a way that it tends to stabilize an "anomalous" electronic distribution of the negative moiety, probably responsible for the "new" observed photoreactivity.

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**Registry No.** 1-Piperidino-5-(2-methoxy-4-nitrophenoxy)pentane, 136616-33-6; 1-piperidino-3-(2-methoxy-4-nitrophenoxy)propane, 136616-34-7; 1-piperidino-2-(2-methoxy-4-nitrophenoxy)ethane, 136616-35-8; 1-piperidino-5-(2-hydroxy-4-nitrophenoxy)pentane, 136616-36-9; 1-piperidino-5-(4-nitrophenoxy)pentane, 136616-37-0; 1-piperidino-2-(4-nitrophenoxy)ethane, 92033-76-6; 1-piperidino-3-(2-hydroxy-4-nitrophenoxy)propane, 136616-38-1; 2-methoxy-4-nitrophenol, 3251-56-7; 1,2-dimethoxy-4-nitrobenzene, 709-09-1; 4-nitrophenol, 100-02-7; 1-(dimethylamino)-2-(4-nitrophenoxy)ethane, 51344-13-9; 1-(dimethylamino)-5-(4-nitrophenoxy)pentane, 91905-11-2.

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# Electrophilic Substitutions on $\eta^2$-Coordinated Arenes: An Unprecedented Michael Addition for Phenol and Aniline

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Symmetrically bound arenes, such as in $[Mn(CO)_3(\eta^6\text{-benzene})]^+$, are activated toward nucleophilic attack, and the utility of these complexes in organic synthesis has been widely demonstrated.[1] Although $\eta^2$-arene species have been reported for several transition metals,[2] their propensity to dissociate or undergo oxidative addition usually precludes an investigation of the arene chemistry. $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$ and its derivatives are stable in this regard,[3] and their facile hydrogenation recently has been demonstrated.[4] Presently, we report a dramatic enhancement of electrophilic reactivity at the para position for anisoles, phenols, and anilines upon their $\eta^2$-coordination.

Crystallographic data have shown that arenes which are $\eta^2$-coordinated have partially localized $\pi$-electron systems.[5] Pentaammineosmium(II) forms complexes with anisole (**1**), phenol (**2**), and *N*,*N*-dimethylaniline (**3**) in which the metal is coordinated across $C_2$ and $C_3$.[3,6] Thus, the uncoordinated portion of the arene resembles a dienyl ether, a dienol, or a dienamine, respectively (Scheme I), and would be expected to undergo electrophilic substitution under milder conditions than the corresponding arene.

Treatment of $[Os(NH_3)_5(\eta^2\text{-anisole})](OTf)_2$ (**1**; 0.06 M) with $CH_3OTf$ (~1 M) in acetonitrile[7] yielded in a new species, **4**, whose $^1H$ and $^{13}C$ NMR,[8] NOE, and $^1H,^1H$-COSY data support the assignment of **4** as $[Os(NH_3)_5[(2,3\text{-}\eta)$-4-methoxy-*N*-methylacetophenone imine$]]^{2+}$, the direct reaction product of *N*-methylacetonitrilium addition to C4 of anisole followed by deprotonation (Scheme I). Exposure of an acetone solution of **4** to air and trace acid resulted in the decomposition of this complex to yield *p*-methoxyacetophenone in 93% yield.[9,10] Although nitrilium additions have been demonstrated for arenes containing electron-donating groups, these reactions are sluggish at room temperature, even at molar concentrations, and are reported to occur in low yield.[11] An acetonitrile solution of anisole (0.3 M) and $CH_3OTf$ (1.5 M) showed less than 5% reaction after 2 weeks.

An acetonitrile solution of the phenol complex (**2**) reacted with maleic anhydride to form **5** (85%),[12] a species whose $^1H$ NMR, $^{13}C$ NMR, and DEPT spectra reveal four olefinic methine, one methylene, and two aliphatic methine carbons. Cyclic voltammetric data of this product showed a reversible couple at 0.85 V (NHE), consistent with an electron-deficient olefinic ligand on pentaammineosmium(II).[13] Infrared data confirmed the integrity of the anhydride linkage and in addition revealed a band at 1641 $cm^{-1}$ consistent with other 2,5-dienone complexes of pentaammineosmium(II).[14] Judging from these data, we assign **5** as the (2,5-cyclohexadienonyl)succinic anhydride species shown in Scheme I, the product of a net Michael addition of the coordinated phenol at C4.[15] $^1H$ and $^{13}C$ data suggest the formation of a single diastereomer (>10:1), although the presence of a second isomer has not been ruled out. The small coupling constant between H3 and H4 ($J$ = 3 Hz) suggests a H4–C4–C3–H3 dihedral angle approaching 90° and the occurrence of Michael addition anti to the osmium, as shown in Scheme I. Refluxing **5** in acidic methanol resulted in the formation of the free diester, **6**,[16] as shown in Scheme I. A retro-Michael reaction hampered efforts to obtain **6** or its anhydride precursor in high yield as the crude organic product was accompanied by varying amounts of phenol and O-alkylated phenols not present prior to attempted esterification.[17]

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(6) The synthesis of $[Os(NH_3)_5(\eta^2\text{-phenol})]^{2+}$ is carried out in a manner similar to that of anisole and aniline as specified in ref 4. $^1H$ NMR (acetone-$d_6$): $\delta$ 8.65 (br. 1 H), 6.59 (t, 1 H), 6.36 (t, 1 H), 5.70 (d, 1 H), 5.32 (t, 1 H), 5.03 (d. 1 H), 4.70 (br, 3 H), 3.45 (br, 12 H). Anal. ($C_8H_{21}OsS_2F_6O_7N_5\cdot{}^1/_4$DMA) C, H, N (DMA = *N*,*N*-dimethylacetamide).

(7) An acetonitrile (1.10 g) solution of **1** (56.0 mg; 0.082 mmol) is treated with $CH_3OTf$ (300 mg; 1.83 mmol) and the solution allowed to stand for 10 min. Addition of $Et_2O$ precipitates **4**.

(8) Characterization of **4**: $^1H$ NMR (acetone-$d_6$): $\delta$ 7.86 (dd, 1 H, CH), 6.10 (dd, 1 H, CH), 5.86 (dd, 1 H, CH), 5.34 (dd, 1 H, CH), 5.02 (br, 3 H, *t*-$NH_3$), 3.95 (s, 3 H, $OCH_3$), 3.64 (br s, 12 H, c-$NH_3$), 3.36 (s, 3 H, $NCH_3$) 2.69 (s, 3 H, $COCH_3$). $^{13}C$ NMR: $\delta$ 184.1, 178.4, 142.5, 125.0, 95.6, 57.1, 53.2, 52.0, 33.0, 16.5. CV ($CH_3CN$; TBAH; 100 mV/s): $E_{1/2} = -0.10$ V.

(9) The $^1H$ NMR spectrum matches that of an authentic sample.

(10) No attempt has been made to recover the osmium in the present study, although an osmium(III) pentaammine precursor has been recovered in high yield for a related system. See ref 4.

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(12) An acetonitrile (1.10 g) solution of $[Os(NH_3)_5(\eta^2\text{-phenol})](OTf)_2$ (**2**) (148 mg; 0.22 mmol) and maleic anhydride (100 mg; 1.02 mmol) is allowed to stand for 20 h. Upon addition of ether (15 mL), an orange precipitate, **5**, is formed (85%). $^1H$ NMR (acetone-$d_6$): $\delta$ 6.60 (br d, 1 H), 6.05 (d, 1 H), 5.1 (br s, 3 H, *trans*-$NH_3$), 4.59 (d, 1 H), 4.42 (d, 1 H), 4.16 (m, 1 H), 3.78 (br s, 13 H, *cis*-$NH_3$, allylic CH), 3.32 (dd, 1 H), 2.83 (dd, 1 H). $^{13}C$ NMR: $\delta$ 198.8, 173.4, 170.7, 143.6, 134.1, 52.5, 51.6, 45.6, 40.0, 31.3. IR (KBr, $cm^{-1}$): 1865, 1782 [$(CO)_2O$], 1641.5 (CO). CV ($CH_3CN$, TBAH, 100 mV/cm): $E_{1/2}$ = +0.85 and +1.04 V (NHE).

(13) For the complex $[Os(NH_3)_5(\eta^2\text{-cyclohexenone})]^{2+}$, $E_{1/2}$ = +0.88 V (NHE, $CH_3CN$).

(14) Kopach, M. E.; Hipple, W. G.; Harman, W. D., manuscript in preparation.

(15) The mechanism for this reaction is currently under investigation.

(16) Characterization of **6**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.12 (d, 2 H, CH), 6.75 (d, 2 H, CH), 6.23 (br, 1 H, OH), 4.02 (dd, 1 H, CH), 3.16 (dd, 1 H, $CH_2$), 2.66 (dd, 1 H, $CH_2$); $^{13}C$ NMR $\delta$ 174.6, 172.9, 156.0, 129.3, 116.2, 52.9, 52.5, 46.7, 38.1; mp 68–69 °C; $M^+$ = 238; lit. mp 76–77 °C. Swain, G.; Todd, A. R.; Waring, W. S. *J. Chem. Soc.* **1944**, 548.

(17) Compound **5** was refluxed in methanol (variable reaction times and $[H^+]$) and the mixture partitioned between water and $CH_2Cl_2$. The crude organic product was eluted down silica with 1:3 ethyl acetate/ether. Overall yield (**6**): 20–40%.

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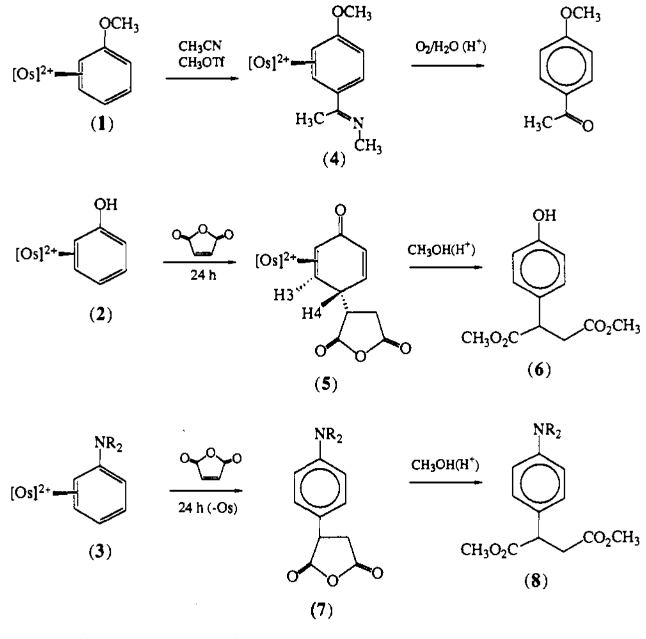
**Scheme I.** Summary of Electrophilic Substitutions Promoted by Pentaammineosmium(II)[a]



[a] $[Os]^{2+} = [Os(NH_3)_5]^{2+}$. R = $CH_3$, H. All reactions carried out at 20 °C in acetonitrile.

When N-substituted maleimides are substituted for maleic anhydride, the isolated yield of the succinyl product ranges from 60 to 80%.[18]

The aniline complex $[Os(NH_3)_5[(2,3\text{-}\eta)\text{-}N,N\text{-dimethylaniline}]](OTf)_2$ (69.5 mg, 0.1 mmol) (**3**) and maleic anhydride (9.8 mg, 0.1 mmol) were combined in $CD_3CN$ (0.5 mL), and the resulting solution was monitored by $^1$H NMR spectroscopy. After 15 min, a $^1$H NMR spectrum indicated a mixture of products, but a pattern of four doublets ranging from 5.5 to 6.4 ppm suggested that one of these species was an $\eta^2$-bound para-disubstituted arene, similar to the products **4** and **5**. Over the next day these peaks diminished, yielding an organic material, **7**, whose $^1$H and $^{13}$C NMR and infrared data are consistent with [4-(dimethylamino)phenyl]succinic anhydride.[19] Treatment of the reaction mixture with acidic methanol resulted in the diester derivative **8** in 50% overall yield from **3** (Scheme I).[20]

The conjugate addition of maleic anhydride to phenol or *N*,*N*-dimethylaniline is unprecedented even in the presence of a Lewis acid, where the dominant reaction is an acylation.[21] Even when the aniline derivative of **3** is employed, conjugate addition to the ring is competitive with N-acylation, resulting in a 30% isolated yield of the corresponding diester. A full investigation of electrophilic additions and substitutions on $\eta^2$-arene complexes and the optimization of resulting organic products is currently in progress.

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[18] Treatment of **2** with 1 equiv of *N*-phenylmaleimide followed by oxidation results in >80% of (4-hydroxyphenyl)-*N*-phenylsuccinimide (yield not optimized).

[19] Characterization of **7**: $^1$H NMR ($CDCl_3$) δ 7.10 (d, 2 H, CH), 6.71 (d, 2 H, CH), 4.23 (dd, 1 H, CH), 3.4 (dd, 1 H, $CH_2$), 3.1 (dd, 1 H, $CH_2$), 2.96 (s, 6 H, $CH_3$); $^{13}$C NMR δ 173, 170, 151, 128, 122, 113, 46, 41, 37; IR ($CD_3CN$) 1861, 1788 cm$^{-1}$.

[20] Characterization of **8**: $^1$H NMR ($CDCl_3$) δ 7.13 (d, 2 H, CH), 6.67 (d, 2 H, CH), 3.99 (dd, 1 H, CH), 3.663 (s, 3 H, $CH_3O$), 3.660 (s, 3 H, $CH_3O$), 3.15 (dd, 1 H, $CH_2$), 2.93 (s, 6 H, $NCH_3$), 2.63 (dd, 1 H, $CH_2$); $^{13}$C NMR 174.4, 172.7, 150.4, 125.6, 113.1, 52.6, 52.2, 46.5, 40.9, 38.2; $M^+$ = 265; mp = 73-74 °C. Anal. ($C_{14}H_{19}NO_4$) C, H, N; C: calcd 63.38; found, 62.84.

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# Geometrical Aspects of the Activation of Enones by Titanium Tetrachloride: Diels-Alder Reactions

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A critical element in the rational design of chiral Lewis acids for effecting stereoselective cycloaddition reactions to achiral enones is an understanding of the geometry of the reactive enone-Lewis acid complex.[1,2] Experimental[3,4] and theoretical[5] studies indicate that an in-plane coordination geometry to carbonyls is thermodynamically preferred for the Lewis acids commonly employed by organic chemists. However, the thermodynamically favored geometry of a molecule or complex is not necessarily the same as the reactive geometry (cf. the Curtin-Hammett principle[6]).

To investigate the nature of the *reactive* geometry of enone-Lewis acid complexes in Diels-Alder reactions, we have examined the relative rate of reaction of cyclopentadiene with $TiCl_4$ complexes of diastereomeric 1-(methoxymethyl)-1-propylhexahydronaphthalen-2-ones **1a** and **1e**. Methoxymethyl groups in **1a** and **1e** are oriented to direct complexation to the π-system and to the plane of the carbonyl, respectively.[7] *n*-Propyl groups are included to minimize conformational differences between the compounds.

Molecular models[8] of **1a**·$TiCl_4$ indicate that while π-coordination of a chelated titanium is geometrically reasonable, in-plane complexation to a *planar* enone is unlikely. In **1e**·$TiCl_4$, complexation could occur either in the plane of the carbonyl or in the π-system on the α-face; however, in the latter position it would block any Diels-Alder reaction from the α-face. $TiCl_4$ seemed to be an apt choice for the activating Lewis acid; while a number

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