxidation reagent indicated the initial formation of the unstable Rh^{III} hydride complex **3** as the only detectable phosphorus-containing product [Eq. (2)]. Remarkably, continuous stirring of the reaction mixture for three days without Ag_2O in a sealed vessel with rigorous exclusion of air resulted in the disappearance of intermediate **3** with formation of the stilbenequinone **2** and complex **5** in a 1:3 molar ratio as judged by $^{31}P\{^1H\}$ NMR spectroscopy.



Complex **5** shows very similar spectroscopic properties to an analogous complex lacking the *p*-methyl group on the aromatic ring.[13] The ^1H NMR spectrum clearly shows a characteristic rhodium-hydride double triplets at $\delta = -27.53$ ppm ($^1J_{Rh,H} = 52.8$ Hz, $^2J_{P,H} = 12.0$ Hz), which collapse into a doublet in the $^1H\{^{31}P\}$ NMR spectrum, whereas the $^{31}P\{^1H\}$ spectrum shows a doublet at $\delta = 74.9$ ppm ($^1J_{Rh,P} = 115.1$ Hz). The product distribution does not change after consumption of intermediate **3**, and the stoichiometry is consistent with the formation of water. Water has been detected by GC-MS. Performing this reaction at 60 °C for three days resulted in the same outcome. Formation of complex **5** by activation of the strong aryl C–O bond at room temperature is unexpected. Only a few cases of aryl–O bond cleavage of ethers or phenols under mild homogeneous reaction conditions have been reported.[6,14,15]

Formation of complex **2** is a clear example of transition-metal-based selectivity. Treatment of compound **1** with 0.5 equivalent of $[\{IrCl(cyclooctene)\}_2]$ resulted in O–H activation and quantitative formation of the fully characterized Ir^{III} phenoxy hydride complex **4** [Eq. (2)]. Orange crystals of **4** were obtained from a benzene solution by slow evaporation of the solvent under N_2 at room temperature (Figure 2).[17] The C–O, Ir–O, Ir···C separations of 1.334(9), 2.083(5), and 2.363(8) Å are in agreement with a phenoxy type structure.[16]

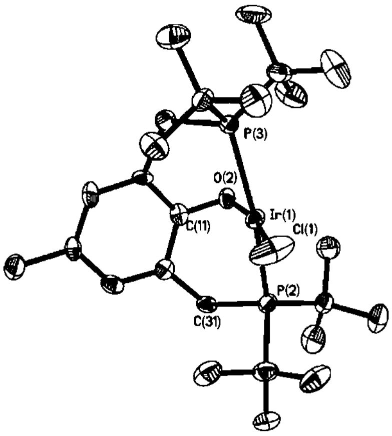


Figure 2. Ortep diagram of complex **4** (thermal ellipsoids set at 50 % probability) Selected interatomic distances [Å] and angles [°]: Ir(1)-O2 2.083(5), Ir(1)···C1(1) 2.363(8), Ir(1)-Cl(1) 2.349(3), Ir(1)-P(2) 2.354(1), Ir(1)-P(3) 2.363(72), C1(1)-O(2) 1.334(9); P(2)-Ir(1)-P(3) 163.97(8).

In sharp contrast to the aforementioned reactivity of the analogous Rh^{III} hydride complex **3**, no formation of bimetallic compounds or other iridium complexes was detected even after three days of heating at 60 °C in THF in a sealed pressure tube. Attempts to oxidize complex **4** with Ag_2O, O_2, ferrocenium hexafluorophosphate, and cyclic voltammetry resulted in an indicative color change from red to purple but $^{31}P\{^1H\}$ NMR spectroscopy measurements showed mixtures of unidentifiable compounds. Apparently the metal center plays an important role in the stilbenequinone complex formation. Although in both cases (**3**, **4**) a d^6 metal center is used, the second-row metal hydride complex **3** is less stable and readily undergoes stilbenequinone formation whereas the third-row metal hydride complex **4** is far more thermally robust but exhibits an unselective reactivity pattern.

Mechanistically, it is likely that the room-temperature dearomatization and dimerization of complex **3** at the methyl group to form **2** proceeds via a *p*-quinonemethide intermediate. An unusual series of monomeric phosphorus–carbon–phosphorus(PCP)-type Rh^I and Ir^I quinone methide complexes (C=C bond bound to the metal center) have been isolated.[11] Formation of a strong metal–olefin bond may contribute to the stability of these compounds, whereas the Rh^I intermediate proposed herein (C=O bond bound to the metal center) undergoes oxidative coupling to afford **2**. However, other mechanistic pathways are also possible. The steric hindrance provided by the two bulky CH_2PtBu_2 groups and stabilization of the *p*-quinonemethide structure by η^2-C=O bond coordination to the low-valent rhodium center may allow this postulated intermediate sufficient lifetime to interact with a second intermediate. No coupling products with complex **5** or solvents were detected. It is remarkable that quantitative formation of the stilbenequinone complex **2** occurs even in the absence of an added oxidant. The Rh^{III} hydride intermediate **3** plays a dual role—as precursor for formation of stilbenequinone complex **2** and as an oxygen-transfer agent. Examples of chemical processes wherein one metal complex fulfills two or more distinctly different tasks are not common.

In summary, a unique oxidative dimerization process of a phenolic compound has been observed with a pincer model system, in which the phenolic oxygen atom itself serves as an oxidant by aryl–oxygen and C–H cleavage, leading to a new metal complex. The oxidative dimerization process can also be affected by an external oxidant. The process is metal selective.

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[16] The $M{-}C_{aryl}$ σ-bond length in cyclometalled pincer complexes is approximately 2.1 Å.[7,15] X-ray characterized Pd^{II} and Rh^{I} phenoxy pincer complexes are reported in ref. [6].

[17] CCDC-236289 (**2**), CCDC-236290 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).