Common Electrophilic Addition Reactions at the Phenol Ring: The Chemistry of TpW(NO)(PMe_3)(η^2-phenol)

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The complex TpW(NO)(PMe_3)(η^2-benzene) was treated with an excess of phenol to generate TpW(NO)(PMe_3)(η^2-2*H*-phenol) as a mixture of two stereoisomers. This complex in the presence of base undergoes reactions with several common classes of electrophiles, including benzaldehyde, alkyl iodides, and Michael acceptors, to form new C−C bonds. Methyl and ethyl iodide react at C2 to form 2-alkyl-2*H*-phenol complexes, whereas the Michael acceptors react at C4 to give 4-alkyl-4*H*-phenol complexes. In both cases, the electrophile adds to the complexed phenol stereoselectively, anti to the metal. In the case of benzaldehyde, an aldol condensation reaction occurs at C2 to form a rare example of a thermally stable *o*-quinone methide complex. Crystal structures of the 2-ethyl-2*H*-phenol and the phenyl *o*-quinone methide complexes are included.

Introduction

Aldehydes, ketones, and their enol and enolate variants play a central role in the formation of carbon−carbon bonds. Reactions that employ them such as the aldol, Mannich, and Michael reactions are staples of modern organic synthesis. Phenols possess the HO−C═C linkage of an enol in a cyclic carbon framework. Although widely available both commercially and in nature,[1,2] the aromatic stabilization of phenols limits their reactivity in the chemistry that is generally facile for enols and enolates. By masking one of the "double bonds" of the aromatic ring through coordination to a transition metal, this aromaticity is diminished, and the latent dienol character exposed. With sufficient loss of aromatic character, these phenol species may also exist as their corresponding dienone tautomers (Figure 1).

Previously, we have demonstrated that dihapto coordination of a phenol with the π-base $[Os(NH_3)_5]^{2+}$ enhances its reactivity toward electrophilic reagents.[3,4] In our endeavor to make this methodology general, we have turned our attention to the recently reported dearomatization agent {TpW((NO)(PMe_3)}, which forms a stable η^2-complex with benzene (**1**).[5]

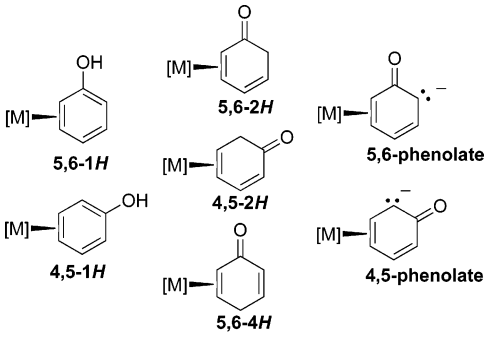
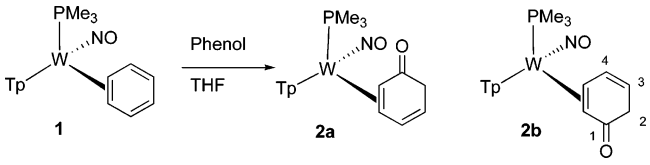


Figure 1. Several possible η^2-phenol complexes, their dienone tautomers (2*H*- and 4*H*-phenols), and their corresponding phenolate isomers.

Scheme 1



Results

The complex TpW(NO)(PMe_3)(η^2-2*H*-phenol) (**2**) was prepared in 91% yield from a ligand exchange reaction in which TpW(NO)(PMe_3)(η^2-benzene) (**1**) was combined with a THF solution of phenol (Scheme 1). On the basis of proton and carbon NMR data, the isolated phenol complex **2** was characterized as a 5,6-η^2-2*H*-phenol complex (see Figure 1) present in a coordination diastereomer ratio (cdr) of 2:1 (**a**:**b**). In contrast to phenol coordinated to osmium(II), for which the 1*H*-phenol complex is the predominant species observed, neither the 1*H*- nor the 4*H*-phenol tautomers were detected in either the proton or the carbon NMR spectrum of **2**.

The diastereomers **2a** and **2b** can be separated using thin-layer chromatography, but low isolated yields (3%) suggest that decomposition of **2** occurs on silica gel. Signals in the ^{13}C NMR spectrum of isomer **2b** at 208.5 and 39.2 ppm correspond to the carbonyl (C1) and the tetrahedral carbon (C2) of the complexed phenol. COSY, HSQC, HMBC, and ^{31}P decoupled proton data confirm that the metal is coordinated across C5 and C6, with the keto oxygen oriented away from the phosphine ligand (see Scheme 1). The spectroscopic features of **2** are

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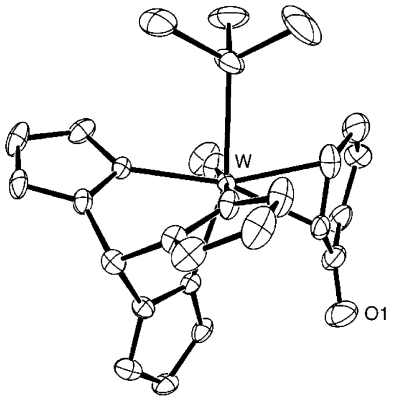

Figure 2. ORTEP diagram (30% ellipsoids) corresponding to **2b**, one of two 2,4-cyclohexadienone isomers for the phenol complex **2**.

similar to those previously reported for the complex $[Os(NH_3)_5$-(3,4-dimethyl-2*H*-phenol)$]^{2+}$.[6] Crystals of **2** were grown from a THF solution of the isomer mixture by vapor diffusion of hexanes, and the ORTEP diagram resulting from an X-ray diffraction study confirms the structure of isomer **2b** as an η^2-phenol (Figure 2). However, internal disorder in the crystal prevented the determination of meaningful bond lengths and angles.

The coordination diastereomers **2a** and **2b** differ by which face of the C5−C6 linkage is coordinated to the metal (vide supra). These coordination diastereomers do not interconvert under neutral or acidic conditions: a d_6-acetone solution enriched in **2b** (dr = 1:4, **a**:**b**) shows no signs of isomerization even after 12 days at 20 °C. However, when this solution mixture was treated with the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the **a**:**b** ratio decreased over a period of 2.5 h until it reached an equilibrium cdr of 2:1 (**a**:**b**).

The infrared absorption spectrum of **2** shows a stretching frequency of 1572 cm^{-1} corresponding to the NO stretch. This value is noticeably blue-shifted from its benzene precursor **1** (1564 cm^{-1}), consistent with an increase in the π-acidity of the organic ligand. In addition, a new carbonyl stretch feature is present in the infrared absorption spectrum at 1619 cm^{-1}. A cyclic voltammogram of **2** shows a chemically irreversible oxidation wave with an $E_{p,a} = +0.80$ V (100 mV/s). This feature, which is over 0.9 V greater than for the benzene analogue (**1**), illustrates the ability of the dienone ligand to stabilize the W(0) oxidation state. In fact, a solution of **2** is stable in air indefinitely, whereas its precursor has a half-life in solution of about an hour at 20 °C in air.

Although the dienone ligand of **2** would not be expected to show reactivity with mild electrophiles at carbon, its conjugate base is an η^2-phenolate ion, which could react at a ring carbon. Correspondingly, when a solution of **2** is treated with DBU and lithium triflate (LiOTf), it readily combines with the Michael acceptors methyl vinyl ketone and methyl acrylate to produce **3** and **4**, respectively (Scheme 2). The addition reactions occur regioselectively at the 4-position of the phenol ligand to produce 5,6-η^2-2,5-cyclohexadienone complexes in moderate yields (56−75%), as mixtures of two coordination diastereomers. The absence of significant H4−H5 coupling in either isomer implies that the corresponding Karplus angle is close to 90°. This observation is consistent with the addition of the Michael acceptor occurring anti to the metal fragment at C4.

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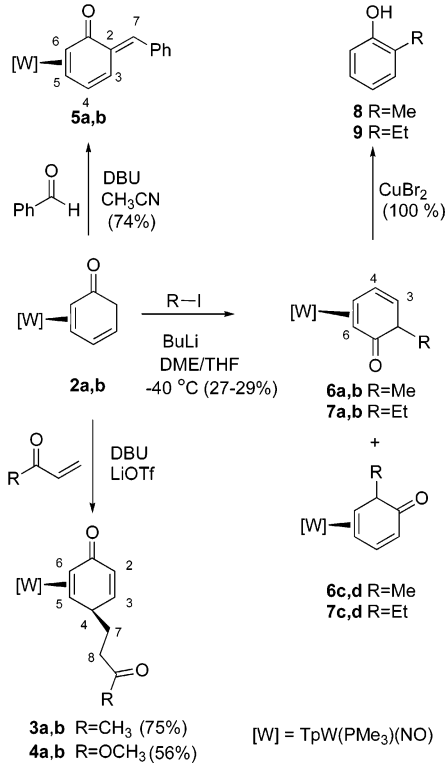
Scheme 2



The cdr of both **3** and **4** is 2:1, the same value found for the phenol complex **2** at equilibrium. When the experiment is repeated without the LiOTf additive, no reaction occurs at 20 °C. Presumably, the lithium ion is needed to stabilize the intermediate phenolate complex through coordination of the oxygen. The reaction proceeds with comparable yields when lower concentrations of either base or acid are used; however, longer reaction times are required. Substituting the DBU with the weaker base, triethylamine, results in no reaction, even in the presence of LiOTf. Chromatography is necessary to isolate pure samples of **3** and **4**, due to competing polymerization of the Michael acceptors. The 2,5-cyclohexadieneone Michael adducts **3** and **4** have slightly higher NO stretching frequencies (1585 and 1580 cm^{-1}, respectively) than their 2*H*-tautomer precursor **2** (1572 cm^{-1}). A key spectroscopic feature in the proton NMR spectrum for these 4*H*-tautomers is a doublet of triplets at 5.9 ppm, corresponding to H2 (see Scheme 2). The redox properties of **3** and **4** are similar to those of **2** with irreversible oxidation waves at $E_{p,a} = +0.82$ and $E_{p,a} = +0.78$ V, respectively. Other Michael acceptors such as acrylonitrile and *N*,*N*-dimethylacrylamide fail to react with **1** under the reaction conditions described above.

Benzaldehyde undergoes an aldol condensation with the phenol complex under basic conditions to produce the *o*-quinone methide complex **5**. When the reaction is run in acetonitrile in the presence of DBU, the *o*-quinone methide complex **5b** precipitates out of solution, while its coordination diastereomer **5a** remains (see Scheme 2). Thus, separation of the coordination diastereomers can be achieved by simple filtration. Complex **5** is synthesized by this method in a combined 76% yield with a cdr of 2:1 (**a**:**b**). This condensation reaction was carried out using DBU or potassium *tert*-butoxide (1 eq) as the catalyst. Alternatively, LiOTf, $Zn(OTf)_2$, $Mg(OTf)_2$, or L-proline can be used, though the rate of the reaction decreases. In addition, the use of $Zn(OTf)_2$ generated a product that was not as clean as that formed under basic conditions.

A key spectroscopic feature for **5** is a singlet near 7 ppm corresponding to the methine proton at the benzyl position and a doublet near 6.2 ppm corresponding to H3. X-ray diffraction analysis for a crystal of **5** confirms that double-bond character exists at C3−C4 (1.34 Å) and C2−C7 (1.35 Å). This crystal structure of **5** also confirms that the condensation reaction results in the *E* stereoisomer of the quinone methide, similar to what was observed for the osmium analogue.[4]

Significantly, the *o*-quinone methide complex **5** can be prepared in air without a noticeable change in yield or diastereoselectivity. Consistent with this observation, **5** shows a chemically irreversible anodic wave in a cyclic voltammogram at $E_{p,a} = +0.71$ V, well positive of the air-reactive benzene precursor **1**. The diastereomers **5a** and **5b** do not interconvert under neutral or basic conditions at 110 °C. Under acidic conditions both diastereomers begin to decompose as the temperature approaches 90 °C, but still no interconversion of the diastereomers was observed.

The reaction of the phenol complex (**2**) with methyl triflate mostly results in O-methylation. However, the C-alkylation of the phenol complex with either methyl or ethyl iodide can be achieved by the prior deprotonation of the phenol at low temperatures (−40 to −80 °C). For example, treatment of **2** with butyllithium followed by ethyl iodide resulted in the selective alkylation of the uncoordinated ortho position of the phenol ligand in **2** to form the corresponding 2-ethyl-2*H*-phenol complex **7** (see Scheme 2). Four different isomers of **7** are formed (**a**−**d**). Complexes **7a** and **7b** were identified as 5,6-η^2-2*H*-phenol coordination diastereomers, while **7c** and **7d** were identified as the previously unobserved 3,4-η^2-2*H*-phenol isomers. While ^{1}H NMR and cyclic voltammetric data showed no indication of other contaminants, it was determined by use of an internal integration standard that the isolated mixture contained only about 30% of **7**. Attempts to improve the yield of **7** by varying the temperature, solvent, concentrations, or base were unsuccessful. In THF, starting with a 2:1 dr (**2a**:**2b**), the ratio of **7a**:**7b**:**7c**:**7d** was 3:5:1.5:1. All attempts to modify this reaction in such a way as to form one dominant isomer were unsuccessful.

The isomers **7b** and **7d** were isolated by column chromatography and have been fully characterized. The proposed structures shown in Scheme 2 are fully consistent with the ^{1}H, ^{13}C, COSY, HSQC, and HMBC data. **7a** and **7c** were characterized as coordination diastereomers of **7b** and **7d**, respectively, on the basis of similar chemical shifts and splitting patterns. The phenol ring protons in 5,6-η^2-diastereomers (**7a**,**b**) are similar to those of the 2*H*-phenol complex (**2a**,**b**). Particularly diagnostic is the splitting pattern for H3, which changes from a ddd in **2a**,**b** to a dd in **7a**,**b**. In contrast, the chemical shifts of the protons for the 4,5-η^2-diastereomers (**7c**,**d**) are different from the 2H-phenol complex (**2a**,**b**). Specifically the doublet at 5.3 ppm, identified as H6, and the dd at 7.6 ppm, identified as H5, are indicative of the shift in coordination to a 3,4-η^2-isomer. As with the other phenol-derived complexes, **2**−**5**, these 2*H*-phenol complexes (**7b**−**d**) can be handled in air without decomposition.

Crystals were obtained for the major isomer **7b**, and an X-ray diffraction study was carried out. The corresponding ORTEP diagram (Figure 3) shows the ethyl group anti to the metal, suggesting that the electrophile added directly to the phenolate ring rather than by way of the tungsten. This is fully consistent with other reactions involving tungsten- and osmium-bound phenols with electrophiles.[7,12,14] The crystal structure also clearly

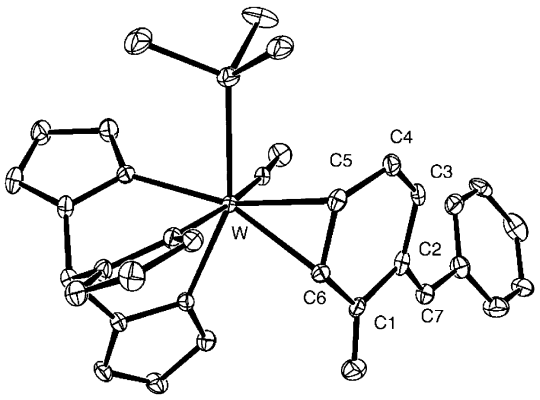


Figure 3. ORTEP diagram for the *o*-quinone methide complex **5** (30% ellipsoids). Selected bond lengths: O1−C1 (1.22 Å), C2−C7 (1.35 Å), C3−C4 (1.33 Å), C5−C6 (1.43 Å).

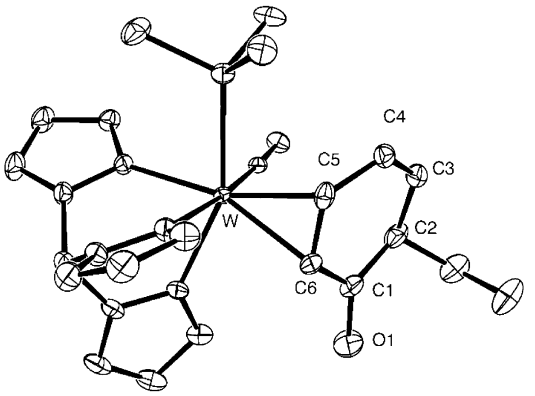


Figure 4. X-ray crystal structure of TpW(NO)(PMe$_3$)(η^2-2-ethylphenol) (**7b**). Selected bond lengths: C1−O1 (1.23 Å), C1−C2 (1.53 Å), C2−C3 (1.50 Å), C3−C4 (1.33 Å), C5−C6 (1.45 Å).

demonstrates the lack of aromaticity, as evidenced by the change in expected bond lengths for the C−C bonds and nonplanarity of the 2*H*-phenol ring. Furthermore, the C−O bond length (1.23 Å) is consistent with a carbonyl group. In a procedure similar to the synthesis of **7**, methyl iodide reacts with the phenolate complex prepared from **2** to produce an *o*-cresol complex (**6**) as a mixture of four isomers. As with **7** these complexes were formed in low yields and the isolated mixture contained mostly paramagnetic materials.

The phenol ligands of complexes **6** and **7** were liberated from the metal by treating the complexes with $CuBr_2$. Substituted phenols *o*-cresol (**8**) and *o*-ethylphenol (**9**) could be isolated in 27% and 29% yields from **2**, respectively.

Discussion

While the dominant mode of coordination for phenol to metals is through the oxygen of a phenoxide, numerous examples also

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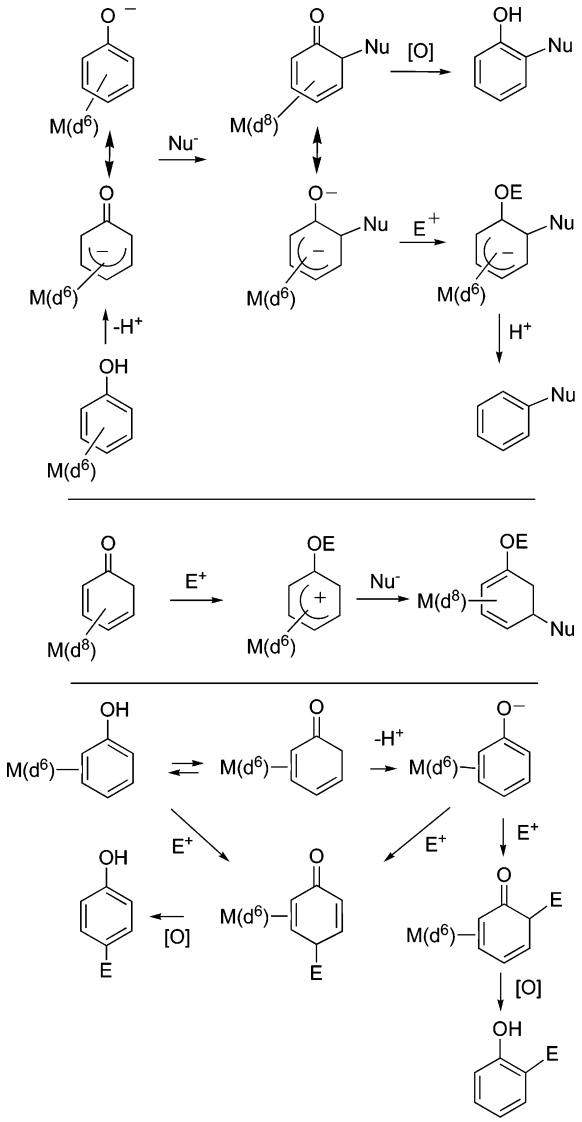
Scheme 3. Summary of Reactivity for η^6, η^4, and η^2 Phenol Complexes (most common electron configurations shown in parentheses)



exist in which the ring is π-coordinated (Scheme 3). The phenol can be coordinated as the 1*H*-tautomer, forming both hexahapto[7−10] and dihapto[6] coordinate complexes, or in its 2*H*-phenolic form, where examples include tetrahapto[11,12] and dihapto coordination.[6] Cresols also have been trapped as 4*H*-phenols on osmium(II).[6] Phenoxides are also known to form π-coordinated complexes. These are typically described as η^5-phenoxide or η^5-oxocyclohexadienyl complexes, and crystallographic and infrared data indicate considerable CO double-bond character in these species.[7,8,13] As illustrated in Scheme 3, the higher coordinate phenol and phenoxide complexes typically undergo reactions with electrophiles at the oxygen atom,[12,14] while reactions with nucleophiles tend to occur at the ortho carbon of the phenol ring.[7,13] These reactions can lead to both ortho-substituted phenols and substituted benzenes (see Scheme 3). The chemistry described in the present work is a rare example of electrophilic additions to coordinated phenols that occur at carbon. Friedel−Crafts alkylations of phenols have been reported,[15] but these reactions are carried out under highly acidic conditions in which cationic rearrangements are commonplace.[16,17]

The only other example of an η^2-phenol complex reported in the literature is $[Os(NH_3)_5(5,6\text{-}\eta^2\text{-}1H\text{-phenol})]^{2+}$, which is present primarily as the phenolic (i.e., 1H) tautomer.[6] This coordination mode is similar to that seen with η^2-anisole complexes of osmium,[18] rhenium,[19] and tungsten[19] and is an arrangement that allows linear conjugation between the uncoordinated segment of the aromatic ring and the oxygen.[18] The purported tungsten η^2-1*H*-phenol complex undoubtedly has the metal coordinated across C5 and C6, which is likely to be the factor that dictates the location of the metal in the 2*H*-phenol isomers (**2**).

Previously we have shown that the barrier to both intrafacial (ring-walk) and interfacial isomerization (face-flip) is much higher for η^2-alkene than for η^2-aromatic complexes.[20] Consistent with this fact is the observation that **2a** and **2b** do not interconvert in absence of a base. Presumably the face-flip or ring-walk, of which either operation would interconvert **2a** and **2b**, occurs for the unobserved phenolate complex intermediate. Studies with osmium(II) and osmium(III) demonstrated that greater metal-to-ligand back-bonding and lower oxidation state of the metal enhance the equilibrium ratio of dienone to phenol tautomers.[6] It is less clear why the 2*H*-phenol **2** is formed in preference to the purported 4*H*-phenol isomer. The 4*H*-phenol complex of pentammineosmium(II) was shown to be thermodynamically favored over the 2*H*-phenol,[6] but the latter was more kinetically accessible. It is possible that the 2*H*-phenol complex **2** is formed for purely kinetic reasons, i.e., that the phenolate is more rapidly protonated at the ortho carbon C2 compared to C4, but we were unable to confirm this by establishing a discernible equilibrium of the 2*H* and 4*H* isomers.

Because its 2*H*-phenol tautomer dominates over the aromatic form, complex **2** is more stable than typical dihapto-arene complexes with respect to oxidation. This is evidenced by the higher oxidation potential of **2** ($E_{p,a} = +0.80$ V) compared to **1** ($E_{p,a} = -0.13$ V).[9] Correspondingly, compound **2** can be handled in air. By comparison, the previously reported pentammineosmium(II) 1*H*-phenol complex was not easily handled outside of a glovebox. The phenol complex **2** also is more inert toward ligand substitution than analogous arene complexes (e.g., benzene, anisole), which have ligand substitution half-lives of about 1 h.[9]

In basic solution, the 2*H*-phenol (**2**) has access to the 1*H*-phenol (or phenolate) form, which reacts with benzaldehyde, alkyl halides, and Michael acceptors to give exclusively C-alkylated products. Interestingly, Michael additions selectively occur at C4, forming 2,5-cyclohexadienones, while aldehydes and alkyl iodides react at the uncoordinated ortho carbon. It has previously been suggested that addition of Michael acceptors to η^2-arenes may occur via a Diels−Alder cycloadduct intermediate or transition state.[3] The Michael addition is proposed to result following ring-opening and protonation of this intermediate. Given that this pathway is not available to the aldehyde or ethyl iodide, it may not be a coincidence that the regiochemical preference changes for the latter two electrophiles.

The reaction of alkyl halides with **2** to form 2-alkylated 2*H*-phenols is, to our knowledge, an unprecedented reaction type.

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Even with the complex $[Os(NH_3)_5(\eta^2\text{-phenol})]^{2+}$, alkylation occurs exclusively at oxygen.[21] The reaction of aldehydes at C2 and subsequent condensation to form *o*-quinone methide complexes has been previously reported, but only for the pentammineosmium(II) system.[4] In contrast to arenes and aromatic heterocycles, which become more reactive as a result of η^2-coordination,[22] *o*-quinone methides are far less so. In dramatic contrast to organic quinone methides, which are observable only at very low temperatures,[23] the quinone methide complex **5** will not react at room temperature with either electron-rich (e.g., 2,3-dihydrofuran) or electron-deficient dienophiles (e.g., *N*-phenylmaleimide). Without the stability associated with the formation of the benzene ring, the *o*-quinone methide ligand in **5** is rendered chemically inert. Similar observations were made with the osmium analogue of **5**.[4] Apart from these two examples, no other examples are known in which an *o*-quinone methide is formed directly from a phenol complex and aldehyde, and the crystal structure of **5** is the first example reported for an η^2-*o*-quinone methide complex. However, Amouri et al. have demonstrated the rich chemistry of η^4-coordinated *o*-quinone methides derived from *o*-alkylated phenols,[13] which undergo reactions with electron-deficient alkenes and alkynes. Novel *p*-quinone methide complexes have also been prepared from 4-(bromomethyl)phenol derivatives by Milstein et al.,[24] which are dihapto-coordinated at the exo-methylene group.

Conclusion

The C-alkylation of the phenol ligand of the complex TpW(NO)(PMe_3)(η^2-phenol) has been accomplished with several common classes of carbon electrophiles. This phenol complex reacts with Michael acceptors to form 4-alkylated 2,5-cyclohexadienone complexes with a high degree of stereo- and regioselectivity. In contrast aldehydes and alkyl halides react at the 2-position to generate *o*-quinone methide or 2,4-cyclohexadienone complexes, respectively. Attempts are currently underway to exploit this unique reactivity as part of a general synthetic methodology for converting phenols into functionalized cyclohexenes.

Experimental Section

General Methods. All NMR spectra were obtained on either a 300 or 500 MHz Varian INOVA, a Bruker Avance 300 or 500 MHz, or a 300 MHz General Electric GN300 spectrometer. All chemical shifts are reported in ppm versus tetramethylsilane using residual shifts of the deuterated solvent as internal standards. ^{31}P NMR spectra are reported using the reported literature value versus H_3PO_4 for triphenyl phosphate ($J = -16.58$ ppm), which is used as the internal standard.[25] Infrared spectra were obtained on a MIDAC Prospect Series spectrometer as a glaze on a horizontal attenuated total reflectance (HATR) cell from Pike Industries. Electrochemical measurements were taken under a nitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetric data were obtained in a three-electrode cell from +1.8 to −1.8 V, with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a platinum wire reference electrode. All data were obtained using a 100 mV/s scan rate with tetrabutylammonium hexaflurophosphate (TBAH) as the electrolyte in *N*,*N*-dimethylacetamide (DMA) unless otherwise noted. All potentials were reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) as the internal standard. For reversible waves the peak-to-peak separation was less than 100 mV. Mass spectra were obtained on a JEOL JMS600 using FAB+ or a Shumadzu CSMS QP5050 by direct inlet; no counterions were observed. The isotopic pattern for the parent ion matches that calculated based on natural abundances. All reactions were performed in a Vacuum Atmospheres Co. glovebox unless otherwise stated. Chromatography was performed on 230−400 mesh silica gel from EMD. Methylene chloride, acetonitrile, and benzene were all eluted on a column packed with activated alumina and purged with nitrogen prior to use. Benzaldehyde and ethyl iodide were distilled prior to use. All other solvents and chemicals were used as received from Sigma-Aldrich, Acros Chemicals, or Fisher Scientific.

TpW(NO)(PMe_3)(5,6-η^2-2*H*-phenol) (2a,b). A solution of phenol (2.427 g, 25.8 mmol) and 10 mL of THF was added to **1** (5.037 g, 8.67 mmol). After 6 h the solution was added into 400 mL of 7:1 pentane/Et_2O. The mixture was filtered with a 60 mL medium-porosity fritted glass disk, washed twice with 50 mL of pentane, and dried in vacuo. A tan precipitate was isolated (**2a**, **2b**, 4.578 g, 91%).

Alternatively, **2a** and **2b** can be prepared by direct reduction from the previously reported complex TpW(NO)(PMe_3)Br.[5] TpW(NO)(PMe_3)Br (14.337 g, 24.6 mmol) was added to a 1 L round-bottom flask charged with a stir bar. Sodium dispersion (10.580 g, 0.138 mol, 30−35% in wax) was added along with 300 mL of benzene. After 20 h the reaction was filtered through 2 cm of Celite in a 350 mL medium-porosity fritted disk into a 2 L filter flask, charged with a stirbar, containing phenol (8.147 g, 86.7 mmol). The Celite was washed with 100 mL of benzene. After 22 h the reaction mixture was chromatographed on silica (6 cm in a 350 mL medium-porosity fritted disk) by first eluting with 1:1 benzene/diethyl ether (1000 mL), then diethyl ether (400 mL), then methylene chloride (800 mL), then ethyl acetate (1200 mL). A separate brown band came off of the column with each change in eluent. The ethyl acetate fraction was stripped to dryness, dissolved in 20 mL of THF, and added to 500 mL of stirring pentane. A light beige precipitate was collected (**2a**, **2b** 6.244 g, 43% yield). Cyclic voltammetry: $E_{p,a} = +0.80$ V. IR: $\nu_{NO} = 1574$, $\nu_{CO} = 1619$ cm^{-1}. Anal. Calcd for $C_{18}H_{25}O_2N_7PBW$: C, 36.21; H, 4.22; N, 16.42. Found: C, 35.99; H, 4.18; N, 16.02. ESI/MS: 597 (M+). **2a**: ^1H NMR (CD_3CN): δ 1.16 (d, 9H, $J = 9.3$ Hz, PMe_3), 1.93 (m, 1H, H_5), 3.01 (br d, 1H, $J = 22.2$ Hz, H2), 3.26 (br d, 1H, $J = 22.2$ Hz, H2), 3.39 (t, 1H, $J = 8.7$ Hz, H_6), 4.94 (ddd, 1H, $J = 11.0$, 4.8, 2.7 Hz, H3), 6.25 (t, 1H, $J = 2.4$ Hz), 6.30 (t, 1H, $J = 2.4$ Hz), 6.39 (t, 1H, $J = 2.4$ Hz), 6.57 (ddd, 1H, $J = 11.0$, 5.1, 3.9 Hz, H4), 7.66 (d, 1H, $J = 2.4$ Hz), 7.83 (d, 1H, $J = 2.4$ Hz), 7.99 (d, 1H, $J = 2.4$ Hz), 8.00 (d, 1H, $J = 2.4$ Hz), 8.01 (d, 1H, $J = 2.4$ Hz), 8.16 (d, 1H, $J = 2.4$ Hz). ^{31}P NMR ($CDCl_3$): δ −10.2. **2b**: ^1H NMR ($CDCl_3$): δ 1.23 (d, 9H, $J = 8.6$ Hz, PMe_3), 2.21 (d, 1H, $J = 9.2$ Hz, H6), 3.07 (br d, 1H, $J = 22.2$ Hz, H_2), 3.15 (br d, 1H, $J = 22.2$ Hz, H2), 3.43 (m, 1H, H5), 5.07 (m, 1H, H3), 6.14 (t, 1H, $J = 2.3$ Hz), 6.24 (t, 1H, $J = 2.3$ Hz), 6.32 (m, 1H, H4), 6.35 (t, 1H, $J = 2.3$ Hz), 7.38 (d, 1H, $J = 2.3$ Hz), 7.55 (d, 1H, $J = 2.3$ Hz), 7.72 (d, 1H, $J = 2.3$ Hz), 7.76 (d, 1H, $J = 2.3$ Hz), 7.81 (d, 1H, $J = 2.3$ Hz), 8.13 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR ($CDCl_3$): δ 13.7 (d, $J = 29$ Hz, PMe_3), 39.2 (s, C2), 58.9 (s, C6), 63.0 (d, $J = 11$ Hz, C5), 106.0 (s), 106.4 (s), 106.1 (s), 116.7 (s, C3), 128.2 (s, C4), 135.9 (s), 136.7 (s), 136.9 (s), 140.3 (s), 142.9 (s), 144.3 (s), 208.5 (s, C1). ^{31}P NMR ($CDCl_3$): δ −12.6.

TpW(NO)(PMe_3)(6,5-η^2-4-(3-oxobutyl)-2,5-cyclohexadien-1-one) (3a, 3b). To a mixture of **2a** and **2b** (0.479 g, 0.802 mmol) and DBU (0.142 g, 0.934 mmol) was added a solution of LiOTf (0.132, 0.846 mmol), methyl vinyl ketone (0.183 g, 2.61 mmol), and about 1 mL of CH_3CN. After 24 h the solution was evaporated down to an oil and run down a 3 cm silica plug with 100 mL of

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THF. The solution was evaporated down to an oil and was dissolved in 1 mL of THF, precipitated into 100 mL of 1:1 pentane/Et_2O, filtered, and dried in vacuo (**3a**, **3b**, 0.400 g, 75%). Cyclic voltammetry: $E_{p,a} = +0.82$ V. IR: $\nu_{NO} = 1585$, $\nu_{CO} = 1648$, $\nu_{CO} = 1702$ cm^{-1}. **3a**: ^{1}H NMR (d_6-acetone): δ 1.23 (d, 9H, $J = 9.3$ Hz, PMe$_3$), 1.53 (br d, 1H, $J = 10.0$ Hz, H5), 1.68 (m, 2H, H7), 2.00 (s, 3H, H7), 2.54 (m, 2H, H8), 3.30 (t, 1H, $J = 10.0$ Hz, H6), 3.64 (br m, 1H, H4), 5.83 (dt, 1H, $J = 10.2$, 1.2 Hz, H2), 6.30 (t, 1H, $J = 2.4$ Hz), 6.38 (t, 1H, $J = 2.4$ Hz), 6.41 (t, 1H, $J = 2.4$ Hz), 6.50 (ddd, 1H, $J = 10.2$, 5.1, 2.1, H3), 7.67 (d, 1H, $J = 2.4$ Hz), 7.86 (d, 1H, $J = 2.4$ Hz), 7.98 (d, 1H, $J = 2.4$ Hz), 8.00 (d, 1H, $J = 2.4$ Hz), 8.08 (d, 1H, $J = 2.4$ Hz), 8.13 (d, 1H, $J = 2.4$ Hz). ^{31}P NMR (d_6-acetone): δ −10.4 (s). **3b**: ^{1}H NMR (CD_3CN): δ 1.09 (d, 9H, $J = 8.7$ Hz, PMe$_3$), 1.78 (dq, 1H, $J = 9.3$, 2.0 Hz, H6), 1.92 (m, 1H, H7), 2.10 (s, 3H, H10), 2.14 (m, 1H, H7), 2.58 (ddd, 1H, 17.4, 9.0, 6.0 Hz, H8), 2.75 (ddd, 1H, 17.4, 9.0, 6.0 Hz, H8), 2.94 (ddd, 1H, $J = 13.2$, 9.3, 1.3 Hz, H5), 3.34 (m, 1H, H4), 5.88 (dt, 1H, $J = 10.0$, 1.3 Hz, H2), 6.16 (t, 1H, $J = 2.3$ Hz), 6.30 (t, 1H, $J = 2.3$ Hz), 6.40 (t, 1H, $J = 2.3$ Hz), 6.43 (ddd, 1H, $J = 10.0$, 5.0, 2.0, H3), 7.55 (d, 1H, $J = 2.3$ Hz), 7.71 (d, 1H, $J = 2.3$ Hz), 7.82 (d, 1H, $J = 2.3$ Hz), 7.87 (d, 1H, $J = 2.3$ Hz), 7.90 (d, 1H, $J = 2.3$ Hz), 8.06 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR (CD_3CN): δ 13.1 (d, $J = 28$ Hz, PMe$_3$), 30.7 (s, C10), 36.7 (s, C7), 40.1 (s, C8), 41.4 (s, C4), 59.6 (s, C6), 64.8 (d, $J = 11$ Hz, C5), 106.8 (s), 107.7 (s), 108.4 (s), 129.8 (s, C2), 137.7 (s), 138.3 (s), 138.6 (s), 142.2 (s), 144.4 (s), 144.8 (s), 145.5 (s, C3), 198.7 (s, C1), 210.4 (s, C9). ^{31}P NMR (d_6-acetone): δ −7.5 (s).

TpW(NO)(PMe$_3$)(6,5-η^2-4-(2-(carbomethoxy)ethyl)-2,5-cyclohexadien-1-one) (4a, 4b). To a mixture of **2a** and **2b** (0.470 g, 0.787 mmol) and DBU (0.130 g, 0.838 mmol) was added a solution of LiOTf (0.129, 0.827 mmol), methyl acrylate (0.217 g, 2.52 mmol), and 1 mL of CH_3CN. After 24 h the reaction was run down a 3 cm silica plug with 60 mL of THF. The solution was evaporated down to an oil. The oil was dissolved in 1 mL of THF, precipitated into 50 mL of diethyl ether, filtered, and dried in vacuo (**4a**, **4b**, 0.299 g, 56%). Cyclic voltammetry: $E_{p,a} = +0.78$ V. IR: $\nu_{NO} = 1580$, $\nu_{CO} = 1640$, $\nu_{CO} = 1731$ cm^{-1}. ESI/MS: 683 (M+). **4a**: ^{1}H NMR (CD_3CN): δ 1.16 (d, 9H, $J = 9.0$, PMe$_3$), 1.49 (dm, 1H, $J = 9.5$ Hz, H5), 1.79 (m, 2H, H7), 2.47 (m, 2H, H8), 3.26 (m, 1H, H6), 3.57 (m, 1H, H4), 3.62 (s, 3H), 5.82 (dt, 1H, $J = 10.3$, 1.5 Hz, H2), 6.27 (t, 1H, $J = 2.5$ Hz), 6.30 (t, 1H, $J = 2.5$ Hz), 6.36 (t, 1H, $J = 2.5$ Hz), 6.51 (ddd, 1H, $J = 10.3$, 5.0, 2.0 Hz, H3), 7.52 (d, 1H, $J = 2.5$ Hz), 7.79 (d, 1H, $J = 2.5$ Hz), 7.87 (d, 1H, $J = 2.5$ Hz), 7.88 (d, 1H, $J = 2.5$ Hz), 8.00 (d, 1H, $J = 2.5$ Hz), 8.04 (d, 1H, $J = 2.5$ Hz). **4b**: ^{1}H NMR (CD_3CN): δ 1.08 (d, 9H, $J = 8.5$ Hz, PMe$_3$), 1.77 (dq, 1H, $J = 9.5$, 1.3 Hz, H6), 2.10 (m, 1H, H7), 2.19 (m, 1H, H7), 2.43 (ddd, 1H, $J = 16.0$, 9.5, 5.5 Hz, H8), 2.61 (ddd, 1H, $J = 16.0$, 9.5, 5.5 Hz, H8), 2.93 (dd, 1H, $J = 9.5$, 2.0 Hz, H5), 3.36 (m, 1H, H4), 3.62 (s, 3H, H10), 5.88 (dt, 1H, $J = 10.5$, 1.3 Hz, H2), 6.17 (t, 1H, $J = 2.3$ Hz), 6.30 (t, 1H, $J = 2.3$ Hz), 6.40 (t, 1H, $J = 2.3$ Hz), 6.43 (ddd, $J = 10.5$, 5.0, 2.0 Hz, H3), 7.55 (d, 1H, $J = 2.3$ Hz), 7.72 (d, 1H, $J = 2.3$ Hz), 7.82 (d, 1H, $J = 2.3$ Hz), 7.87 (d, 1H, $J = 2.3$ Hz), 7.90 (d, 1H, $J = 2.3$ Hz), 8.06 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR (CD_3CN): δ 13.1 (d, $J = 29$ Hz, PMe$_3$), 31.0 (s, C8), 37.9 (s, C7), 41.4 (s, C4), 52.4 (s, C10), 59.6 (s, C6), 64.3 (d, $J = 12$ Hz, C5), 106.8 (s), 107.8 (s), 108.4 (s), 130.1 (s), 137.7 (s), 138.3 (s), 138.7 (s), 142.3 (s), 144.4 (s), 144.8 (s), 144.8 (s), 175.6 (s, C1), 198.3 (s, C9).

TpW(NO)(PMe$_3$)(5,6-η^2-2-Benzylidenecyclohexa-3,5-dienone) (5a, 5b). TpW(NO)(PMe$_3$)(η^2-phenol) (**2a**,**b**) (0.824 g, 1.38 mmol), DBU (0.250 g, 1.64 mmol), and benzaldehyde (1.705 g, 16.9 mmol) were dissolved in 1 mL of CH_3CN and stirred for 42 h. The orange precipitate was filtered and washed with 1 mL of acetone and dried in vacuo (**5b**, 0.230 g, 24.3%). The filtrate was removed under vacuum. The resulting oil was dissolved in 1 mL of CH_2Cl_2 and added to Dowex 50 × 8−400 resin (0.998 g) and stirred for 30 min. The mixture was filtered and washed three times with 2 mL of CH_2Cl_2. The filtrate was evaporated under vacuum, and the resulting oil was dissolved in 2 mL of CH_2Cl_2 and added to 75 mL of pentane. The resulting orange precipitate was collected by filtration and was dried in vacuo (**5a**, 0.513 g, 54.3%). **5a**,**b**: Cyclic voltammetry: $E_{p,a} = +0.71$ V. IR: $\nu_{NO} = 1590$, $\nu_{CO} = 1621$ cm^{-1}. Anal. Calcd for $C_{25}H_{29}O_2N_7PBW\cdot H_2O$: C, 42.70; H, 4.44; N, 13.94. Found: C, 42.98; H, 4.22; N, 14.22. ESI/MS: 685 (M+). **5a**: ^{1}H NMR (d_6-acetone): δ 1.27 (d, 9H, $J = 9.3$ Hz, PMe$_3$), 2.38, (dd, 1H, $J = 8.0$, 5.5 Hz, H5), 3.78 (ddd, 1H, $J = 10.0$, 8.0, 1.0 Hz, H6), 6.11 (d, 1H, $J = 9.8$ Hz, H3), 6.31 (t, 1H, $J = 2.3$ Hz), 6.41 (t, 1H, $J = 2.3$ Hz), 6.43 (t, 1H, $J = 2.3$ Hz), 6.95 (dd, 1H, $J = 9.8$, 5.5 Hz, H4), 7.18 (t, 1H, $J = 7.7$ Hz, Ph), 7.22 (s, 1H, H7), 7.34 (t, 2H, $J = 7.7$ Hz, Ph), 7.61 (d, 2H, $J = 7.7$ Hz, Ph), 7.84 (d, 2H, $J = 2.3$ Hz), 8.01 (d, 2H, $J = 2.3$ Hz), 8.04 (d, 2H, $J = 2.3$ Hz), 8.12 (d, 2H, $J = 2.3$ Hz), 8.23 (d, 2H, $J = 2.3$ Hz). ^{13}C NMR (d_6-acetone): δ 13.9 (d, $J = 29$ Hz, PMe$_3$), 61.4 (s, C6), 62.3 (d, $J = 6$ Hz, C5), 107.1 (s), 107.7 (s), 108.2 (s), 116.5 (s, C3), 120.3 (d, $J = 20$ Hz, C4), 127.7 (s, C11), 127.9 (s), 129.3 (s, C10), 130.7 (s, C9), 132.3 (s),137.2 (s), 138.0 (s), 138.5 (s), 138.7 (s), 143.0 (s), 145.4 (s), 145. 6 (s), 197.9 (s, C1). ^{31}P NMR (d_6-acetone): δ −10.1 (s). **5b** ^{1}H NMR ($CDCl_3$): δ 1.27 (d, 9H, $J = 8.4$ Hz, PMe$_3$), 2.68 (d, 1H, $J = 9.0$ Hz, H6), 3.79 (m, 1H, H5), 6.21 (t, 1H, $J = 2.4$ Hz), 6.24 (d, 1H, $J = 9.3$ Hz, H3), 6.28 (t, 1H, $J = 2.4$ Hz), 6.34 (t, 1H, $J = 2.4$ Hz), 6.56 (dd, 1H, $J = 9.3$, 4.8 Hz, H4), 7.19 (t, 1H, $J = 7.5$ Hz, H11), 7.33 (t, 2H, $J = 7.5$ Hz, H10), 7.44 (d, 1H, $J = 2.4$ Hz), 7.53 (s, 1H, H7), 7.59 (d, 1H, $J = 2.4$ Hz), 7.63 (d, 2H, $J = 7.5$ Hz, H9), 7.74 (d, 1H, $J = 2.4$ Hz), 7.76 (d, 1H, $J = 2.4$ Hz), 7.82 (d, 1H, $J = 2.4$ Hz), 8.11 (d, 1H, $J = 2.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 13.8 (d, $J = 29$ Hz, PMe$_3$), 62.0 (s, C6), 63.3 (d, $J = 10$ Hz, C5), 106.0 (d, $J = 5$ Hz), 106.6 (d, $J = 5$ Hz), 107.2 (d, $J = 4$ Hz), 117.3 (d, $J = 5$ Hz, C3), 127.0 (s, C11), 128.0 (s, C7), 128.2 (s, C10), 131.3 (s, C9), 131.7 (s, C4), 134.5 (s, C2), 136.1 (s), 136.9 (s), 137.8 (s, C8), 140.3 (s), 142.3 (s), 144.0 (d, $J = 8.1$ Hz), 197.6 (s, C1). ^{31}P NMR (d_6-acetone): δ −9.5 (s).

TpW(NO)(PMe$_3$)(5,6-η^2-2-methyl-2*H*-phenol) (6). To a solution of **2** (0.149 g, 0.250 mmol) in 3.68 g of THF at −40 °C was added a 2.5 M solution of BuLi in hexanes (0.13 mL, 0.33 mmol). Iodomethane (0.977 g, 6.89 mmol) was added immediately. After 16 h the solution was warmed to room temperature, and the solvent was removed in vacuo. The residue was dissolved in 1.5 mL of THF, precipitated in 100 mL of pentane, and collected on a 15 mL medium-porosity fritted glass disk, yielding a crude product mixture (**6(a−d)**, 0.175 g). ESI/MS: 612 (MH+). Cyclic voltammetry: $E_{p,a} = +0.76$ V. Selected NMR data: ^{1}H NMR (d_6-acetone): minor isomer δ 4.82 (dd, 1H, $J = 9.6$, 2.7 Hz, H_3); minor isomer δ 4.85 (dd, 1H, $J = 9.6$, 2.7 Hz, H_3); minor isomer δ 5.28 (d, 1H, $J = 9.3$ Hz, H_6); major isomer δ 1.23 (d, 9H, $J = 8.4$ Hz, PMe$_3$), 5.33 (d, 1H, $J = 9.6$ Hz, H_6).

TpW(NO)(PMe$_3$)(5,6-η^2-2-ethyl-2*H*-phenol) (7). To a solution of **2a** and **2b** (0.255 g, 0.427 mmol) in THF (2 mL) and dimethoxymethane (5 mL) at −40 °C was added *n*-butyllithium (0.2 mL, 0.5 mmol, 2.5 M in hexanes). Ethyliodide (0.856 g, 5.52 mmol) at −40 °C in 0.5 mL of THF was immediately added. After 17 h the solvent was removed by evaporation in vacuo. The residue was dissolved in THF (1 mL) and added to stirring pentane (100 mL). The yellow-beige precipitate was collected by filtration using a 15 mL medium-porosity fritted glass disk, yielding a crude product mixture (**7**, 0.288 g). **7b**: Cyclic voltammetry: $E_{p,a} = +0.79$ V. ^{1}H NMR (d_6-acetone): δ 0.90 (t, 3H, $J = 7.4$ Hz, H_8), 1.26 (d, 9H, 7.4 Hz, PMe$_3$), 1.80 (m, 2H, H7), 1.99 (dm, 1H, $J = 8.6$ Hz, H6), 3.18 (br m, 1H, H2), 3.44 (m, 1H, H5), 4.88 (dd, 1H, $J = 9.6$, 2.4 Hz, H3), 6.17 (t, 1H, $J = 2.2$ Hz), 6.36 (t, 1H, $J = 2.2$ Hz), 6.46 (t, 1H, $J = 2.2$ Hz), 6.46 (buried m, 1H, H4), 7.71 (d, 1H, $J = 2.2$ Hz), 7.76 (d, 1H, $J = 2.2$ Hz), 7.91 (d, 1H, $J = 2.2$ Hz), 7.98 (d, 1H, $J = 2.2$ Hz), 8.01 (d, 1H, $J = 2.2$ Hz), 8.22 (d, 1H, $J = 2.2$ Hz). ^{13}C NMR (d_6-acetone): δ 11.9 (s, C_8), 13.9 (d,

J = 29, PMe_3), 25.7 (s, C7), 47.7 (s, C2), 59.2 (s, C6), 63.1 (d, J = 10, C5), 106.5 (s), 107.6 (s), 108.3 (s), 121.3 (s, C3), 129.8 (s, C4), 137.2 (s), 138.0 (s), 138.5 (s), 142.4 (s), 143.9 (s), 145.6 (s), 208.9 (s, C1). **7c**: ^{1}H NMR (d_6-acetone): δ 1.05 (t, 3H, J = 7.2 Hz), 1.23 (d, 9H, J = 8.7 Hz) 1.84 (m, 2H), 3.07 (dd, 1H, J = 11.7, 8.7 Hz), 3.30 (t, 1H, J = 6.3 Hz), 5.38 (d, 1H, J = 9.5 Hz), 6.30 (t, 1H, J = 2.1 Hz), 6.38 (t, 1H, J = 2.1 Hz), 6.43 (t, 1H, J = 2.1 Hz), 7.81 (d, 1H, J = 2.1 Hz), 7.83 (d, 1H, J = 2.1 Hz), 7.96 (dd, 1H, J = 9.5, 5.7 Hz), 8.00 (m, 2H), 8.04 (d, 1H, J = 2.1 Hz), 8.12 (d, 1H, J = 2.1 Hz). **7d**: IR: ν_{NO} = 1585, ν_{CO} = 1630 cm^{-1}. Cyclic voltammetry: $E_{p,a}$ = +0.70 V. ^{1}H NMR (d_6-acetone): δ 0.88 (t, 3H, J = 7.4 Hz, H_8), 1.28 (d, 9H, 8.5 Hz, PMe_3), 1.53 (dm, 1H, J = 9.8 Hz, H4), 1.65 (m, 2H, H7), 3.20 (m, 1H, H3), 3.30 (t, 1H, J = 6.9 Hz, H2), 5.26 (d, 1H, J = 9.5 Hz, H6), 6.32 (t, 1H, J = 2.2 Hz), 6.37 (t, 1H, J = 2.2 Hz), 6.40 (t, 1H, J = 2.2 Hz), 7.58 (ddd, 1H, J = 9.5, 5.1, 1.4 Hz, H5), 7.70 (d, 1H, J = 2.2 Hz), 7.84 (d, 1H, J = 2.2 Hz), 7.96 (d, 1H, J = 2.2 Hz),7.98 (d, 1H, J = 2.2 Hz), 8.01 (d, 1H, J = 2.2 Hz), 8.09 (d, 1H, J = 2.2 Hz). ^{13}C NMR (d_6-acetone): δ 12.4 (s, C7), 14.1 (d, J = 29 Hz, PMe3), 36.2 (s, C7), 52.5 (d, J = 8 Hz, C5), 53.7 (s, C2), 57.6 (s, C6), 107.1 (s), 107.6 (s), 107.9 (s), 118.9 (s), 137.5 (s), 137.7 (s), 138.3 (s), 142.5 (s), 142.6 (s), 145.2 (s), 153.8 (s), 200.1 (s, C1).

2-Methylphenol (8). To a mixture of **2** (0.502 g, 0.841 mmol) in 7 mL of THF at −40 °C was added *n*-butyllithium (0.44 mL, 1.1 mmol, 2.5 M in hexanes). Methyl iodide (1.166 g, 7.98 mmol) in 0.5 mL of THF at −40 °C was immediately added. After 19 h the reaction was warmed to room temperature and the solvent was evaporated. The residue was dissolved in 3 mL of CH_2Cl_2, and $CuBr_2$ (0.374 g, 1.67 mmol) was added. After 1 h the reaction was filtered and the solvent was evaporated. The product was isolated using a 20 cm SiO_2 column using a 1:9 solution of EtOAc/hexanes (v:v) as the eluent (0.025 g, 27% yield). The ^{1}H NMR was consistent with a spectrum of authentic *o*-cresol.

2-Ethylphenol (9). To a mixture of **2** (0.503 g, 0.843 mmol) in 7 mL of THF at −40 °C was added *n*-butyllithium (0.44 mL, 1.1 mmol, 2.5 M in hexanes). Ethyliodide (1.245 g, 7.98 mmol) in 0.5 mL of THF at −40 °C was immediately added. After 19 h the reaction was warmed to room temperature and the solvent was evaporated. The residue was dissolved in 3 mL of CH_2Cl_2, and $CuBr_2$ (0.374 g, 1.67 mmol) was added. After 1 h the reaction was filtered and the solvent was evaporated. The product was isolated by preparative TLC using a 20 × 20 cm, 1500 μM SiO_2 plate using a 1:4 solution of EtOAc/hexanes (v:v) as the eluent (0.030 g, 29% yield). R_f = 0.66. The ^{1}H NMR spectrum was consistent with the spectrum obtained from Sigma-Aldrich.[26]

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Supporting Information Available: Crystallographic details for compounds **5** and **7b** and spectra for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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