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Facile η^5–η^1 Ring Slippage of the Cycloolefin Ligands in Osmocene and Bis(η^5-indenyl)ruthenium(II)

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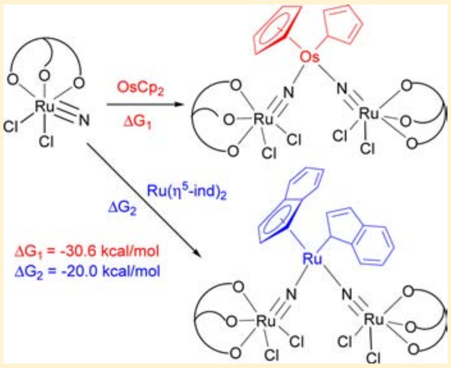
Supporting Information

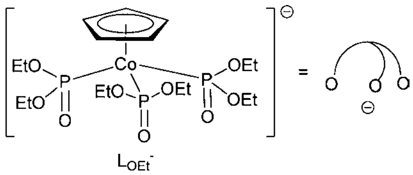


ABSTRACT: η^5–η^1 ring slippage of [OsCp$_2$] (Cp = η^5-C$_5$H$_5$) and [Ru(η^5-ind)$_2$] (ind = indenyl) resulting from reaction with the ruthenium(VI) nitride [Ru(L$_{OEt}$)(N)Cl$_2$] (**1**; L_{OEt}^- = [CoCp{P(O)(OEt)$_2$}$_3$]$^-$) is reported. The treatment of [OsCp$_2$] or [Ru(η^5-ind)$_2$] with **1** resulted in η^5-η^1 ring slippage of the cycloolefin ligands and formation of the trinuclear nitrido complexes [Cp(η^1-C$_5$H$_5$)Os(NRuL$_{OEt}$Cl$_2$)$_2$] (**2**) or [(η^5-ind)(η^1-ind)Ru(NRuL$_{OEt}$Cl$_2$)$_2$] (**3**). No reactions were found between [OsCp$_2$] and amines, such as pyridine and 2,2′-bipyridyl, or other metal nitrides, such as [Os(L$_{OEt}$)(N)Cl$_2$], indicating that the electrophilic property of **1** is essential for ring slippage. The crystal structures of **2** and **3** have been determined. The short Os–N distances in **2** [1.833(5) and 1.817(5) Å] and the (ind)Ru–N distances in **3** [1.827(5) and 1.852(5) Å] are indicative of multiple bond character, consistent with density functional theory (DFT) calculations. Therefore, **2** and **3** may be described by two resonance forms: Ru^{VI}–M^{II}–Ru^{VI} and Ru^{IV}–M^{VI}–Ru^{IV} (M = Os, Ru). Also, DFT calculations indicate that for the reaction of **1** with [OsCp$_2$] or [Ru(η^5-ind)$_2$], η^5–η^1 ring slippage is energetically more favorable than the η^5–η^3 counterpart. The driving force for η^5–η^1 ring slippage is believed to be the formation of the strong M–N (M = Os, Ru) (multiple) bonds. By contrast, the same reaction with acetonitrile is energetically uphill, and thus no ring slippage occurs.

INTRODUCTION

Although osmocene, [OsCp$_2$] where Cp = η^5-cyclopentadienyl, has been known for a long time, its reaction chemistry has not been well explored.[1] Electron-rich [OsCp$_2$] can be oxidized readily to higher-valent osmocenes such as dinuclear [(OsCp$_2$)$_2$]$^{2+}$, [(OsCp$_2$S)$_2$]$^{2+}$, and [{OsCp(η^5-C$_5$H$_4$)}$_2$]$^{2+}$ containing Os–Os single bonds and mononuclear [OsCp$_2$(X)]$^{n+}$ [X = neutral (n = 2) or anionic (n = 1) ligand],[1,2] indicating its potential for multi-electron transfer. Our interest in high-oxidation-state osmocene complexes is stimulated by a recent report that [OsCp$_2$] can mediate the photochemical oxidation of water, possibly via CpOs^{IV} oxo or hydroxo intermediates.[3,4] This finding suggests that osmocene derivatives containing metal–ligand multiple bonds can display rich redox and catalytic chemistry.

Chart 1. Klӓui Tripodal Ligand L_{OEt}^-



Previously, we reported that the ruthenium(VI) nitride [Ru^{VI}(L$_{OEt}$)(N)Cl$_2$] (**1**), where L_{OEt}^- is the Klӓui's tripodal ligand [CoCp{P(O)(OEt)$_2$}$_3$]$^-$ (Chart 1), exhibits electrophilic behavior and can act like a π-acceptor ligand for late transition metals.[5,6] For example, **1** can insert into the Ru–H bond in [Ru^{II}(L$_{OEt}$)(H)(CO)(PPh$_3$)][5b] and the Rh–C bond in [Rh^{III}(mes)$_3$] (mes = mesityl)[5c] to give Ru^{IV}–Ru^{II} and Ru^{IV}–Rh^{III}–Ru^{IV} μ-imido complexes, respectively. Also, **1** reacts with [Ru^{II}(η^6-p-cymene)Cl$_2$]$_2$ to afford a tetranuclear nitrido complex featuring symmetric Ru^{IV}=N=Ru^{IV} bridges.[6] These results indicate that **1** can function as an "inner-sphere" two-electron oxidant for lower-valent organometallic complexes. As an extension of this study, we set out to explore the reactivity of **1** with metallocenes. In this work, we found that the reactions of **1** with [OsCp$_2$] and [Ru(η^5-ind)$_2$] (ind = indenyl) result in η^5–η^1 ring slippage of the cycloolefin ligands and formation of trinuclear Ru(N)M(N)Ru (M = Os, Ru) complexes.

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X-ray crystallography revealed that the Os−N and (ind)Ru−N bonds in these nitrido complexes possess multiple-bond character. Density functional theory (DFT) calculations have been performed in order to better understand the electronic structures and pathway of formation of these μ-nitrido complexes.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer operating at 400, 376.5, and 162.0 MHz for ^{1}H, ^{19}F, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C) and H_3PO_4 (^{31}P). Electrospray ionization mass spectra were recorded on an Applied Biosystem QSTAR mass spectrometer. UV/vis spectra were recorded on a Perkin-Elmer LAMBDA D 900 UV/vis/near-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K. The compounds $[Ru(L_{OEt})(N)Cl_2]$ (**1**)[5] and $[Ru(\eta^5\text{-ind})_2]$ (ind = indenyl)[7] were prepared according to literature methods. $[OsCp_2]$ was purchased from Strem Ltd. and used as received.

Synthesis of $[Cp(\eta^1\text{-}C_5H_5)Os(NRuL_{OEt}Cl_2)_2]$ (2). To a purple solution of **1** (50.0 mg, 0.069 mmol) in benzene (5 mL) was added $[OsCp_2]$ (11.1 mg, 0.035 mmol). The resulting brown mixture was stirred overnight at room temperature, and the volatiles were removed in vacuo. The residue was washed with hexane and extracted with Et_2O/tetrahydrofuran (THF). Recrystallization from Et_2O/THF/hexane gave brown crystals that were suitable for X-ray analysis. Yield: 52.4 mg (85%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.17 (t, J = 6.8 Hz, 6H, CH_3), 1.21 (t, J = 6.8 Hz, 6H, CH_3), 1.28 (t, J = 6.8 Hz, 6H, CH_3), 1.32 (t, J = 6.8 Hz, 6H, CH_3), 1.44 (t, J = 6.8 Hz, 6H, CH_3), 1.54 (t, J = 7.2 Hz, 6H, CH_3), 4.26−4.52 (m, 24 H, OCH_2), 4.85 (s, 10 H, Cp of L_{OEt}^-), 6.09 (s, 5H, Cp), 6.44 (br, 2H, η^1-C_5H_5), 7.53 (br, 1H, η^1-C_5H_5), 7.85 (br, 2H, η^1-C_5H_5). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 114.45 (m), 119.95 (m). Anal. Calcd for $C_{44}H_{80}Cl_4Co_2N_2O_{18}P_6OsRu_2$: C, 29.98; H, 4.57; N, 1.59. Found: C, 29.68; H, 4.46; N, 1.60.

Synthesis of $[(\eta^5\text{-ind})(\eta^1\text{-ind})Ru(NRuL_{OEt}Cl_2)_2]$ (3). To a purple solution of **1** (50.0 mg, 0.069 mmol) in Et_2O (5 mL) was added $[Ru(\eta^5\text{-ind})_2]$ (10.9 mg, 0.035 mmol). The resulting deep-red mixture was stirred overnight at room temperature. Hexane was added to the reaction mixture, which led to the precipitation of a red solid. Upon filtration, the red solid was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2−hexane−Et_2O gave air-stable deep-red crystals. Yield: 52.8 mg (85%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.72−0.85 (m, 6H, CH_3), 1.17−1.29 (m, 12H, CH_3), 1.35−1.39 (m, 9H, CH_3), 1.55 (m, 9H, CH_3), 4.01 (m, 2H, OCH_2), 4.24−4.51 (m, 18H, OCH_2), 4.70 (m, 4H, OCH_2), 4.80 (s, 5H, Cp), 4.91 (s, 5H, Cp), 6.24 (m, 1 H, ind), 6.48 (m, 1 H, ind), 6.65 (d, J = 5.3 Hz, 1H, ind), 6.78 (m, 1H, ind), 6.91 (m, 2H, ind), 7.01 (m, 1H, ind), 7.21−7.32 (m, 3H, ind), 7.43 (m, 1H, ind), 7.61 (m, 1H, ind), 7.67 (d, J = 8.3 Hz, 1H, ind), 8.78 (m, 1H, ind). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 115.79 (m), 120.67 (m). Anal. Calcd for $C_{52}H_{86}Cl_4Co_2N_2O_{18}P_6Ru_3 \cdot {}^1/_2C_4H_{10}O$: C, 35.21; H, 4.77; N, 1.58. Found: C, 35.01; H, 4.63; N, 1.52.

X-ray Crystallography. Crystallographic data and refinement details for complexes **2** and **3** are listed in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption using the program *SADABS*. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL* software package.[8,9] In **2**, the two osmium-bound Cp rings are disordered and the 10 carbon atoms C51−C60 are split into two parts with 0.5 occupancy each. The carbon atoms C53A and C57 are overlapped on a single site. The carbon atoms C6−C10 of the Cp ring in one L_{OEt}^- ligand are 67:33 disordered. The carbon atoms C14, C19, and C20 (67:33), C39 and C41 (50:50), and C40 and C42 (33:33:33) of the ethoxy groups are also disordered. In **3**, the carbon atoms C11 and C12 of an ethoxy group of a tripod ligand are 50:50 and 50:25:25 disordered, respectively.

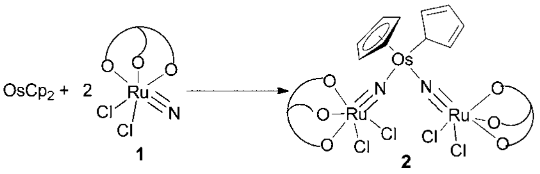
Table 1. Crystallographic Data and Refinement Details for $2 \cdot C_4H_8O$ and $3 \cdot 0.75C_6H_{14} \cdot CH_2Cl_2$

	$2 \cdot C_4H_8O$	$3 \cdot 0.75C_6H_{14} \cdot CH_2Cl_2$
formula	$C_{48}H_{88}Cl_4Co_2N_2O_{19}OsP_6Ru_2$	$C_{57.5}H_{96.5}Cl_6Co_2N_2O_{18}P_6Ru_3$
M_r	1835.02	1923.46
a, Å	13.2605(15)	14.3744(3)
b, Å	15.9640(18)	18.0585(3)
c, Å	19.194(2)	31.6395(7)
α, deg	99.384(2)	
β, deg	96.206(2)	97.010(2)
γ, deg	113.496(1)	
V, Å^3	3608.6(7)	8151.6(3)
Z	2	4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
ρ_{calcd}·g·cm^{-3}	1.689	1.567
T, K	298	173
μ, mm^{-1}	2.956	1.316
F(000)	1836	3910
no. of reflns	37311	37436
no. of indep reflns	14072	14954
R_{int}	0.0446	0.0587
R1, wR2 [$I > 2\sigma(I)$]	0.0472, 0.1080	0.0728, 0.1676
R1, wR2 (all data)	0.0739, 0.1150	0.0919, 0.1783
GOF	1.028	1.089

Computational Details. All structures were optimized at the B3LYP level of theory.[10−12] In addition, the frequency calculations were performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the ruthenium, osmium, cobalt, phosphorus, and chlorine atoms, whereas the standard 6-31G(d) basis set was used for the carbon, oxygen, nitrogen, and hydrogen atoms.[13] Polarization functions[14] were added for ruthenium [ζ(f) = 1.235], osmium [ζ(f) = 0.886], cobalt [ζ(f) = 2.780], chlorine [ζ(d) = 0.514], and phosphorus [ζ(d) = 0.34]. The calculated bond lengths in Figure S5 in the Supporting Information (SI) are consistent with the experimental values, indicating the reliability of our calculations. All of the optimizations were performed with the *Gaussian 09* software package.[15] The natural bond orbital (*NBO*) program,[16] as implemented in *Gaussian 09*, was used to obtain Wiberg bond indices (bond orders),[17] which are a measure of the bond strength.

■ RESULTS AND DISCUSSION

Reaction of 1 with [OsCp$_2$]. The treatment of $[OsCp_2]$ with 2 equiv of **1** in benzene at room temperature afforded the trinuclear nitrido complex **2** containing an η^1-cyclopentadienyl ligand (eq 1). This is a rather unusual reaction for $[OsCp_2]$ because the group 8 metallocene is expected to be stable because of the 18-electron rule. Attempts to prepare an analogous dinuclear osmium−ruthenium complex (containing an η^3-C_5H_5 ligand) failed. ^{1}H NMR spectroscopy indicates that the reaction of $[OsCp_2]$ with 1 equiv of **1** gave a ca. 1:1 mixture of **2** and



(1)

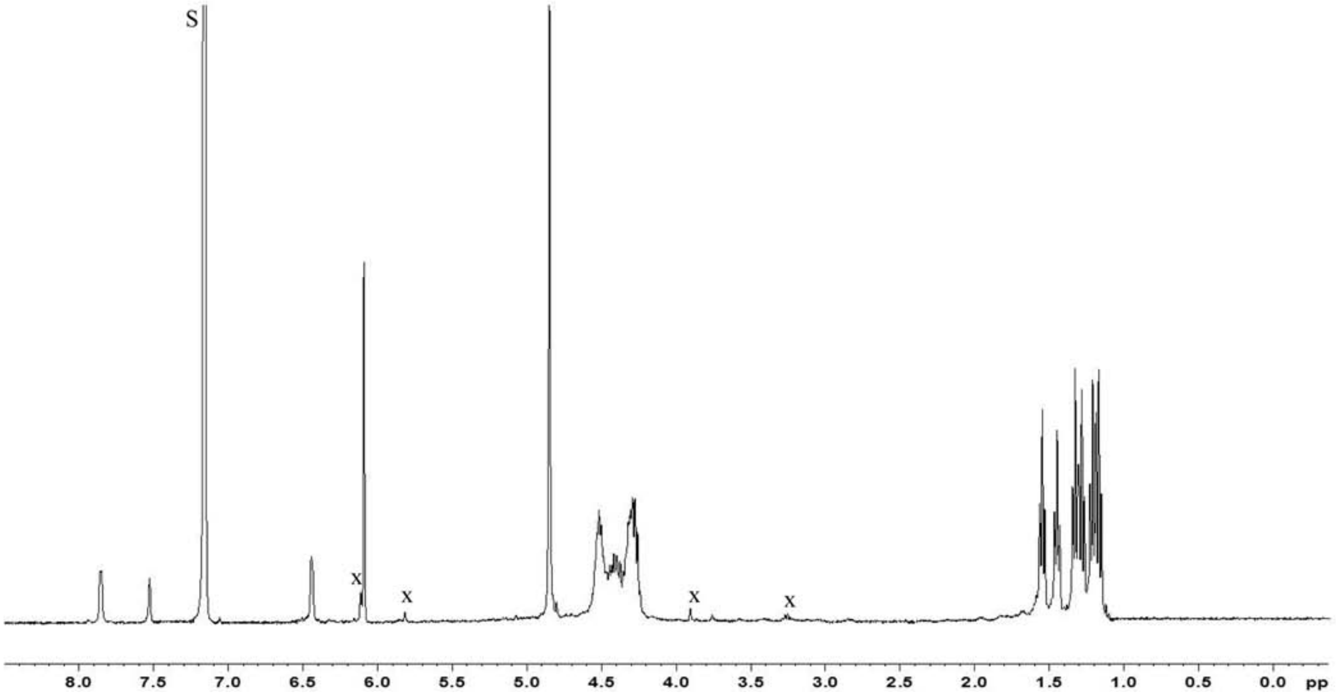


Figure 1. ^{1}H NMR (400 MHz) spectrum of **2** in C_6D_6 at 25 °C. S = solvent; x = impurities.

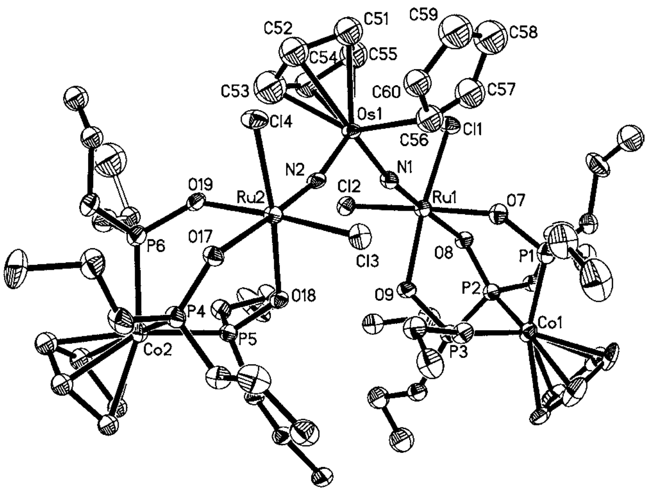


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Os1−N1 1.833(5), Os1−N2 1.817(5), Ru1−N1 1.699(4), Ru2−N2 1.706(4), Os−C(Cp) 2.246(15)−2.348(14), Os−C56 2.177(13); Ru1−N1−Os1 165.6(3), Ru2−N2−Os1 166.7(3).

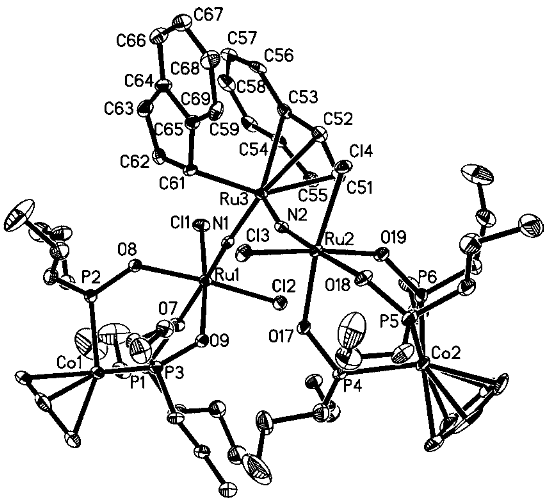
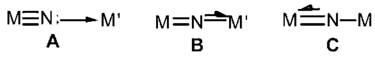


Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru1−N1 1.684(5), Ru2−N2 1.690(5), Ru3−N1 1.852(5), Ru3−N2 1.827(5), Ru3−C(η^5-ind) 2.236(7)−2.438(7), Ru3−C61 2.195(7); Ru1−N1−Ru3 168.0(3), Ru2−N2−Ru3 165.0(3).

Scheme 1. Resonance Forms of Nitrido-Bridged Complexes



unreacted [$OsCp_2$]. To our knowledge, this is the first report of η^5−η^1 ring slippage for a group 8 metallocene,[18] although a similar conversion has been found for the strained metallocenophanes [1]ferrocenophanes and [1]- and [2]ruthenocenophanes.[19] The closest analogue of reaction (1) in the literature is the formation of [$CrCp(\eta^1$-$C_5H_5)(NO)_2$] from 16-electron [$CrCp_2$] and NO.[20] It may also be noted that rapid interconversion between the η^5- and η^1-cyclopentadienyl ligands in [$TiCp_2(\eta^1$-$C_5H_5)_2$][21] and [$MCp_2(\eta^1$-$C_5H_5)$(N-*t*-Bu)] (M = Mo,[22] Nb[23]) has been observed.

Unlike [$Fe^{II}Cp(\eta^1$-$C_5H_5)(CO)_2$],[24] **2** is nonfluxional in solution and shows three signals at δ 6.09, 6.44, and 7.53 due to the η^1-C_5H_5 protons in the ^{1}H NMR spectrum (Figure 1) even at 60 °C. In addition, two singlets at δ 4.85 and 6.09 assignable to the Cp protons of the magnetically equivalent L_{OEt}^- ligands and the CpOs moiety were observed.

In the solid state, complex **2** exhibits a three-legged piano-stool structure with the osmium atom coordinated to one Cp, one η^1-C_5H_5, and two ruthenium nitrides (Figure 2). The Ru−N−Os units are roughly linear [166.7(3) and 165.6(3)°], and the N−Os−N angle is 102.9(2)°. The average Os−C distance for the

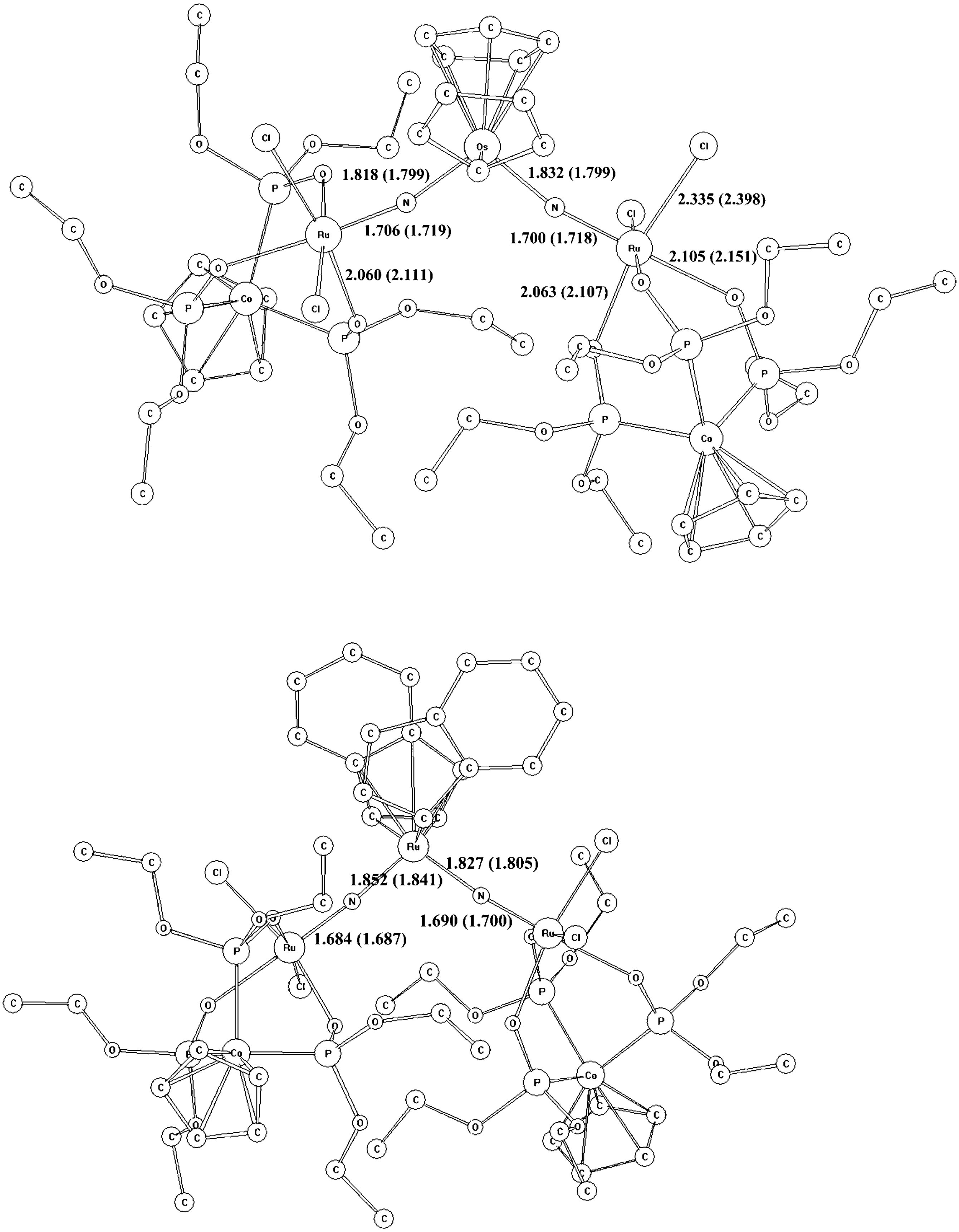
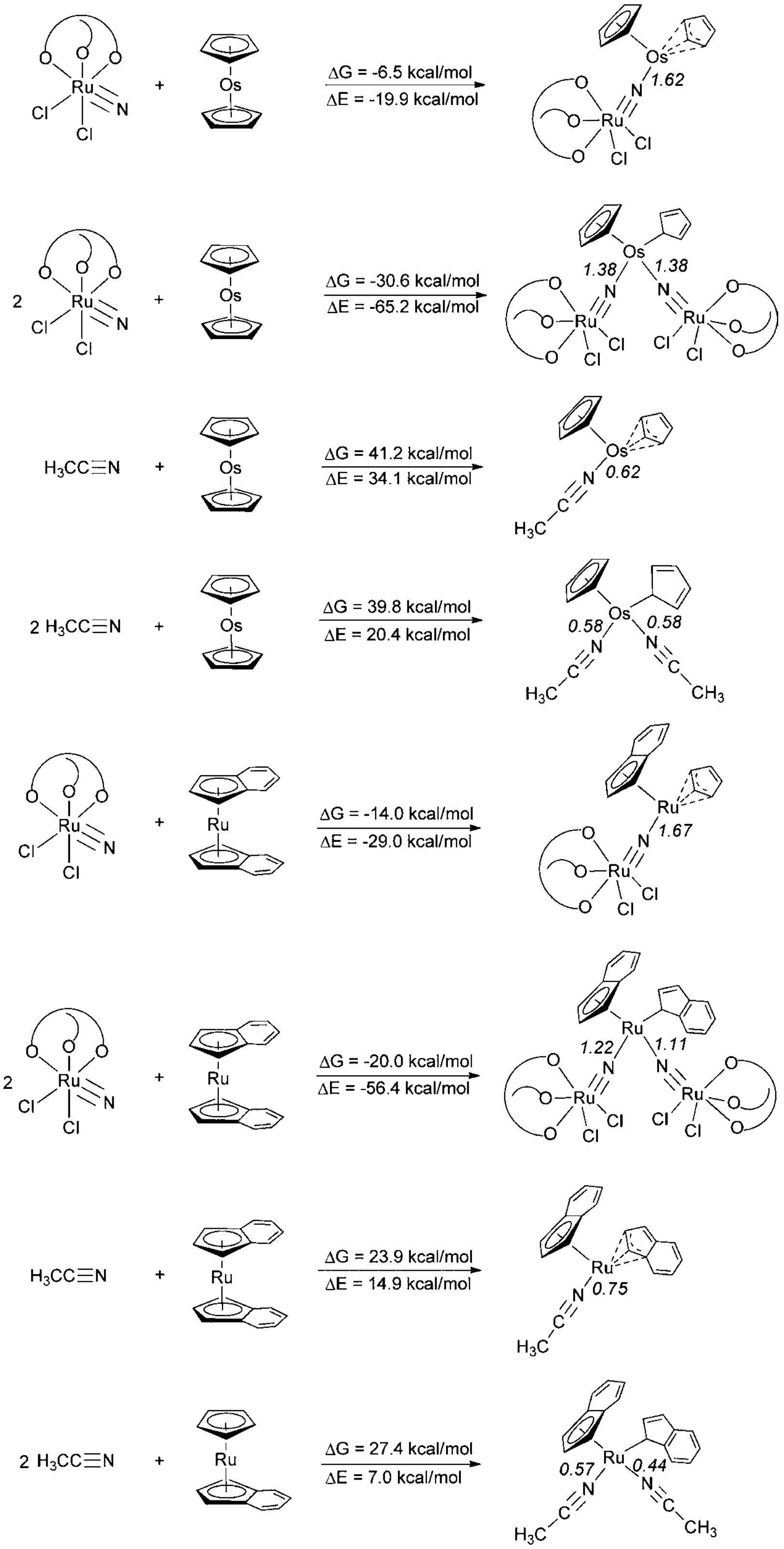


Figure 4. Selected experimental and calculated (in parentheses) bond lengths (Å) for **2** (top) and **3**. For clarity, hydrogen atoms are omitted.

η^5-Cp ligand (2.29 Å) is longer than that in $[(OsCp_2S)_2]^{2+}$ [2.22(1) Å],[2] possibly because of steric effects, whereas that for the η^1-C_5H_5 ligand is 2.177(13) Å. The Os−N distances [1.833(5) and 1.817(5) Å] are quite short, indicative of

Scheme 2. Calculated Free Energy (ΔG) and Electronic Energy (ΔE) Changes for η^5–η^3 and η^5–η^1 Ring Slippage for the Reactions of $[\mathrm{OsCp_2}]$ and $[\mathrm{Ru}(\eta^5\text{-ind})_2]$ with 1 and Acetonitrile[a]

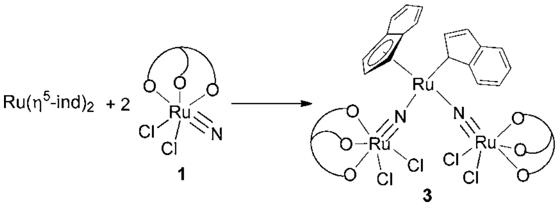


[a]The bond orders of the M–N (M = Os, Ru) bonds formed are indicated in italic.

multiple-bond character. By comparison, the Os–N bonds in $[\mathrm{Os^{IV}_2}(\mu\text{-N})(\mathrm{S_2CNMe_2})_5]$[25] and $[(\mathrm{Me_2PhP})_3(\mathrm{PhCN})\mathrm{ClRe^V}(\mu\text{-N})\mathrm{Os^{II}Cl_2(CO)_3}]^+$[26] are 1.76(3) and 1.75(3) and 2.061(8) Å, respectively. The Ru–N distances in **2** [1.699(4) and 1.706(4) Å] are between those of **1** [1.573(6) Å][5a] and $[\{\mathrm{Ru^{IV}L_{OEt}Cl_2}\}_2(\mu\text{-N})]^-$ [1.728(11)–1.727(11) Å],[7] suggestive of a Ru−N bond order between 3 and 2. It may be noted that in a related trinuclear cobalt/osmium nitrido complex, $[CpCo(NOsTpCl_2)_2]$ [Tp^- = hydrido(trispyrazolyl)borate], the Co−N(Os) bonds also possess multiple-bond character.[27]

Reactions of osmocene with nitrogen ligands and other metal nitrido complexes have been examined in order to confirm that the ruthenium(VI) nitride **1** is a special ligand for ring slippage. No reactions were found when osmocene was treated with unidentate [e.g., acetonitrile, pyridine, 4-(*N*,*N*-dimethylamino)-pyridine, aniline] or bidentate (e.g., 2,2′-bipyridyl) nitrogen ligands, nor were there any reactions between osmocene and the nitrido complexes $[Ru(N)Cl_4]^-$,[28] $[L_{OEt}Os(N)Cl_2]$, and $[L_{OEt}Re(N)(PPh_3)Cl]$.[29] This result suggests that the electrophilic property of **1** is crucial for ring slippage of osmocene.

Reaction of 1 with [Ru(η^5-ind)$_2$]. Reactions of **1** with other metallocenes have been studied. No reaction was found between **1** and ferrocene. The treatment of **1** with $[CoCp_2]$ and $[NiCp_2]$ at −20 °C resulted in the formation of dark insoluble precipitates, indicative of decomposition of the metallocenes. The reaction of **1** with $[RuCp_2]$ gave a mixture of products according to NMR spectroscopy. We have not been able to separate these products for characterization. On the other hand, **1** reacted rapidly[30] with $[Ru(\eta^5\text{-ind})_2]$ to give **3** containing an η^1-indenyl ligand (eq 2).



(2)

Unlike in **2**, the two $\{RuL_{OEt}\}$ moieties in **3** are not magnetically equivalent presumably because of the lower symmetry of the η^5-indenyl ligand compared with that of Cp. Two singlets at δ 4.71 and 4.91 due to the Cp rings of the L_{OEt}^- ligands were observed in the ^1H NMR spectrum. The molecular structure of **3** is shown in Figure 3. The Ru−N−Ru units are roughly linear [165.0(3) and 168.0(3)°], and the N−Ru(ind)−N angle is 101.5(2)°. The (ind)Ru−N distances in **3** [1.827(5) and 1.852(5) Å] are quite short, indicative of multiple-bond character. The (L_{OEt})Ru−N distances [1.684(5) and 1.690(5) Å] are similar to those in **2**. The Ru−C distances for the η^5-indenyl ligands [2.236(7)−2.438(7) Å] are longer than those of reported ruthenium(II) η^5-indenyl complexes, e.g., $[Ru(\eta^5\text{-ind})(PPh_3)(PPh_2H)Cl]$ [2.161(3)−2.357(3) Å],[31] possibly because of steric effects, whereas that for the η^1-indenyl ligand is 2.195(7) Å.

DFT Calculations. DFT calculations were performed in order to elucidate the electronic structures of **2** and **3** and the possible mechanism for their formation. The computed bond lengths for both compounds are in good agreement with the experimental ones (Figure 4), indicative of the reliability of the calculations. Three resonance forms, **A**−**C** (Scheme 1), can be used to describe the bonding in the nitrido bridges in **2** and **3**. Specifically, in structure **A**, the nitrogen donates its lone pair to M′, whereas in structure **B**, there is an additional σ bond besides the dative bond. In structure **C**, only a σ bond exists between M′ and N. Structure **B** has the strongest M′−N bond among the three resonance forms.

In **2**, the average Os−N bond order is calculated to be 1.38, consistent with the short observed Os−N distances. The average Ru−N bond order of 1.66 is significantly reduced compared with that of **1** (2.70), suggesting that structure **B** is the predominant resonance form for **2**. A similar situation is found for **3**, in which the average (ind)Ru−N and (L_{OEt})Ru−N bond orders are calculated to be 1.16 and 1.84, respectively. Therefore, **2** and **3** may be described as $Ru^{IV}-Os^{VI}-Ru^{IV}$ and $Ru^{IV}-Ru^{VI}-Ru^{IV}$ complexes, respectively, containing Os−N and (ind)Ru−N multiple bonds.

To gain insight into the mechanism for the formation of **2** and **3**, we calculated the reaction energies for $\eta^5-\eta^3$ and $\eta^5-\eta^1$ ring slippage for the products of the reactions of **1** with $[OsCp_2]$ and $[Ru(\eta^5\text{-ind})_2]$ (Scheme 2). In both cases, $\eta^5-\eta^1$ conversion is thermodynamically more favorable than the $\eta^5-\eta^3$ counterpart. This is in sharp contrast with a previous study on the ferrocene system, which suggests that $\eta^5-\eta^1$ ring slippage is a high-energy process.[32] We reason that the formation of strong M−N (M = Os, Ru) multiple bonds in **2** and **3** is responsible for the exothermicity of $\eta^5-\eta^1$ ring slippage.

The energies for the same reactions with acetonitrile were also calculated in order to show that ruthenium(VI) nitride is a unique ligand for ring slippage. Indeed, both the reaction of acetonitrile with $[OsCp_2]$ and that with $[Ru(\eta^5\text{-ind})_2]$ are endothermic, and therefore no ring slippage occurs. The average M−N(acetonitrile) bond orders in the hypothetical acetonitrile adducts $[OsCp(\eta^1\text{-}C_5H_5)(MeCN)_2]$ and $[Ru(\eta^5\text{-ind})(\eta^1\text{-ind})(MeCN)_2]$ are calculated to be 0.58 and 0.51, respectively, which are significantly smaller than those in **2** and **3** and indicative of dative interactions only.

■ CONCLUSIONS

In summary, while $[OsCp_2]$ and $[Ru(\eta^5\text{-ind})_2]$ do not react with nitrogen ligands such as aniline and pyridine, we found that they undergo facile $\eta^5-\eta^1$ ring slippage upon reaction with the ruthenium(VI) nitride **1**. To our knowledge, this is the first report of such ring slippage for osmocene. This is an unusual reaction for group 8 metallocenes because they are expected to be stable because of the 18-electron rule. No reactions were found when $[OsCp_2]$ was treated with amine ligands or analogous osmium and rhenium nitrido complexes, suggesting that the electrophilic behavior of **1** is important for ring slippage. DFT studies reveal that the driving force for ring slippage is the formation of strong Os−N and Ru−N (multiple) bonds in **2** and **3**, respectively. In these reactions, $\eta^5-\eta^1$ conversion is found to be thermodynamically more favorable than $\eta^5-\eta^3$ conversion. This is in sharp contrast with a previous theoretical study on ferrocene,[32] which suggests that $\eta^5-\eta^1$ ring slippage is a high-energy process. Reactions (1) and (2) can serve as a new strategy for the synthesis of higher-valent group 8 metallocene derivatives containing multiply bonded ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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