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Easy Access to Bio-Inspired Osmium(II) Complexes through Electrophilic Intramolecular C(sp^2)-H Bond Cyclometalation

Ricardo Cerón-Camacho,[†] David Morales-Morales,[†] Simon Hernandez,[†] Ronan Le Lagadec,*[,†] and Alexander D. Ryabov[‡]

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, 04511 México DF, Mexico, and Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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Mild electrophilic C(sp^2)-H cyclometalation of 2-phenylpyridine and *N,N*-dimethylbenzylamine by the chloro-bridged osmium(II) dimer $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ in acetonitrile affords cyclometalated pseudotetrahedral Os^{II} complexes $[Os(C\sim N)(\eta^6\text{-}C_6H_6)(NCMe)]PF_6$ (C∼*N* = *o*-C_6H_4py-$\kappa C,N$ (**2**) and *o*-$C_6H_4CH_2NMe_2$-$\kappa C,N$ (**5**), respectively) in good to excellent yields. The cyclometalation reactions are super sensitive to the nature of an external base. Sodium hydroxide is essential for cyclometalation of 2-phenylpyridine, but NaOH retards metalation of *N,N*-dimethylbenzylamine, the tertiary amine being self-sufficient as a base. Further reactions of compounds **2** and **5** with 1,10-phenanthroline or 2,2′-bipyridine (N∼N) lead to the substitution of the η^6-bound benzene to produce octahedral species $[Os(C\sim N)(N\sim N)(NCMe)_2]PF_6$ or $[Os(C\sim N)(N\sim N)_2]PF_6$ in MeCN or MeOH as solvent, respectively. The cis configuration of the MeCN ligands in $[Os(C\sim N)(phen)(NCMe)_2]PF_6$ has been confirmed by an X-ray crystallographic study. Electrochemical investigation of the octahedral osma(II)cycles by cyclic voltammetry showed a pseudoreversible $M^{III/II}$ redox feature at (−50)−(+109) and 190−300 mV versus Ag/AgCl in water and MeCN, respectively. As a possible application of the compounds, a rapid electron exchange between the reduced active site of glucose oxidase enzyme from *Aspergillus niger* and the electrochemically generated Os^{III} species has been demonstrated. The corresponding second-order rate constants cover the range $(0.7-4.8) \times 10^6$ M^{-1} s^{-1} at 25 °C and pH 7.

Introduction

Intramolecular cleavage of C−H bonds by osmium complexes to produce cyclometalated compounds is a matter of precedent.[1−8] The reported examples of synthesis of bidentate C∼N osmacycles through C−H bond cleavage are limited.[9−15] Most of cyclometalated osmium compounds are synthesized through transmetalation of ortho-mercurated aryl derivatives thus eliminating the most challenging C−H bond activation step.[10,16] When osmium compounds do cyclom-

* To whom correspondence should be addressed. E-mail: ronan@servidor.unam.mx.
† Universidad Nacional Autónoma de México.
‡ Carnegie Mellon University.

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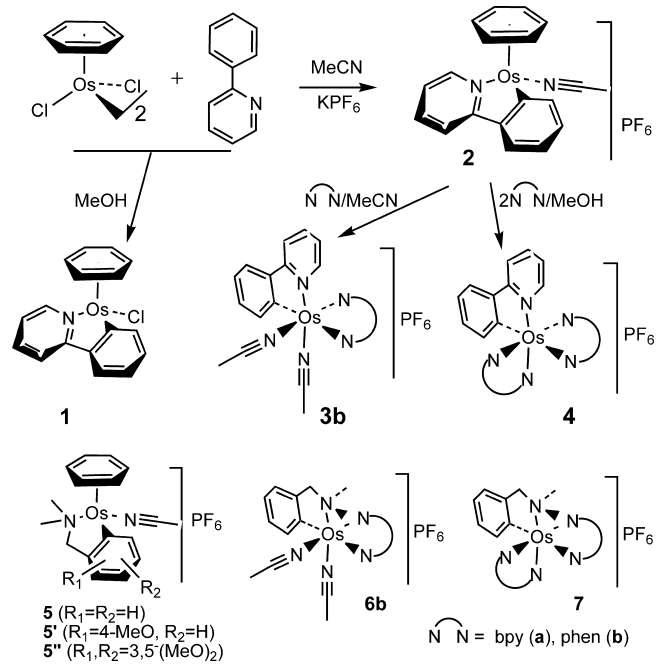
etalate C−H bonds to form bidentate metalacycles, the C−H bond cleavage occurs predominantly via the oxidative addition mechanism involving d^6 osmium(II) reactive species.[15] The oxidative addition usually requires rather sophisticated osmium compounds for an easy generation of coordinatively unsaturated intermediates.[1] For example, Esteruelas et al. recently reported density-functional theory (DFT) mechanistic studies of the intramolecular activation of methyl C(sp^3)−H bonds of 8-methylquinoline or 2-(dimethylamino)pyridine by the eight-coordinated hexahydride $OsH_6(P^iPr_3)_2$ which starts with the dissociation of two H_2 molecules to produce Os^{II} species followed by oxidative addition of the C−H bond to form trihydride seven-coordinated osma(IV)cycles.[15] However this exciting chemistry might not be synthetically appealing as a route to cyclometalated bidentate osmium complexes because of its complexity.

Electrophilic cyclometalation of C−H bonds by transition metal complexes is less demanding. It requires simpler starting compounds and is therefore a handier synthetic procedure.[1,17–19] Partially because of this ease, the chemistry of bidentate pallada-, platina-, and ruthenacycles has developed extensively, and the compounds have found various applications.[18,20–24] Therefore, the addition of osmium to the electrophilic cyclometalation list is a tempting challenge, and this work reports on the successful cycloosmation of 2-phenylpyridine and *N,N*-dimethylbenzylamine using the common osmium(II) chloro-bridged dimer $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ as starting material.

The present work emerged from our previous investigations[25] aimed at the synthesis of cyclometalated osmium(II) compounds structurally identical to the corresponding Ru^{II} metalacyles,[26,27] which proved to be versatile electron shuttles between the active sites of several oxidoreductases and the electrode.[28] In the earlier work, we have found that the dimer $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ reacts with symmetric ortho-mercurated 2-phenylpyridine to obtain **1**, a precursor to targeted compounds of type **5** (Scheme 1). Compound **1** could also be synthesized through the direct C−H cyclometalation of 2-phenylpyridine though in a very low yield.[25] We are pleased to report here that the mercury-involved transmetalation pathway should now be abandoned and replaced by the much "greener"[29] synthesis via electrophilic cyclometalation of C(sp^2)−H bonds. X-ray structural characterization of representative osma(II)cycles, tentative mechanistic considerations, and electrochemical and bioelectrochemical properties of new compounds with respect to glucose oxidase (GO) from *Aspergillus niger* are also described within.

Scheme 1. Synthetic Procedures Used for Synthesis of 2-Phenylpyridine Complexes **1**−**4**; Corresponding Procedures Applied to *N,N*-Dimethylbenzylamine Afford **5**−**7**



Experimental Section

General Information. All experiments were performed under dry argon using Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. *N,N*-dimethylbenzylamine, 2-phenylpyridine, potassium hexafluorophosphate, tetra-*n*-butylammonium hexafluorophosphate, 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 1,3-cyclohexadiene, and glucose oxidase from *A. niger* (type VII) were purchased from Sigma Aldrich Chemical and were used as received. Sodium hexachloroosmate(IV) was purchased from Strem Chemicals and converted into $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ as described elsewhere.[30] Substituted *N,N*-dimethylbenzylamines were prepared according to the literature procedures.[31] The activity of glucose oxidase in terms of catalytically active FAD was determined spectrophotometrically using the extinction coefficient of $1.31 \times 10^4\ M^{-1}\ cm^{-1}$ at 450 nm.[32] All NMR spectra were recorded on a JEOL GX300 (^1H at 300.53 MHz) spectrometer in CD_3CN. Chemical shifts (δ) are in ppm and referenced to the residual solvent peaks. Coupling constants (J) are in Hz. The adopted numbering schemes are shown in Chart 1. Mass spectra (FAB^+) were obtained using a JEOL JMS-SX102A instrument with *m*-nitrobenzyl alcohol as a matrix. IR spectra were recorded on a Bruker-Tensor 27 FT-IR apparatus (KBr disks, diffuse reflection

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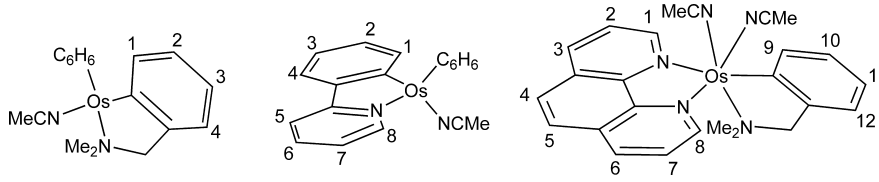
Chart 1. Carbon Numbering for Osmium Complexes Adopted in This Work



mode). Elemental analyses were carried out by USAI-UNAM on an EA 1108 FISONS Instruments analyzer.

Electrochemical measurements were performed on a PC-interfaced potentiostat-galvanostat AUTOLAB PGSTAT 12. A three-electrode setup was used with a BAS working glassy carbon electrode, Ag/AgCl reference electrode, and auxiliary Pt electrode. Before each measurement, the working electrode was polished with a diamond paste and rinsed with acetone and distilled water. Anodic peak currents (i_o) were obtained from cyclic voltammograms in the absence of the enzyme. Catalytic currents (i_{cat}) were obtained in the presence of GO and D-glucose under nitrogen. The rate constants, k_3, were calculated from the slopes of linear plots of the ratio i_{cat}/i_o against $([GO]/v)^{1/2}$ (v is the scan rate), as originally described elsewhere[33] and applied in our previous studies.[25,26,34,35]

[OsCl(o-C_6H_4py-κC,N)(η^6-C_6H_6)] (1). To a suspension of [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ (50 mg, 0.0735 mmol) in 15 mL of methanol was added 2-phenylpyridine (23 μL, 0.162 mmol). The mixture was refluxed for 24 h. The solvent was evaporated under vacuum, and the residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered through Al_2O_3, using CH_2Cl_2 as eluent. The bright yellow fraction was collected and concentrated to about 1 mL. Crystallization from CH_2Cl_2/diethylether (slow diffusion) gave yellow crystals, which were washed with diethylether and dried under vacuum (40 mg, 59%). ^{1}H NMR: 9.20 (d, 1H, ^3J = 5.2, H-8), 8.12 (d, 1H, ^3J = 7.4, H-1), 7.82 (d, 1H, ^3J = 8.2, H-4), 7.69 (m, 2H, H-6 + H-7), 7.16 (dd, 1H, ^3J = 8.1, ^4J = 1.3, H-5), 7.03 (m, 2H, H-2 + H-3), 5.57 (s, 6H, C_6H_6). MS-FAB$^+$: 459 (20%) [M + H]$^+$, 424 (18%) [(M + H) − Cl]$^+$, 381 (5%) [(M + H) − C_6H_6]$^+$.

[Os(o-C_6H_4py-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 (2). To a suspension of [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ (100 mg, 0.147 mmol), NaOH (12 mg, 0.294 mmol) and KPF_6 (91 mg, 0.588 mmol) in 15 mL of acetonitrile was added 2-phenylpyridine (49 μL, 0.294 mmol). The mixture was stirred at 40 °C for 48 h. The solvent was evaporated under vacuum, and the dark residue was dissolved in 20 mL of CH_2Cl_2. The solution was filtered through Al_2O_3, using a 10:1 CH_2Cl_2/NCMe mixture as eluent. The bright yellow fraction was collected and concentrated to about 1 mL. Addition of 10 mL of diethyl ether caused precipitation of a yellow solid (95 mg, 54%). ^{1}H NMR: 9.20 (dd, 1H, ^3J = 6.6, ^4J = 0.8, H-8), 8.09 (dd, 1H, ^3J = 6.3, ^4J = 0.5, H-5), 8.03 (dd, 1H, ^3J = 8.3, ^4J = 0.8, H-1), 7.93 (td, 1H, ^3J = 8.3, ^4J = 1.7, H-7), 7.84 (dd, 1H, ^3J = 7.2, ^4J = 1.7, H-4), 7.25−7.13 (m, 3H, H-2 + H-3 + H-6), 5.79 (s, 6H, C_6H_6), 2.23 (s, 3H, NCMe). MS-FAB$^+$: 569 (2%) [(M + H) − NCMe]$^+$, 465 (18%), 424 (44%) [(M + H) − (NCMe + PF_6)]$^+$. IR (cm^{-1}): 2287 (weak, $\nu_{N\equiv C}$), 837 (strong, ν_{PF6}). Anal. Calcd for $C_{19}H_{17}F_6N_2OsP\cdot 0.5CH_2Cl_2$: C, 35.98; H, 2.79; N, 4.30. Found: C, 36.15; H, 2.85; N, 4.38%.

[Os(o-$C_6H_4CH_2NMe_2$-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 (5). To a suspension of [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ (50 mg, 0.073 mmol) and KPF_6 (27 mg, 0.147 mmol) in 10 mL of acetonitrile was added *N,N*-dimethylbenzylamine (0.2 mL,1.33 mmol). The mixture was stirred at 30 °C for 24 h. The solvent was evaporated under vacuum, and the dark residue was dissolved in 10 mL of dichloromethane. The solution was filtered through Al_2O_3 using a 10:1 CH_2Cl_2/NCMe mixture as eluent. The bright yellow fraction was collected and concentrated to about 1 mL. Addition of diethyl ether (ca. 10 mL) caused precipitation of a yellow solid (69 mg, 83%). ^{1}H NMR: 7.94 (dd, 1H, ^3J = 6.0, H-1), 7.10 (m, 1H, H-4), 6.96 (m, 2H, H-2 + H-3), 5.67 (s, 6H, C_6H_6), 3.94 (d, 1H ^2J = 13.7, CH_2), 3.54 (d, 1H, ^2J = 13.7, CH_2), 3.18 (s, 3H, NMe_2), 2.94 (s, 3H, NMe_2), 2.14 (s, 3H, NCMe). MS-FAB$^+$: 445 (5%) [(M + H) − PF_6]$^+$, 404 (20%) [(M + H) − (NCMe + PF_6)]$^+$. IR (cm^{-1}): 2284 (weak, $\nu_{N\equiv C}$), 842 (strong, ν_{PF6}). Anal. Calcd for $C_{17}H_{21}F_6N_2OsP\cdot 2CH_2Cl_2$: C, 30.09; H, 3.32; N, 3.60. Found: C, 29.02; H, 2.80; N, 3.74%.

[Os(o-4-MeO$C_6H_3CH_2NMe_2$-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 (5′). [Os(o-4-MeO$C_6H_3CH_2NMe_2$-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 was obtained using the same procedure from [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ (20 mg, 0.0294 mmol), KPF_6 (11 mg, 0.0588 mmol), and 4-MeO-*N,N*-dimethylbenzylamine (9 mg, 0.052 mmol) in 28% (26 mg) yield. RMN ^{1}H: 7.50 (s, 1H, H-1), 7.03 (d, 1H, ^3J = 7.9, H-2), 6.55 (dd, 1H, ^3J = 8.2, ^4J = 1.9, H-3), 5.69 (s, 6H,C_6H_6), 3.93 (d, 1H, ^2J = 13.7, CH_2), 3.78 (s, 3H, OMe), 3.51 (d, 1H, ^2J = 13.7, CH_2), 3.14 (s, 3H, Me), 2.95 (s, 3H, Me), 1.96 (s, 3H, NCMe). MS-FAB$^+$: 618 (<1%) [(M + H)]$^+$, 473 (<5%) [(M + H) - PF_6]$^+$, 732 (100%) [(M + H) - (NCMe + PF_6)]$^+$. IR: 837 (strong, ν_{PF6})

[Os(o-3,5-$(MeO)_2C_6H_2CH_2NMe_2$-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 (5″). [Os(o-3,5-$(MeO)_2C_6H_2CH_2NMe_2$-κC,N)(η^6-C_6H_6)(NCMe)]PF_6 was obtained using the same procedure from [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ (20 mg, 0.0294 mmol), KPF_6 (11 mg, 0.0588 mmol), and 3,5-bis-MeO-*N,N*-dimethylbenzylamine (11 mg, 0.052 mmol) in 21% (8 mg) yield. RMN ^{1}H 6.40 (d, 1H, ^4J = 2.1, H-2), 6.29 (d, 1H, ^4J = 2.4, H-4), 5.80 (s, 6H, C_6H_6), 3.93 (d, 1H, ^2J = 13.8, CH_2), 3.84 (s, 3H, 3-OCH_3), 3.73 (s, 3H, 5-OCH_3), 3.56 (d, 1H, ^2J = 13.8, CH_2), 3.15 (s, 3H, Me), 2.91 (s, 3H, Me), 1.96 (s, 3H, NCMe). MS-FAB$^+$: 650 (1%) [(M + H)]$^+$, 505 (<5%) [(M + H) − PF_6]$^+$, 464 (80%) [(M + H) − (NCMe + PF_6)]$^+$. IR: 839 (strong, ν_{PF6}).

[Os(o-$C_6H_4CH_2NMe_2$-κC,N)(phen)(NCMe)$_2$]PF_6 (6b). A solution of **5** (30 mg, 0.051 mmol) with 1,10-phenanthroline (9 mg, 0.051 mmol) in acetonitrile (10 mL) was stirred at room temperature for 72 h. The solvent was evaporated under vacuum, and the dark brown residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered through Al_2O_3 using a 10:0.5 CH_2Cl_2/NCMe mixture as eluent. The purple fraction was collected and evaporated to dryness under vacuum. Crystallization from acetone/pentane (slow diffusion) gave dark purple crystals, which were washed with pentane and dried under vacuum (22 mg, 59%). ^{1}H NMR: 9.52 (d, 1H, ^3J = 5.2, H-8), 8.91 (d, 1H, ^3J = 5.5, H-1), 8.34 (d, 1H, ^3J = 8.3, H-6), 8.10 (dd, 3H, ^3J = 8.8, H-3 + H-4 + H-5), 7.96 (m, 1H, H-9), 7.54 (dd, 2H, ^3J = 5.5), 7.14 (dd, 2H, ^3J = 7.1, H-10 + H-11), 6.76 (dd, 1H, ^3J = 7.1, H-12), 4.14 (d, 1H, ^2J = 13.5, CH_2),

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3.52 (d, 1H, ^2J = 13.5, CH_2), 2.98 (s, 3H, Me), 2.34 (s, 3H, Me), 2.26 (s, 3H, NCMe), 2.14 (s, 3H, NCMe). MS-FAB$^+$: 733 (19%) $[(M + H)]^+$, 588 (60%) $[(M + H) - PF_6]^+$, 547 (5%) $[(M + H) - NCMe]^+$, 504 (90%) $[(M + H) - 2\ NCMe]^+$ IR (cm^{-1}): 2260 (medium, $\nu_{N\equiv C}$), 845 (strong, ν_{PF6}). Anal. Calcd for $C_{25}H_{26}F_6N_5OsP$: C, 41.04; H, 3.58; N, 9.57. Found: C, 40.85; H, 3.53; N, 9.05%.

[Os(o-C_6H_4py-κC,N)(phen)(NCMe)$_2$]PF_6 (3b). A solution of **2** (40 mg, 0.068 mmol) with 1,10-phenanthroline (15 mg, 0.082 mmol) in acetonitrile (10 mL) was refluxed for 48 h. The solvent was evaporated under vacuum, and the dark brown residue was dissolved in 10 mL of CH_2Cl_2 and filtered through Al_2O_3 using a 10:0.5 CH_2Cl_2/NCMe mixture as eluent. The purple fraction was collected and evaporated to dryness under vacuum. Crystallization from CH_2Cl_2/pentane or acetone/pentane (slow diffusion) gave dark purple crystals, which were washed with diethyl ether and dried under vacuum (33 mg, 64%). ^{1}H NMR: 9.55 (d, 1H, ^3J = 5.2), 8.49 (d, 1H, ^3J = 7.9), 8.17−7.90 (m, 6H), 7.82 (d, 1H, ^3J = 7.7), 7.37−7.27 (m, 3H), 7.05 (d, 1H, ^3J = 5.5), 2.84 (s, 3H, Me), 2.38 (s, 3H, Me). MS-FAB$^+$: 753 (10%) $[(M + H)]^+$, 608 (45%) $[(M + H) - PF_6]^+$, 526 (43%) $[(M + H) - (2\ NCMe + PF_6)]^+$. IR ($cm^{-1}$): 2361, 2249 (medium, $\nu_{N\equiv C}$), 843 (strong, ν_{PF6}). Anal. Calcd for $C_{27}H_{22}F_6N_5OsP\cdot 0.5CH_2Cl_2$: C, 41.59; H, 2.92; N, 8.82. Found: C, 41.69; H, 2.91; N, 8.64%.

General Method of Synthesis of Complexes 4 and 7. A solution of **2** or **5** with 1,10-phenanthroline or 2,2′-bipyridine in methanol (10 mL) was refluxed for 24 h (except 48 h for **7a**). The solvent was evaporated under vacuum, and the dark brown residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered through Al_2O_3 using a 90:10 CH_2Cl_2/NCMe mixture as eluent. The purple fraction was collected and evaporated to dryness under vacuum. Crystallization from acetone/pentane or dichloromethane/pentane (slow diffusion) gave dark purple microcrystals, which were washed with pentane and dried under vacuum

[Os(o-$C_6H_4CH_2NMe_2$-κC,N)(phen)$_2$]PF_6 (7b). [Os(o-$C_6H_4CH_2$-NMe_2-κC,N)(phen)$_2$]PF_6 was obtained from **5** (40 mg, 0.068 mmol) and 1,10-phenanthroline (27 mg, 0.149 mmol) in 78% yield (44 mg). ^{1}H NMR: 9.72 (d, 1H, ^3J = 5.5), 9.12 (d, 1H, ^3J = 4.9), 8.36 (d, 1H, ^3J = 4.4), 7.29−7.58 (m, 11H), 7.45 (m, 1H), 6.95 (dd, ^3J = 5.5, 2H), 6.56−6.52 (m, 2H), 5.91 (d, ^3J = 6.6, 1H), 4.99 (d, 1H, ^2J = 14.3), 3.63 (d, 1H, ^2J = 14.3), 2.70 (s, 3H, Me), 2.16 (s, 3H, Me). MS-FAB$^+$: 831 (1%) $[(M + H)]^+$, 686 (18%) $[(M + H) - PF_6]^+$, 552 (4%) $[(M + H) - (dmba + PF_6)]^+$. IR ($cm^{-1}$): 843 (strong, ν_{PF6}). Anal. Calcd for $C_{33}H_{28}F_6N_5OsP$: C, 47.76; H, 3.40; N, 8.44. Found: C, 47.87; H, 3.52; N, 8.63%.

[Os(o-$C_6H_4CH_2NMe_2$-κC,N)(bpy)$_2$]PF_6 (7a). [Os(o-$C_6H_4CH_2$-NMe_2-κC,N)(bpy)$_2$]PF_6 was obtained from **5** (30 mg, 0.053 mmol) and 2, 2′-bipyridine (17 mg, 0.112 mmol) in 36% yield (15 mg). ^{1}H NMR: 9.31 (d, 1H, ^3J = 5.5), 8.81 (dd, 1H, ^3J = 5.8, ^4J = 0.55), 8.44 (d, 1H, ^3J = 8.3), 8.38 (d, 1H, ^3J = 8.3), 8.16−8.10 (m, 2H), 8.04 (d, 1H, ^3J = 7.9), 7.72 (ddd, 1H, ^3J = 7.5, ^4J = 1.4), 7.64 (ddd, 1H, ^3J = 7.5, ^4J = 1.4), 7.56 (ddd, 1H, ^3J = 7.6, ^4J = 1.4), 7.47−7.30 (m, 4H), 7.20 (ddd, 1H, ^3J = 7.2, ^4J = 1.4), 6.88 (d, 1H, ^3J = 7.4), 6.77 (ddd, 1H, ^3J = 7.4, ^4J = 1.4), 6.72−6.67 (m, 1H), 6.56 (ddd, 1H, ^3J = 7.4, ^4J = 1.4), 5.87 (dd, 1H, ^3J = 6.0, ^4J = 1.1), 4.79 (d, 1H, ^2J = 14.0), 3.54 (d, 1H, ^2J = 14.0), 2.56 (s, 3H, Me), 2.14(s, 3H, Me). MS-FAB$^+$: 638 (5%) $[(M + H) - PF_6]^+$, 504 (<5%) $[(M + H) - dmba]^+$. IR (cm^{-1}): 843 (strong, ν_{PF6}). Anal. Calcd for $C_{29}H_{28}F_6N_5OsP$: C, 44.55; H, 3.61; N, 8.96. Found: C, 44.57; H, 3.65; N, 8.20%.

[Os(o-C_6H_4py-κC,N)(phen)$_2$]PF_6 (4b). [Os(o-C_6H_4py-κC,N)-(phen)$_2$]PF_6 was obtained from **2** (35 mg, 0.057 mmol) and 1,10-phenanthroline (23 mg, 0.127 mmol) in 82% yield (40 mg). ^{1}H NMR: 8.36 (d, 1H, ^3J = 4.7), 8.24 (d, 1H, ^3J = 8.3), 8.12−7.87 (m, 12H), 7.76 (d, 1H, ^3J = 5.2), 7.58−7.45 (m, 4H), 7.28−7.18 (m, 2H), 6.72−6.60(m, 3H). MS-FAB$^+$: 851 (5%) $[(M + H)]^+$, 706 (58%) $[(M + H) - PF_6]^+$, 526(9%) $[(M + H) - (phen + PF_6)]^+$. IR ($cm^{-1}$): 843 (strong, ν_{PF6}). Anal. Calcd for $C_{35}H_{24}F_6$-$N_5OsP.CH_2Cl_2$: C, 46.26; H, 2.80; N, 7.49. Found: C, 46.36; H, 3.22; N, 7.69%.

[Os(o-C_6H_4py-κC,N)(bpy)$_2$]PF_6 (4a). [Os(o-C_6H_4py-κC,N)-(bpy)$_2$]PF_6 was obtained from **2** (35 mg, 0.057 mmol) and 2,2-bipyridine (23 mg, 0.127 mmol) in 68% yield (37 mg). ^{1}H NMR: 8.38−8.31 (m, 2H), 8.26 (m, 2H), 8.02−7.97 (m, 1H), 7.79−7.75 (m, 3H), 7.64 (m, 1H), 7.57−7.46 (m, 4H), 7.34 (m, 1H), 7.26−7.21 (m, 3H), 6.87−6.75 (m, 3H), 6.15 (m, 1H). MS-FAB$^+$: 803 (<5%) $[(M + H)]^+$, 658 (52%) $[(M + H) - PF_6]^+$, 502 (15%) $[(M + H) - (bpy + PF_6)]^+$. IR ($cm^{-1}$): 842 (strong, ν_{PF6}). Anal. Calcd for $C_{31}H_{24}F_6N_5OsP$: C, 46.44; H, 3.02; N, 8.74. Found: C, 46.05; H, 3.19; N, 8.65%.

X-Ray Structural Study of Complexes 3b, 5, and 6b. Diffraction intensities data were collected with a SMART APEX diffractometer equipped with a graphite monochromated Mo Kα radiation and a CCD area detector at room temperature. The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3 in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package[36] using a narrow-frame integration algorithm. The intensity data were corrected by Lorentz and polarization effects, and an analytical absorption correction was applied in all cases. The data integration was done using a monoclinic unit cell for **3b** and **5**, triclinic for **6b** to yield a total of 15454, 10529, and 13233 reflections for **5**, **3b**, and **6b**, respectively, of which 3391 to **5**, 4597 to **3b**, and 5798 to **6b** were independent. Analysis of the data showed negligible decay during the data collection in all cases. The structures were solved by Patterson method using the SHELXS-97[37] program, completed by subsequent difference Fourier synthesis map, and refined by full matrix least-squares procedures on F^2. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the aromatic groups using U_{eq} = 1.2 Å and U_{eq} = 1.5 Å for methyl groups to precedent atom in all cases. For all complexes, the final cycle of refinement was carried out on all nonzero data using SHELXL-97 and anisotropic thermal parameters for all non-hydrogen atoms. The structures have incorporated solvent molecules, which were refined isotropically. The distorted anions PF_6^- in all crystal structures were modeled and refined anistropically in two major contributors. Compound **6b** was solved in the noncentrosymmetric monoclinic spatial group *Cc*. The solution in the monoclinic *C*2/*c* group was not possible and various factors such as E^2-1, the Flack parameter for absolute configuration of −0.003(1), and the packing of the molecules allowed us to assign the noncentrosymmetric *Cc* spatial group. All calculations were performed using the SHELXTL (6.12) program package. Additional details are summarized in Table 1.

Results and Discussion

Electrophilic C−H Cyclometalation of 2-Phenylpyridine and *N,N*-Dimethylbenzylamine. The synthetic procedures described in this work are shown in Scheme 1 by the example of the cyclometalation and derivatization of 2-phenylpyridine. These lead to osmacycles **1**−**4**. Essentially, the same

(36) *AXS, SAINT Software Reference Manual*; Bruker: Madison, WI, 1998.
(37) Sheldrick, G. M. *SHELXTL (Version 6.10). Bruker AXS Inc*; Madison, WI, 2000.

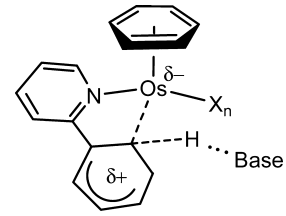
Table 1. Crystallographic Data for Compounds **5**, **6b**, and **3b**

	5	**6b**	**3b.acetone**
empirical formula	$C_{17}H_{21}N_2OsPF_6$	$C_{25}H_{26}F_6N_5OsP$	$C_{30}H_{28}F_6N_5OOsP$
formula weight	588.53	731.68	809.74
temperature (K)	291(2)	291(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	Cc	$P2(1)/c$
unit cell dimensions (in Å and °)	$a = 10.8424(12)$, $\alpha = 90$ $b = 12.7042(13)$, $\beta = 95.302(2)$ $c = 14.0603(15)$, $\gamma = 90$	$a = 11.2693(7)$, $\alpha = 90$ $b = 12.4643(8)$, $\beta = 96.271(10)$ $c = 18.8585(12)$, $\gamma = 90$	$a = 9.9527(7)$, $\alpha = 101.997(10)$ $b = 12.0274(9)$, $\beta = 90.836(10)$ $c = 14.3999(11)$, $\gamma = 100.940(10)$
volume (Å^3)	1928.4(4)	2633.1(3)	1652.8(2)
Z	4	4	2
density (mg/m^3, calculated)	2.027	1.846	1.627
absorption coeff. (mm^{-1})	6.755	4.971	3.970
$F(000)$	1128	1424	792
crystal size (mm)	0.24 × 0.12 × 0.06	0.03 × 0.09 × 0.07	0.32 × 0.11 × 0.11
θ range for data collection (°)	2.16 to 25.00	2.17 to 25.00	1.77 to 25.00
index ranges	$-12 \le h \le 12$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-13 \le h \le 13$ $-14 \le k \le 14$ $-22 \le l \le 22$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-17 \le l \le 17$
reflections collected	15454	10529	13233
independent reflections	3391 [R(int) = 0.0375]	4597 [R(int) = 0.0403]	5798 [R(int) = 0.0397]
absorption correction	analytical	integration	analytical
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	3391/411/302	4597/337/402	5798/404/451
goodness-of-fit on F^2	0.952	0.880	0.897
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0212$, $wR2 = 0.0459$	$R1 = 0.0278$, $wR2 = 0.0518$	$R1 = 0.0335$, $wR2 = 0.0685$
R indices (all data)	$R1 = 0.0259$, $wR2 = 0.0467$	$R1 = 0.0356$, $wR2 = 0.0534$	$R1 = 0.0445$, $wR2 = 0.0704$
largest diff. peak and hole (e Å^{-3})	0.461 and −0.510	0.764 and −0.395	1.045 and −0.672

reactions run using *N,N*-dimethylbenzylamine afford structurally similar compounds **5**−**7**.

There is a remarkable, mechanistically relevant difference between reactions of 2-phenylpyridine and *N,N*-dimethylbenzylamine. Complex $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ reacts with 2-phenylpyridine in acetonitrile at 30 °C to give **2** in a very low yield (ca. 9%). The yield did not improve at higher temperatures. The presence of a strong base such as NaOH is essential for increasing the yield up to 54%. The reaction is complete in a matter of 24−48 h. The situation is opposite for *N,N*-dimethylbenzylamine, and **5** is obtained in 83% isolated yield at 30 °C in the absence of NaOH, though when NaOH is added the yield of **5** drops to as low as 10%. Obviously, the bases in the scene, that is, 2-phenylpyridine, *N,N*-dimethylbenzylamine, and hydroxide, play an important role in the cyclometalation by osmium, and this is important evidence for the electrophilic mechanism of intramolecular C−H bond activation.[1] The phenyl group of *N,N*-dimethylbenzylamine is more electron-rich than that of 2-phenylpyridine, and therefore, *N,N*-dimethylbenzylamine operates both as a substrate and as a base in such a way that no extra NaOH is required. The basicity of 2-phenylpyridine is by several orders of magnitude lower than that of *N,N*-dimethylbenzylamine,[38] and the pyridine base cannot assist in the dissociation of hydrogen as a proton. Therefore, the nucleophilic assistance of NaOH as external base is essential for the formation of **2** (Scheme 2). Deeper mechanistic discussion without kinetic data is speculative at the moment, but the mechanism is presumably similar to the C(sp^2)-H cyclopal-

Scheme 2. Postulated Transition State for the Electrophilic Cycloosmation of N-Coordinated 2-Phenylpyridine with the Nucleophilic Assistance That Involves a Base (Hydroxide) As a Proton Acceptor[a]



[a] A similar mechanism is assumed for *N,N*-dimethylbenzylamine with the amine acting as a base. Only partial charges are shown for clarity.

ladation where the nucleophilic assistance during the rate-limiting electrophilic attack is reliably documented experimentally[39] and theoretically.[40] The electrophilic nature of the cycloosmation is also supported by the fact that methoxy-substituted *N,N*-dimethylbenzylamines (4-MeO and 3,5-$(MeO)_2$) afford metalacycles **5′** and **5″** respectively, which are similar to **5**, whereas 4-NO_2-*N,N*-dimethylbenzylamine is unreactive under the same reaction conditions.

Cyclometalation of 2-phenylpyridine by $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ occurs also in refluxing methanol to afford the previously reported[25] compound **1** in 60% yield. The osmium reactions in acetonitrile proceed differently as compared to those with Ru^{II} chloro-bridged dimer $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$.[41,42] Cycloruthenation in the presence of NaOH involves dissociation of the η^6-bound benzene and the formation of $[Ru(o\text{-}C_6H_4py\text{-}\kappa C,N)(MeCN)_4]PF_6$. No such product was detected when $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ was used as metalating agent. Attempts to prepare $[Os(o\text{-}C_6H_4py\text{-}$

(38) Smith, R. M.; Martell, A. E. *Critical Stability Constants, Vol. 2: Amines*; Plenum Press: NY and London, 1975.
(39) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629–2638.
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(41) Fernandez, S.; Pfeffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390–2394.
(42) Ryabov, A. D.; Estevez, H.; Alexandrova, L.; Pfeffer, M.; Le Lagadec, R. *Inorg. Chim. Acta* **2006**, *359*, 883–887.

$\kappa C,N)(MeCN)_4]PF_6$ were unsuccessful. In particular, refluxing a solution of **2** in acetonitrile for 48 h leads to the quantitative recovery of **2**. The η^6-benzene ring is obviously more tightly bound to osmium(II) than to ruthenium(II), and its displacement by acetonitrile is more difficult in the Os^{II} case. A similar tendency has been experimentally observed for metalocenes Cp_2M (M = Fe, Ru, Os)[43] and theoretically predicted by DFT for Ru^{II} and Os^{II} η^6-complexes of benzene and *p*-cymene.[44]

Derivatization of 2 and 5: Synthesis of Complexes 3, 4, 6, and 7. Compounds **3b** and **6b** were obtained from **2** and **5**, respectively, on prolonged treatment with 1,10-phenanthroline in acetonitrile. Despite many efforts, compounds **3a** and **6a** with bpy could not be prepared. In the ruthenium case, coordination of 2,2′-bipyridine is also much more difficult than that of 1,10-phenanthroline,[42] but $[Ru(o\text{-}C_6H_4py\text{-}\kappa C,N)(bpy)(MeCN)_2]PF_6$ was obtained by using dichloromethane instead of acetonitrile as solvent.[45] The same approach did not work in the present case, and an increase in temperature and/or reaction time was not successful either. In particular, after complex **2** and 1.2 equiv of 2,2′-bipyridine were kept at 35 °C in CH_2Cl_2 for 100 h, **2** was recovered quantitatively along with a small amount of decomposition products. We have previously discussed in detail the lower reactivity of bpy compared to phen toward similar ruthena(II)cycles.[45] Arguments put forward previously are applicable for the osmium compound reported here. A new factor is a stronger binding of the benzene ligand to the osmium center. Therefore, its substitution by both 2,2′-bipyridine and acetonitrile should be even more difficult.

Protic methanol is a better medium for ligand substitution, and compounds **4a**,**b** and **7a**,**b** were synthesized by refluxing methanolic solutions of **2** or **5** in the presence of 2,2′-bipyridine or 1,10-phenanthroline in good yields. It is worth mentioning that the bpy complexes **4a** and **7a** were isolated in lower yields compared to the corresponding phen species **4b** and **7b**.

X-ray Structural Studies. Structures of *N,N*-dimethylbenzylamine compounds **5** and **6b**, as well as that of 2-phenylpyridine derivative **3b**, were confirmed by single crystal X-ray diffraction studies (Figure 1). The crystallographic data are summarized in Table 1. As seen in Figure 1, osmium in complex **5** is at the center of a pseudotetrahedron with bond distances and angles within the usual range observed for such compounds. The mean $Os-C_{benzene}$ distance of 2.203 Å should be compared with that of 2.212 Å for **1**[25] and 2.206 Å for $[Ru(o\text{-}C_6H_4CH_2NMe_2\text{-}\kappa C,N)(\eta^6\text{-}C_6H_6)(NCMe)]PF_6$.[35] Octahedral structures **3b** and **6b** are also similar to their ruthenium counterparts. The higher trans effect of the C atom σ-bound to the metal is reflected in longer Os−N distances for the nitrogen atoms trans to the carbon atom.

There are intermolecular π-π interactions in the solid-state structure of **3b** involving phenanthroline ligands. The closest distance between the rings equals 3.624 Å (Figure 2). It is a noteworthy fact that although the 2-phenylpyridine moiety is also prone to exhibit π-π stacking, this does not occur probably because of the symmetry adopted by the molecule in the solid state and the fact that the counterions present in the lattice hinder a close proximity of other flat fragments (e.g., 1,10-phenanthroline or 2-phenylpyridine).

Electrochemical Properties. Cyclic voltammograms of selected osma(II)cycles obtained in acetonitrile are shown in Figure 3 together with the data for the corresponding ruthena(II)cycles for comparison. The data for all osmium compounds listed in Scheme 1 and for the corresponding ruthenium species[42] obtained in both acetonitrile and water containing about 5% acetonitrile for increasing solubility are summarized in Table 2. As seen in Figure 3, the M^{II}/M^{III} redox feature is well defined for both Os and Ru metalacycles, and the reduction potentials of osmium derivatives are by 260−310 mV more cathodic than those of the ruthenium counterparts. At the scan rate of 0.1 V s^{-1} the peak separation for Os species is usually in the range of 0.056−0.063 and 0.060−0.079 V in MeCN and water, respectively, indicating a higher level of reversibility when acetonitrile is used as solvent.

Electron transfer with Glucose Oxidase (GO) from *A. niger*. The relatively low reduction potentials of these cyclometalated octahedral osmium(II) complexes and the numerous applications of other Os^{II} species as electron carriers to/from active sites of oxidoreductases[28,46–50] encouraged us to test complexes **3**, **4**, **6**, and **7** as mediators of GO enzyme. GO, the biological function of which is to oxidize β-D-glucopyranose into the corresponding γ-lactone,[51] is a kind of model enzyme for probing a mediator capability of a low-molecular-weight electron carrier.[28] If it mediates electron transport with GO well, then the mediator is worth testing with other less available or more expensive enzymes.

The high capability of **7b** to exchange electrons with the active site of GO, that is, to be a mediator, is demonstrated in Figure 4. Cyclic voltammograms of **7b** with and without GO and D-glucose in water illustrate a significant current increase when GO and D-glucose are present. The current growth is accounted for in terms of eqs 1–3.

$$\text{GO(ox)} + \text{D-glucose} \rightarrow \text{GO(red)} + \delta\text{-D-gluconolactone} + 2H^+ \quad (1)$$

$$\text{GO(red)} + 2Os^{III} \xrightarrow{k_3} \text{GO(ox)} + 2Os^{II} \quad (2)$$

$$2Os^{II} - 2e \rightarrow 2Os^{III} \qquad \text{(electrode)} \quad (3)$$

Step 2 is known to follow second-order kinetics, and the corresponding rate constants k_3 for step 2, calculated by means of the procedure of Bourdillon et al.,[33] are shown in Table 2.

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(45) Ryabov, A. D.; Le Lagadec, R.; Estevez, H.; Toscano, R. A.; Hernandez, S.; Alexandrova, L.; Kurova, V. S.; Fischer, A.; Sirlin, C.; Pfeffer, M. *Inorg. Chem.* **2005**, *44*, 1626–1634.
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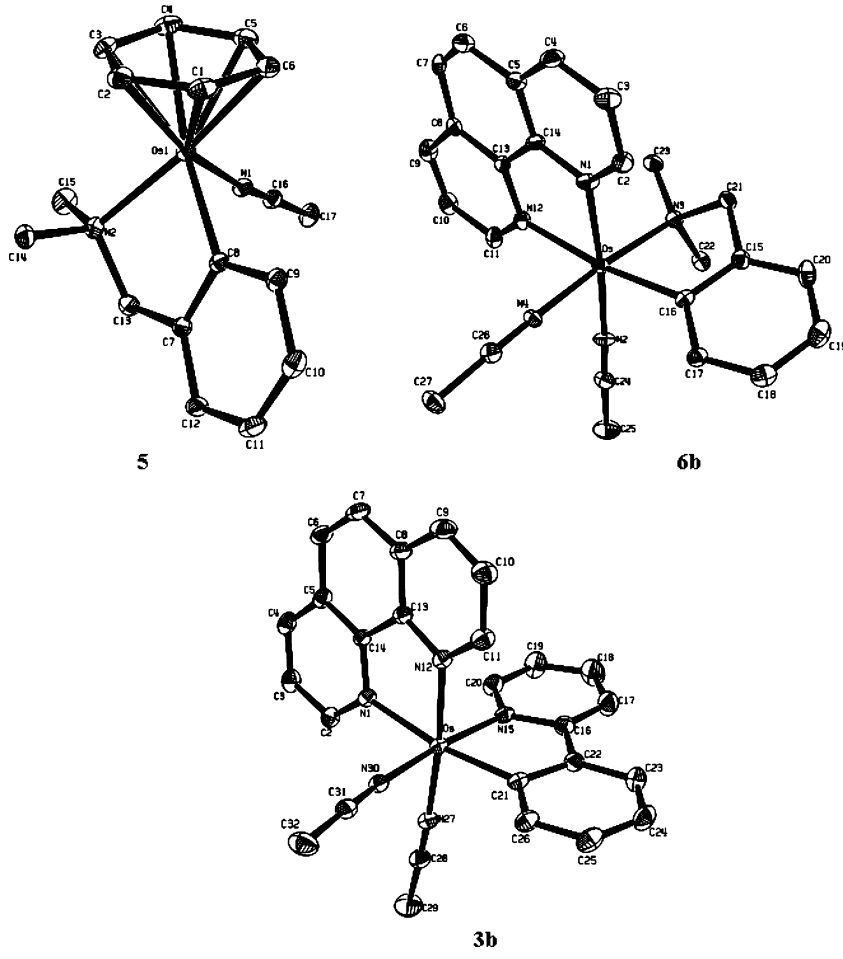

Figure 1. ORTEP views of osmacycles **3b**, **5**, **6b**. Thermal ellipsoids are drawn with 50% probability level. Hydrogen atoms and PF_6^- anions are omitted for clarity. Selected bond lengths (in Å) and angles (in °). **5**: Os1−N1 2.043(4), Os1−C8 2.082(4), Os1−N2 2.178(4), Os1−C1 2.175(5), Os1−C2 2.175(5), Os1−C3 2.215(5), N1−Os1−C8 85.57(16), N1−Os1−N2 84.94(15), N2−Os1−C8 77.57(17), C16−N1−Os1 174.4(4). **3b**: Os−N27 2.005(5), Os−N30 2.008(5), Os−N15 2.048(5), Os−N12 2.050(5), Os−N1 2.134(4), Os−C21 2.040(5), N27−Os−N15 91.07(19), N30−Os−N15 172.86(18), C21−Os−N15 79.6(2), N27−Os−N12 172.14(19), C21−Os−N1 171.1(2). **6b**: Os−N1 2.056(14), Os−N2 1.984(14), Os−N3 2.168(7), Os−N4 2.003(7), Os−N12 2.126(6), Os−C16 2.053(8), N2−Os−N1 174.4(2), C16−Os−N12 171.7(4), N2−Os−N3 90.5(4), N4−Os−N3 175.2(3), C16−OsN3 79.0(3).

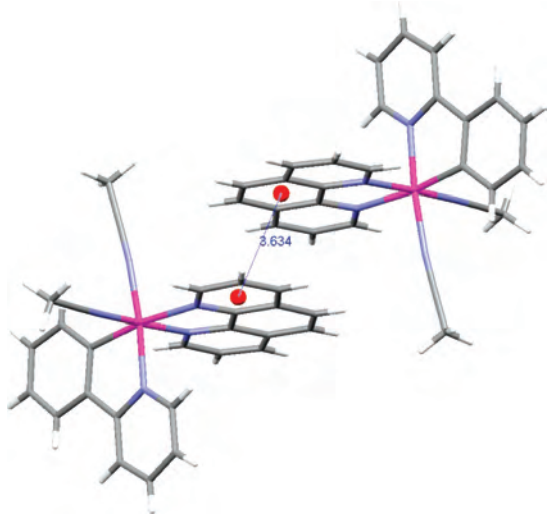

Figure 2. Stacking interactions in the crystal structure of complex **3b** with the centroid−centroid distance of 3.634 Å.

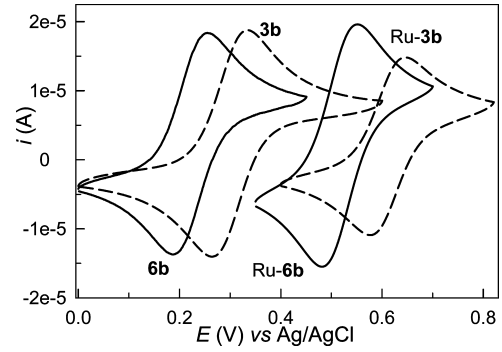

Figure 3. Comparison of cyclic voltammograms of selected cyclometalated osmium compounds reported here and the corresponding ruthenium counterparts. Conditions: complexes 10^{-3} M, glassy carbon working electrode, 25 °C, scan rate 0.1 V s^{-1}, 0.1 M $(n\text{-Bu})_4NPF_6$ in MeCN.

The rate constants k_3 are rather high for all compounds. There is no significant difference between the complexes, but compound **7a** has the lowest value of k_3. Interestingly, the k_3 for **7b** is higher almost by the order of magnitude though **7b** contains phen instead of bpy as in **7a**. One may also notice that the reduction potentials of **7a** and **7b** are the same in acetonitrile, but **7b** is more oxidizing than **7a** by about 60 mV in water. Curiously, this effect is not observed for the **4a**,**b** pair of 2-phenylpyridine complexes. It should also be mentioned that in this study we were unable to

Table 2. Reduction Potentials (in mV versus Ag/AgCl) at 25 °C, Scan Rate 0.1 V s^{-1}, 0.1 M (n-Bu)$_4$NPF$_6$ in CH_3CN or Water, and the Rate Constants k_3 (in M^{-1} s^{-1}) for Oxidation of GO(red) by the Electrochemically Generated Os^{III} Species at pH 7.0 (0.01 M phosphate)

	M = Os		M = Ru		
compound	MeCN	H_2O	MeCN	H_2O	$10^6 \times k_3$
[M(o-$C_6H_4CH_2NMe_2$-$\kappa C,N$)(bpy)$_2$]PF_6 (**7a**)	191	−51	479	231	0.67 ± 0.02
[M(o-$C_6H_4CH_2NMe_2$-$\kappa C,N$)(phen)$_2$]PF_6 (**7b**)	192	13	471	250	4.80 ± 0.3
[M(o-$C_6H_4CH_2NMe_2$-$\kappa C,N$)(phen)(NCMe)$_2$]PF_6 (**6b**)	221	32	510	332	2.0 ± 0.3
[M(o-C_6H_4py-$\kappa C,N$)(bpy)$_2$]PF_6 (**4a**)	271	84	531	329	3.9 ± 0.1
[M(o-C_6H_4py-$\kappa C,N$)(phen)$_2$]PF_6 (**4b**)	282	31	537	324	1.8 ± 0.2
[M(o-C_6H_4py-$\kappa C,N$)(phen)(NCMe)$_2$]PF_6 (**3b**)	299	109	605	423	2.9 ± 0.3

achieve the k_3 of 10^7 M^{-1} s^{-1} for **4b** as previously reported.[25] We could not suggest obvious reasons for this inconsistency. The value of k_3 could be affected by slightly different properties of the GO sample used in this study and by the fact that determination of the i_{cat}/i_o ratio from the data such as in Figure 4 is rather arbitrary. This might explain the fluctuation in k_3. It should be noted that in some cases the reported values of k_3 differ by a factor of 100.[28] In any case, the values of the rate constants k_3 summarized in Table 2 do sound reasonable[28] and, supported by the fact that these now easier accessible complexes have low reduction potentials in aqueous medium, make the complexes promising materials for biochemical and related applications.

Conclusions

Electrophilic C(sp^2)-H cyclometalation by chloro-bridged osmium(II) dimer [OsCl(μ-Cl)(η^6-C_6H_6)]$_2$ affords a set of easy to derivatize cyclometalated osmium(II) compounds such as **1**, **2**, and **5** in good yields under very mild conditions. This procedure is obviously cleaner than the synthesis of the compounds using toxic mercurated precursors and makes bidentate osma(II)cycles more accessible. The octahedral compounds are readily reduced/oxidized at the electrode and have, by about 0.3 V, lower reduction potentials compared to the corresponding Ru^{II} counterparts. New compounds may find applications in various fields including bioamperometric biosensors[52] because they have been shown to possess high activity as mediators of glucose oxidase.

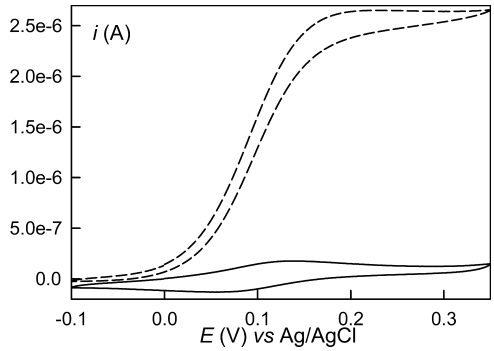

Figure 4. Cyclic voltammogram of complex **7b** (1×10^{-4} M) without (solid line) and in the presence (dotted line) of GO (1×10^{-6} M) and 0.05 M of D-glucose at pH 7.0, scan rate 3 mV s^{-1}.

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Supporting Information Available: Crystallographic CIF files for compounds **3b**, **5**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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