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Migratory Insertion and Reductive Coupling of Tetraarylruthenium(IV) Complexes

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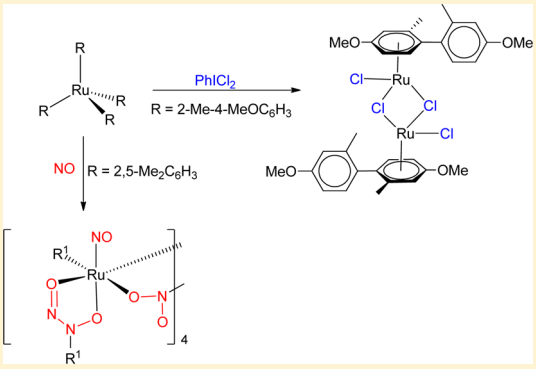
Supporting Information

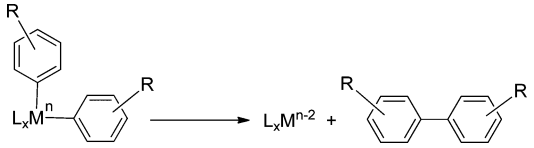
ABSTRACT: Tetraarylruthenium(IV) complexes have been synthesized and their migratory insertion, reductive coupling, and bromination reactions investigated. Treatment of $[Ru(acac)_3]$ ($acac^-$ = acetylacetonate) with RMgBr, followed by column chromatography in air afforded the tetraaryl complexes $[RuR_4]$ (R = 2,5-dimethylphenyl (R^1); 4-methoxy-2-methylphenyl (R^2)). Oxidation of $[RuR^2_4]$ with $AgBF_4$ gave the Ru(V) complex $[Ru^VR^2_4](BF_4)$, which has a measured μ_{eff} of 1.8 μ_B. $[RuR_4]$ and can catalyze the oxidation of methyl *p*-tolyl sulfide with PhIO. Reaction of $[RuR^2_4]$ with $PhICl_2$ led to C−C reductive coupling and the formation of the Ru(II) η^6-biaryl complex $[(\eta^6\text{-}R^2\text{-}R^2)RuCl_2]_2$ (**1**). Treatment of $[RuR^1_4]$ with excess NO gave the tetranuclear Ru(II) aryl-*N*-nitrosohydroxylaminato complex $[RuR^1(N)\{\kappa_2\text{-}O,O'\text{-}ON(R^1)NO\}(\mu\text{-}NO_2)]_4$ (**2**). Bromination of $[RuR^1_4]$ with *N*-bromosuccinimide resulted in formation of $[RuR'_4]$ (R′ = 4-bromo-2,5-dimethylphenyl) (**3**). The crystal structures of $[RuR^2_4]$, $[RuR^2_4](BF_4)$, and **1**−**3** have been determined.



INTRODUCTION

One pathway for decomposition of transition-metal σ-aryl complexes is reductive coupling of the aryl ligands to give biaryls (Scheme 1).[1−3] It has been shown that the reductive coupling of some σ-aryl complexes can be inhibited by ortho substituents of the aryl ligands. Thus, transition-metal complexes with ortho-substituted aryl ligands such as 2,4,6-trimethylphenyl (mes) and 2-methylphenyl (2-MeC_6H_4) are generally more stable than the phenyl analogues.[4]

Scheme 1. Reductive Coupling of Metal σ-Aryl Complexes



Previously, Wilkinson and co-workers have synthesized a series of homoleptic 2-methylphenyl complexes $[M(2\text{-}MeC_6H_4)_4]$ (M = Re, Ru, Os, Mo, Cr)[5−8] and studied their reactivity. $[M(2\text{-}MeC_6H_4)_4]$ (M = Re, Cr, Mo, W) reacted with phosphines to give η^2-aryne complexes via ortho hydrogen abstraction.[7−9] Analogous Nb and W η^2-aryne complexes have been synthesized similarly from the corresponding tetraaryl precursors.[10] By contrast, the treatment of $[Os(2\text{-}MeC_6H_4)_4]$ with L (L = CO, PMe_3) led to reductive coupling of the aryls and formation of $[\{\eta^6\text{-}2(2\text{-}MeC_6H_4)MeC_6H_4\}Os^{II}(2\text{-}MeC_6H_4)_2L]$, whereas $[Os^{II}(2\text{-}MeC_6H_4)_2(CNR)_4]$ and cyclometalated $[Os^{II}\{C,N\text{-}3\text{-}Me(2\text{-}C(2\text{-}MeC_6H_4)NCMe_3)C_6H_3\}(2\text{-}MeC_6H_4)(CNR)_3]$ were obtained from the reactions with RNC (R = *tert*-butyl-2,6-dimethylphenyl).[3] Oxidation of tetraarylosmium(IV) with $AgBF_4$ and PhIO afforded Os(V)[11] and oxo-Os(VI)[12] complexes, respectively. Also, we found that $[OsR^1_4]$ (R^1 = 2,5-dimethylphenyl) can be brominated with pyridinium tribromide to $[OsR'_4]$ (R′ = 4-bromo-2,5-dimethylphenyl), which underwent Suzuki coupling with arylboronic acids to give homoleptic Os(IV) σ-biaryl complexes.[13]

Compared with the osmium analogues, the reaction chemistry of tetraarylruthenium(IV) has not been well explored. This may be due, in part, to lack of general methods to synthesize $[RuR_4]$ complexes in high yield. In an effort to study the electronic factors affecting the stability/reactivity of $[RuR_4]$ complexes, we sought to synthesize homoleptic 2,5-dimethylphenyl (R^1) and 4-methoxy-2-methylphenyl (R^2) complexes of Ru and investigate their organometallic chemistry. Herein, we report the synthesis of $[RuR_4]$ (R = R^1, R^2) by alkylation of $[Ru(acac)_3]$ with Grignard reagents. We found that $[RuR^2_4]$ undergoes reductive coupling with $PhICl_2$ to give a dinuclear Ru(II) η^6-biaryl complex. Furthermore, reaction of

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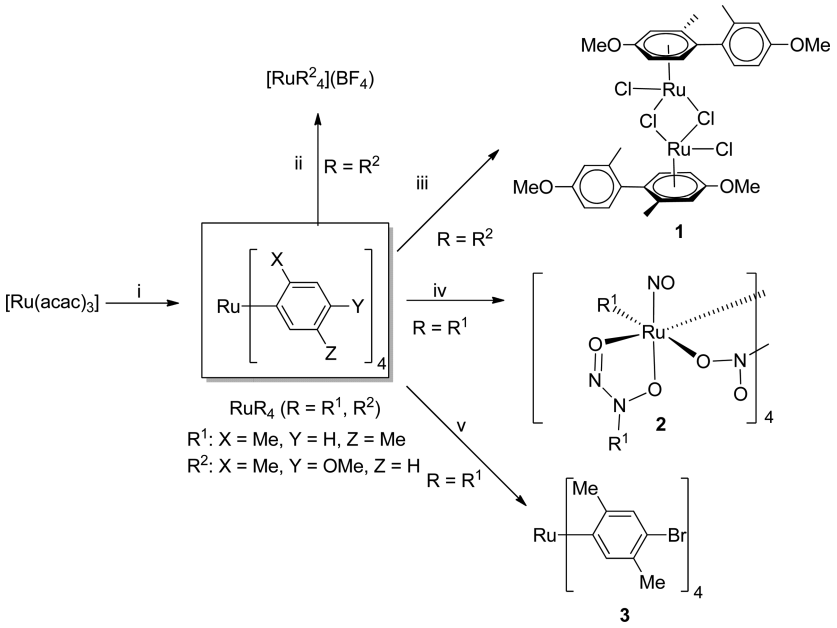
Scheme 2. Synthesis and Reactivity of $[RuR_4]$ (R = R^1, R^2)[a]



[a]Reagents and conditions: (i) 7 equiv of RMgBr, THF, silica chromatography in air; (ii) $AgBF_4$, CH_2Cl_2; (iii) $PhICl_2$, CH_2Cl_2; (iv) NO(g), CH_2Cl_2; (v) CH_2Cl_2, NBS, 1 M H_2SO_4.

$[RuR^1_4]$ with NO resulted in insertion of NO into the Ru−C bond and the formation of a tetranuclear aryl-*N*-nitrosohydroxylaminato complex. The bromination of $[RuR^1_4]$ with *N*-bromosuccinimide (NBS) has also been studied.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were dried, distilled, and degassed before use. ^{1}H NMR spectra were recorded at room temperature on a Bruker AV 400 MHz NMR spectrometer operating at 400 (for ^{1}H) and 100 (for ^{13}C) MHz. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$. Cyclic voltammetry was performed using a CH Instrument model 600D potentiostat. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in MeCN), respectively. Gas chromatography was performed with a Bruker 430-GC instrument equipped with a FID detector. Elemental analyses were performed by Medac Ltd., Surrey, U.K. The compound $[Ru(acac)_3]$ ($acac^-$ = acetylacetonate) was prepared according to a literature method.[14]

Syntheses. *$[RuR^1_4]$ (R^1 = 2,5-Dimethylphenyl).* To a solution of $[Ru(acac)_3]$ (400 mg, 1.01 mmol) in tetrahydrofuran (THF) (10 mL) was added 7 equiv of R^1MgBr (7 mL of 1 M solution in THF, 7 mmol). The resulting brown mixture was stirred at room temperature overnight, and the volatiles were removed in vacuo. The residue was extracted into diethyl ether and subjected to column chromatography in air (silica gel, CH_2Cl_2/hexanes, 1:1, v/v). Recrystallization from hexanes afforded brown crystals. Yield: 15 mg, 28%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 6.75−6.82 (m, 2H, Ph), 6.99 (s, 1H, Ph). ^{13}C {^{1}H} NMR (100, MHz, $CDCl_3$): δ 20.55 (s, CH_3), 24.34 (s, CH_3), 127.18 (s, Ph), 127.58 (s, Ph), 132.92 (s, Ph), 133.41 (s, Ph), 134.90 (s, Ph), 160.62 (s, C_{ipso} Ph). Anal. Calcd for $C_{32}H_{36}Ru$: C, 73.72; H, 7.03. Found: C, 73.36; H, 7.12.

$[RuR^2_4]$ (R^2 = 4-Methoxy-2-methylphenyl). This compound was synthesized similarly as for $[RuR^1_4]$ using R^2 MgBr (1 M in THF) as the alkylating agent. The product was eluted with Et_2O/CH_2Cl_2 (1:1, v/v). Recrystallization from hexanes afforded purple crystals which were suitable for X-ray diffraction analysis. Yield: 17 mg, 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.56−6.62 (m, 2H, Ph), 7.07 (m 1H, Ph). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 24.96 (s, CH_3), 54.47 (s, OCH_3), 109.27 (s, Ph), 114.51 (s, Ph), 133.96 (s, Ph), 140.06 (s, Ph), 149.47 (s, Ph), 158.96 (s, C_{ipso} Ph). Anal. Calcd for $C_{32}H_{36}O_4Ru$: C, 65.62; H, 6.20. Found: C, 65.51; H, 6.24.

$[RuR^2_4](BF_4)$. To a solution of $[RuR^2_4]$ (30 mg, 0.051 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of $AgBF_4$ (10 mg, 0.051 mmol). The green solution was stirred at room temperature for 1 h, and the volatiles were removed in vacuo. The residue was washed with hexanes and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes afforded dark green crystals which were suitable for X-ray analysis. Yield: 22 mg, 67%. μ_{eff} (Evans method,[12] chloroform) = 1.8 μ_B. Anal. Calcd for $C_{32}H_{36}BF_4O_4Ru$: C, 57.15; H, 5.40. Found: C, 56.63; H, 5.17.

*$[Ru(\eta^6\text{-}R^2\text{-}R^2)Cl_2]_2$ (**1**).* To a solution of $[RuR^2_4]$ (30 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was added 4 equiv of $PhICl_2$. The yellowish orange solution was stirred at room temperature for 1 h, and the volatiles were removed in vacuo. The residue was washed with hexanes and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/Et_2O/hexanes afforded dark yellow crystals which were suitable for X-ray analysis. Yield: 10 mg, 48% (with respect to Ru). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 3.80 (s, 6H, OCH_3), 4.10 (s, 6H, OCH_3), 5.12−5.22 (m, 2H, Ph), 5.40−5.52 (m, 2H, Ph), 5.59−5.61 (m, 2H, Ph), 6.70 (s, 2H, Ph), 6.78−6.81 (m, 2H, Ph), 7.95−7.98 (m, 2H, Ph) Anal. Calcd for $C_{32}H_{36}Cl_4O_4Ru_2{\cdot}0.5CH_2Cl_2$: C, 45.16; H, 3.92. Found: C, 44.81; H, 4.28.

*$[RuR^1(NO)\{\kappa_2\text{-}O,O'\text{-}ON(R^1)NO\}(\mu\text{-}NO_2)]_4$ (**2**).* To a solution of $[RuR^1_4]$ (30 mg, 0.058 mmol) in CH_2Cl_2 (10 mL) was bubbled NO(g) for 5 min at 0 °C, during which the dark solution turned reddish orange. The resulting mixture was stirred at room temperature overnight, and the volatiles were removed in vacuo. Recrystallization from CH_2Cl_2/Et_2O/hexanes afforded orange-red crystals which were suitable for X-ray analysis. Yield: 8 mg, 35% (based on Ru). ^{1}H NMR (400 MHz, C_6D_6): δ 1.84 (s, 12H, CH_3), 2.08 (s, 12H, CH_3), 2.43 (s, 12H, CH_3), 2.64 (s, 12H, CH_3), 6.56−6.90 (m, 16H, Ph), 7.68 (m, 8H, Ph). IR (KBr, cm^{-1}): 1879 [ν(N−O)], 1509 [$\nu_s(NO_2)$], 1261 [$\nu_{as}(NO_2)$]. Anal. Calcd for $C_{64}H_{72}N_{16}O_{20}Ru_4$: C, 42.95; H, 4.06; N, 12.52. Found: C, 43.08; H, 4.32; N, 12.32.

*$[RuR'_4]$ (R' = 4-Bromo-2,5-dimethylphenyl) (**3**).* To a solution of $[RuR^1_4]$ (80 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was added 6 equiv of *N*-bromosuccinimide (160 mg, 0.90 mmol) in H_2O/1 M H_2SO_4 (1:1, v/v) (10 mL). The resulting mixture was then stirred at room temperature for 1 h and water (10 mL) was added. The purple organic

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layer was separated, washed with brine solution, and dried with $MgSO_4$. The filtrate was concentrated and subjected to column chromatography (silica gel, hexanes). Recrystallization from hexanes afforded purple crystals which were suitable for X-ray analysis. Yield: 52 mg, 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 6.94 (s, 1H, Ph), 7.10 (s, 1H, Ph). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.97 (s, CH_3), 23.96 (s, CH_3), 124.20 (s, Ph), 131.45 (s, Ph), 133.60 (s, Ph), 133.76 (s, Ph), 137.07 (s, Ph), 158.42 (s, C_{ipso} Ph). Anal. Calcd for $C_{32}H_{32}Br_4Ru$: C, 45.90; H, 3.85. Found: C, 45.41; H, 3.91.

Ru-Catalyzed Decomposition of PhIO. To a solution of [RuR_4] (R = R^1, R^2; 2 mg) in CH_2Cl_2 (5 mL) was added 100 equiv of PhIO (85 mg, 0.384 mmol). The resulting mixture was stirred at room temperature for 1 h. The yield of PhI formed was determined by GLC.

Ru-Catalyzed Sulfide Oxidation. A mixture of methyl *p*-tolyl sulfide (1.49 mmol), PhIO (0.03 mmol), and Ru catalyst (0.0015 mmol) in 1 mL of CH_2Cl_2 was stirred under nitrogen at room temperature for 2 h. The yield of the organic product was determined by GLC and based on PhI formed.

X-ray Crystallography. Intensity data were collected on a Bruker APEX 1000 CCD diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[13,14] Atomic positions of non-hydrogen atoms were refined with anisotropic parameters and with suitable restraints. However, disordered atoms were refined isotropically. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

RESULTS AND DISCUSSION

Synthesis of [RuR_4]. The synthesis and reactivity of tetraarylruthenium(IV) complexes are summarized in Scheme 2. Previously, homoleptic alkyls and aryls of Ru(IV) have been prepared by alkylation of $(Et_4N)[RuCl_5(THF)]$, $[RuO_4]^-$, $[Ru_2(CH_3CO_2)_4Cl]$, or $[RuCl_3(THF)_3]$ (THT = tetrahydrothiophene) with Grignard reagents.[5,18,19] However, attempts to synthesize [RuR_4] (R = 2,5-dimethylphenyl (R^1), 4-methoxy-2-methylphenyl (R^2)) by alkylation of these Ru starting materials led to isolation of the desired products in very low yield (<5%). On the other hand, we found that [RuR_4] could be obtained in ca. 28% yield (unoptimized) from the reaction of $[Ru(acac)_3]$ ($acac^-$ = acetylacetonate) with RMgBr, followed by column chromatography in air. It seems likely that the alkylation of $[Ru(acac)_3]$ initially gave an Ru(III) intermediate, possibly $[RuR_4]^-$, which was subsequently air oxidized to [RuR_4] during the workup. Attempts to isolate the Ru(III) intermediates by carrying out the workup under nitrogen failed.

Like the 2-methylphenyl analogue, [RuR^1_4] and [RuR^2_4] are air-stable and diamagnetic. X-ray quality single crystals of [RuR^2_4] were obtained by slow evaporation of a saturated CH_2Cl_2/hexanes solution in air. Figure 1 shows the molecular structure of [RuR^2_4]. Similar to $[Ru(2\text{-}MeC_6H_4)_4]$,[5b] the structure of [$RuR^2_4$] exhibits a 4-fold symmetry, and the geometry around Ru is roughly tetrahedral [C−Ru−C′ angles = 105.99(15) and 111.24(8)°]. The Ru−C distance [1.986(3) Å] and C−Ru−C′ angles [105.99(15) and 111.24(8)°] compare well with those in $[Ru(2\text{-}MeC_6H_4)_4]$.[5b]

Oxidation of [RuR_4]. The cyclic voltammograms of [RuR^1_4] and [RuR^2_4] in acetonitrile displayed reversible couples at 0.5 and 0.2 V vs $Cp_2Fe^{+/0}$, respectively, which are assigned to the metal-centered Ru(V/IV) couple. The Ru(V/IV) potential for [RuR^2_4] is lower than those for $[Ru(2\text{-}MeC_6H_4)_4]$ (0.51 V vs $Cp_2Fe^{+/0}$, CH_2Cl_2),[7] indicating the ability of the methoxy substituent in stabilizing the Ru(V) state.

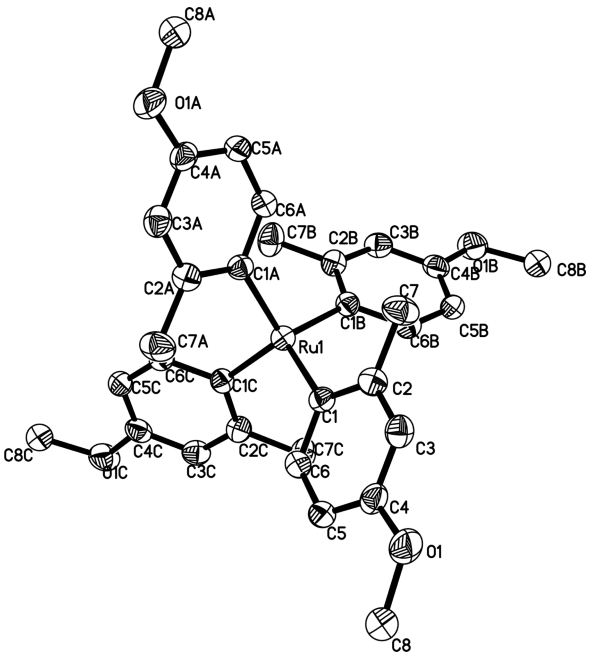

Figure 1. Molecular structure of [RuR^2_4]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond length (Å) and angles (deg): Ru−C 1.986(3); C−Ru−C′ 105.99(15), 111.24(8).

Treatment of [RuR^2_4] with 1 equiv of $AgBF_4$ afforded $[Ru^VR^2_4](BF_4)$, which was isolated as green crystals. The measured magnetic moment of ca. 1.8 μ_B is consistent with the S = 1/2 spin state. A similar Ru(V) complex, $[Ru^V(mes)_4]^+$ ($E_{1/2}$ = 0.32 V), has been isolated previously, but its structure has not been determined.[19] While $[RuR^2_4](BF_4)$ is air-stable in solution, it is reduced to [RuR^2_4] readily when reacted with PPh_3 and nucleophiles such as N_3^-. Figure 2 shows the molecular structure of $[RuR^2_4](BF_4)$. Similar to isoelectronic $[Os(2\text{-}MeC_6H_4)_4]^+$,[6b] and $[Re(2\text{-}MeC_6H_4)_4]$,[5b] the complex

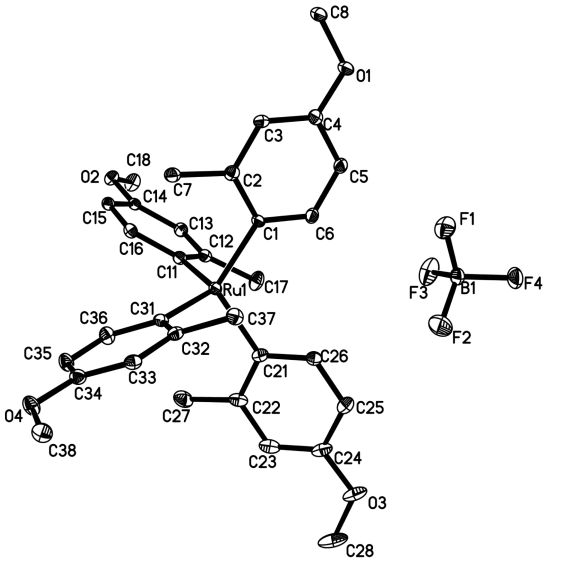

Figure 2. Molecular structure of $[RuR^2_4](BF_4)$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru−C 1.970(3)−1.979(3); C−Ru−C′ 99.21(10)−116.54(11).

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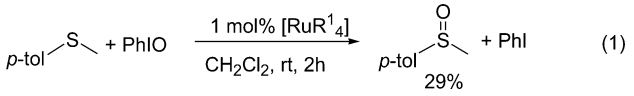
cation $[RuR^2_4]^+$ features a pseudo 4-fold symmetry. The range of C−Ru−C′ angles [99.21(10)−116.54(11)°] in $[RuR^2_4]^+$ is obviously larger than that for $[RuR^2_4]$, due to the Jahn−Teller effect associated with the low-spin d^3 electron configuration.[7,19] The Ru−C bond lengths in $[RuR^2_4]^+$ [1.970(3)−1.979(3) Å] are slightly shorter than those in $[RuR^2_4]$.

Reaction of [RuR$_4$] with PhIO. The reaction between tetraarylruthenium(IV) complexes and PhIO was studied because the Os(VI) mono-oxo complex $[Os^{VI}(O)R^1_4]$ has been synthesized by oxidation of $[OsR^1_4]$.[12] Treatment of $[RuR^1_4]$ in $CDCl_3$ with 1 equiv of PhIO at room temperature resulted in a purple solution. GLC analysis showed that PhI was produced in ca. 90% yield. ^{1}H NMR spectroscopy indicated the reaction mixture contained $[RuR^1_4]$ along with some other diamagnetic species. We have not been able to separate the product mixture by recrystallization. $[RuR^1_4]$ was found to be a catalyst for decomposition of PhIO. Thus, in the presence of 1 mol % of $[RuR^1_4]$, PhIO was converted to PhI in over 95% yield in 1 h. The byproduct oxygen has been identified by GC analysis. It seems likely that the reaction of $[RuR^1_4]$ with PhIO afforded a reactive intermediate, possibly a high-valent oxo or PhIO complex,[20] which decomposed rapidly to $[RuR^1_4]$ with elimination of oxygen. In the presence of an organic substrate, $[RuR^1_4]$ can catalyze the oxo transfer of PhIO (presumably via the intermediacy of an oxo or PhIO complex). For example, treatment of methyl *p*-tolyl sulfide with PhIO in the presence of 1 mol % of $[RuR^1_4]$ afforded methyl *p*-tolyl sulfoxide in 29% yield (based on PhI formed) (eq 1); no methyl *p*-tolyl sulfone was detected. A similar yield (28%) was found when $[RuR^2_4]$ was used as catalyst.



(1)

Reductive Coupling of [RuR$^2_4$]. Reactions of $[RuR^1_4]$ with other hypervalent iodine reagents have also been examined. $[RuR^1_4]$ reacted readily with PhINTs (Ts = tosyl) to produce a purple species along with PhI and $TsNH_2$. We have not been able to crystallize the purple species for characterization. No reaction was found between $[RuR^1_4]$ and $PhI(OAc)_2$ (OAc = acetate), whereas $[RuR^1_4]$ reacted with $PhICl_2$ to produce a brown species that exhibited ^{1}H NMR signals at δ 5−6 ppm, which can be attributed to an η^6-arene ligand. We have not been able to crystallize this brown product for further characterization. On the other hand, reaction of $[RuR^2_4]$ with $PhICl_2$ afforded a brown crystalline solid, which was identified as the Ru(II) η^6-biaryl complex $[(\eta^6\text{-}R^2\text{-}R^2)RuCl_2]_2$ (**1**) by X-ray diffraction. The ^{1}H NMR spectrum of **1** displayed resonances at δ 5.12−5.61 ppm due to the phenyl protons of the η^6-bonded aryl ring along with multiplets at δ 6.70−6.98 ppm corresponding to the uncoordinated aryl ring of the biaryl ligand. Figure 3 shows the molecular structure of **1**. The structure consists of two symmetry-related $[(\eta^6\text{-biaryl})RuCl_2]$ fragments linked together by two bridging chlorides. The Ru−C [2.153(4)−2.231(3) Å] and Ru−Cl [2.4404(9) and 2.4311(8) Å] distances are typical for $[(\eta^6\text{-arene})RuCl_2]$-type complexes, e.g. $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$.[21] The two aryl rings in the biaryl ligand are roughly perpendicular to each other (dihedral angle = 96.63°).

The C−C and C−Cl reductive elimination of high-valent transition-metal aryl halide complexes is well documented. Recently, Whitfield and Sanford reported that upon heating *cis*-$[Pd^{IV}(ppy)_2Cl_2]$ (ppy = 2-(2-pyridyl)phenyl), which was prepared by the chlorination of *cis*-$[Pd^{II}(ppy)_2]$ with $PhICl_2$, underwent C−C and C−Cl reductive elimination to afford 4,4′-bi(2-phenylpyridine) and 2-(2-chlorophenyl)pyridine, respectively.[22] Therefore, we believe that a similar pathway is involved in the formation of **1**. Reaction of $[RuR^2_4]$ with $PhICl_2$ gives a high-valent Ru chloride complex (possibly a Ru^{VI} species because Ru^V aryl complexes such as $[RuR^1_4]^+$ and $[RuR^2_4]^+$ are stable with respect to reducing elimination), which undergoes C−C and C−Cl reductive elimination to afford $[(\eta^6\text{-}R^2\text{-}R^2)RuCl_2]$, which dimerizes to **1**. Consistent with this proposal, the aryl chloride 4-chloro-3-methylanisole (R^2Cl) has been detected in the reaction mixture by GLC analysis. It may also be noted that Os(II) η^6-biaryl complexes have been obtained from the ligand-induced reductive coupling of $[Os(2\text{-}MeC_6H_4)_4]$.[3] Attempts to characterize the reactive Ru chloride intermediate(s) by monitoring the reaction of $[RuR^2_4]$ with 1 equiv of $PhICl_2$ in $CDCl_3$ by using NMR spectroscopy failed. Only a complex ^{1}H NMR spectrum showing peaks

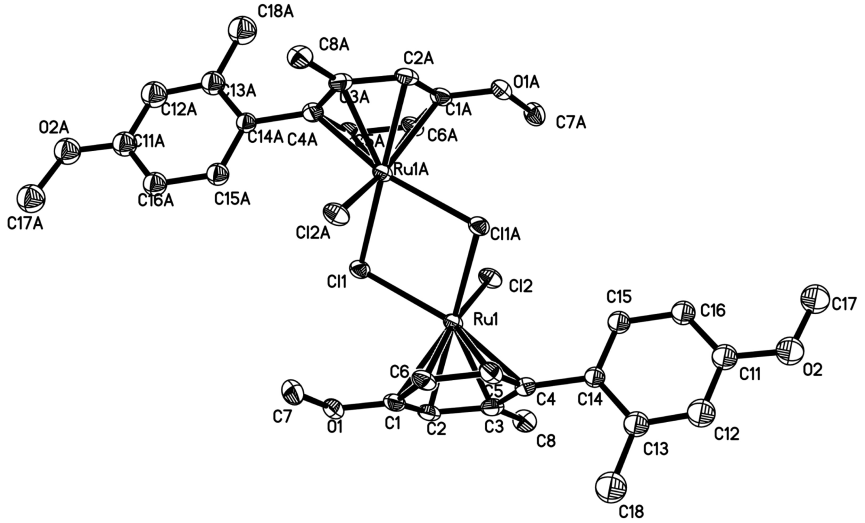


Figure 3. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): Ru1−C 2.153(4)−2.231(3), Ru1−Cl1, 2.4404(9), Ru1−Cl1A 2.4311(8), Ru1−Cl2 2.4017(9).

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corresponding to **1** and unreacted [RuR$^2_4$], along with some unidentified species, was observed.

Migratory Insertion of [RuR$^1_4$] with NO. Treatment of [RuR$^1_4$] with excess NO led to formation of the tetranuclear aryl-*N*-nitrosohydroxylaminato complex [Ru(NO)R^1{κ_2-*O*,*O*′-ON(R^1)NO}(μ-NO$_2$)]$_4$ (**2**). Complex **2** is diamagnetic and exhibits sharp ^{1}H NMR signals, consistent with the {Ru(NO)}^{6} electron configuration. The IR N−O stretching frequency of 1879 cm^{-1} is typical for the linear nitrosyl ligand.[23] Figure 4

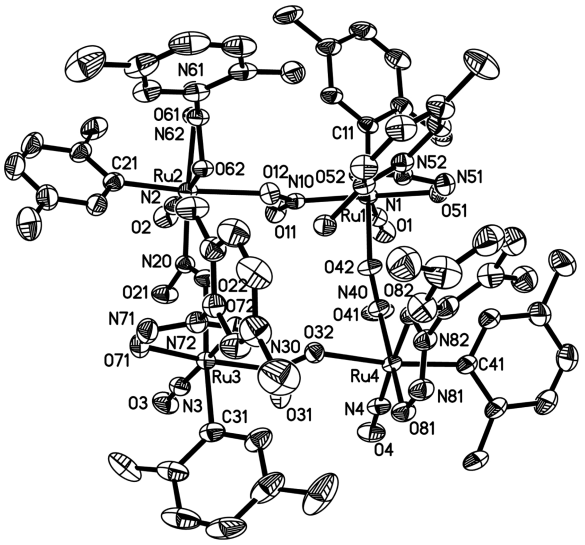
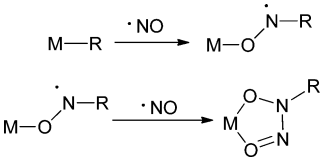


Figure 4. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru−C 2.067(4)−2.080(3), Ru−N(nitrosyl) 1.731(3)−1.738(3), Ru−O(nitrosohydroxylaminato) 1.997(3)−2.055(3), Ru−O(nitrito) 2.029(3)−2.045(3), Ru−N-(nitrito) 2.230(3)−2.255(2); Ru−N−O (nitrosyl) avg 177.7°.

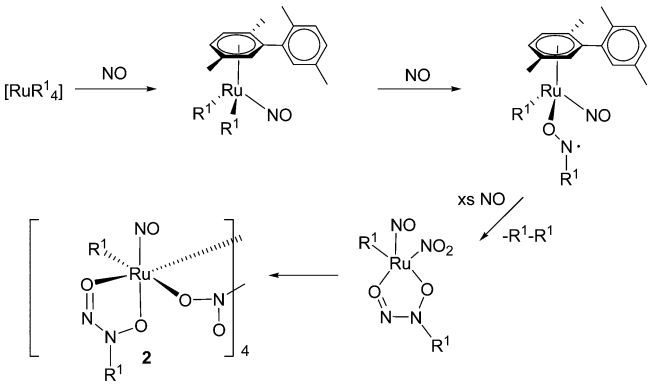
shows the crystal structure of **2**. The structure consists of four [Ru(NO)(R^1){κ_2-*O*,*O*′-ON(R^1)NO}]$^+$ units that are bridged by four bidentate-*N*,*O* nitrite ligands. The geometry around each Ru center is *pseudo* octahedral with the nitrosyl opposite to an oxygen of the nitrosohydroxylaminate chelate and the aryl ligand trans to an oxygen of the nitrite. The nitrosyl binds to Ru in a linear fashion (average Ru−N−O angle = 177.7°). The Ru−C distances [2.067(4)−2.080(3) Å] are similar to those in [RuR$^1_4$]. The O−N (O−N 1.330(4)−1.352(3) Å, O═N 1.294(4)−1.323(4) Å) and N−N (1.263(5)−1.276(4) Å) bond lengths in the Ru[ON(R^1)NO] metallacycles compare well with those in reported alky-*N*-nitrosohydroxylaminato complexes.[24]

Reactions of metal alkyls with NO leading to the formation of alkyl-*N*-nitrosohydroxylaminato complexes are well documented. It is believed that the insertion of NO into the metal−alkyl bond gives a radical intermediate, which reacts rapidly with another molecule of NO to yield an alkyl-*N*-nitrosohydroxylaminato group (Scheme 3).[24,25] Therefore, a plausible mechanism for the formation of **2** is proposed in Scheme 4. Reaction of [RuR$^1_4$] with NO results in reductive coupling of aryl groups and formation of a Ru(II) η^2-biaryl intermediate. Migratory insertion of the Ru aryl with NO gives the Ru[ON(R^1)NO] metallacycle. Dissociation of the labile η^6-biaryl ligand[26] and coordination of NO$_2^-$, which is presumably derived from disproportionation of NO,[27] affords five-coordinated Ru[ON(R^1)NO](R^1)(NO)(NO$_2$), which is finally

Scheme 3. Proposed Pathway for the Formation of Alky-*N*-nitrosohydroxylaminato Complexes[25]



Scheme 4. Plausible Mechanism for the Formation of 2



converted to the tetramer **2**. It should be noted that the formation of Ru(II) nitrosyl nitrito complexes by reactions of Ru porphyrin and Schiff base complexes with excess nitric oxide is well precedented.[27,28]

Bromination of [RuR$^1_4$]. In previous work, we reported that the aryl ligands in [OsR$^1_4$] could be brominated selectively by pyridinium tribromide.[13] In this work, we found that under the same conditions the bromination of [RuR$^1_4$] with excess pyridinium tribromide led to formation of a mixture of mono- and dibrominated products, characterized by mass spectrometry. On the other hand, reaction of [RuR$^1_4$] with NBS yielded the tetrabrominated complex [RuR′$_4$] (R′ = 4-bromo-2,5-dimethylphenyl) (**3**) as the sole product. Similar to the Os analogue, the aryl ligands in [RuR$^1_4$] were brominated selectively at the para position with respect to the Ru−C bond. The crystal structure of **3** has been determined (Figure 5). The Ru−C distance [1.984(5) Å] and C−Ru−C′ angles [106.3(3) and 111.06(14)°] in **3** are similar to those in [RuR$^1_4$], indicating that the bromo substituents have very little influence on the Ru−C bonds. The synthesis of Ru complexes with functionalized aryl ligands using **3** as the starting material is underway.

CONCLUSIONS

In summary, we have synthesized the Ru(IV) tetraaryl complexes [RuR$^1_4$] and [RuR$^2_4$] by alkylation of [Ru(acac)$_3$] with Grignard reagents. [RuR$^1_4$] can catalyze the oxo transfer of PhIO, possibly via the intermediacy of an oxo species or PhIO complex. Reaction of [RuR$^2_4$] with PhICl$_2$ afforded a Ru(II) η^6-biaryl complex, presumably via the C−C and C−Cl reductive elimination. Migratory insertion of [RuR$^1_4$] with NO led to formation of the aryl-*N*-nitrosohydroxylaminato complex [Ru(NO)R^1{κ_2-*O*,*O*′-ON(R^1)NO}(μ-NO$_2$)]$_4$. [RuR$^1_4$] can be selectively brominated with NBS to give a homoleptic Ru(IV) bromoaryl complex. The results of this work demonstrate that both the Ru center and aryl ligands in tetraarylruthenium(IV) complexes display rich reaction chemistry.

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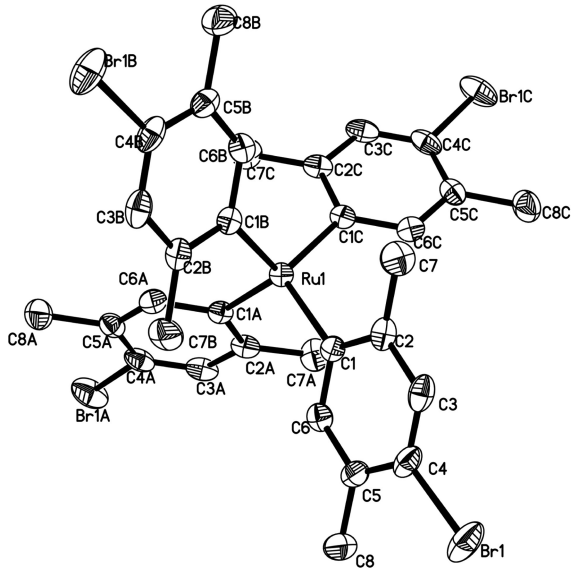

Figure 5. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond length (Å) and angles (deg): Ru−C 1.984(5); C−Ru−C′ 106.3(3), 111.06(14).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data and experimental details, crystal structures and selected bond lengths and angles, and CIF data. 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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