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σ-Acetylide Complexes of Ruthenium(IV) and Osmium(IV) Thiolates

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Summary: Treatment of [M(Sxylyl)$_3$(MeCN)Cl] (M = Ru, Os; xylyl = 2,6-dimethylphenyl) with PhC≡CH in the presence of Et$_3$N afforded [Et$_3$NH][M(Sxylyl)$_3$(C≡CPh)Cl]. The crystal structure of [Et$_3$NH][Ru(Sxylyl)$_3$(C≡Ctol)Cl] (tol = 4-tolyl) has been determined. The average Ru−S, Ru−C, and Ru−Cl distances are 2.1980, 1.991(5), and 2.5131(13) Å, respectively. Interaction of [Et$_4$NH][Ru(Sxylyl)$_3$(C≡CPh)Cl] with excess t-BuNC gave trans-[Ru(t-BuNC)$_4$(Sxylyl)$_2$].

Introduction

Transition-metal−sulfur systems are of significance due to their central roles in biology[1] and heterogeneous catalysis.[2] Of interest are binary sulfides of noble metals, notably Ru, which are active catalysts for the industrially important hydrodesulfurization process.[3] Recently, molecular Ru thiolato and sulfido complexes have also been synthesized to model the active sites of metal−sulfide catalysts[4] and metalloenzymes.[5] While Ru(II) thiolate complexes are well documented, the analogous Ru(IV) system has received relatively less attention.[6−8] Trigonal-bipyramidal Ru(IV) and Os(IV) thiolate complexes [M(SAr)$_4$(MeCN)] (M = Ru, Os; Ar = aryl group such as 2,4,5,6-tetramethylphenyl and 2,4,6-triisopropylphenyl) were first synthesized by Koch and Millar and co-workers.[7a] The solid-state structures of these complexes feature the characteristic trigonal-planar [M(SAr)$_3$]$^+$ core that is also found for the isoelectronic Mo(II),[9] Tc(III),[10] and Re(III)[11] analogues. Interestingly, [M(SAr)$_4$(MeCN)] reacted with CO to give [M(SAr)$_4$(CO)]. Therefore, one may expect that the electron-rich {Ru(SAr)$_3$}$^+$ core should exhibit rich organometallic chemistry. Nevertheless, relatively few organometallic compounds of Ru(IV) thiolates are known to date.[6d,7c,12,13] Herein we report the synthesis and characterization of the first *σ*-acetylide complexes of Ru(IV) and Os(IV) thiolates.

Results and Discussion

Millar and Koch and co-workers synthesized [Ru(SAr)$_3$(MeCN)] by reaction of [Et$_4$N][RuCl$_4$(MeCN)$_2$] with LiSAr in the presence of Ar$_2$S$_2$ in refluxing EtOH/MeCN.[7a] We found that reaction of [Et$_4$N][RuCl$_4$(MeCN)$_2$] with NaSxylyl (xylyl = 2,6-dimethylphenyl) afforded [Ru(Sxylyl)$_4$(MeCN)] (**1**) along with [Et$_4$N][Ru(Sxylyl)$_4$Cl] (**2**); the latter has been characterized by X-ray diffraction. As previously reported,[7d] protonation of **1** with HCl afforded [Ru(Sxylyl)$_3$(MeCN)Cl] (**3**) in good yield. The solid-state structures of **2** and **3** are shown in Figures 1 and 2, respectively. Similar to [Ru(SAr)$_4$(MeCN)],[7a] the geometry around Ru in complexes **2** and **3** is trigonal-bipyramidal with the equatorial thiolate ligands adopting a “two-up one-down” conformation, which can be explained in terms of the π interaction between 3p$_\pi$ orbitals the two equatorial sulfurs and the empty 2e (d$_{xy}$, d$_{x^2-y^2}$) Ru orbitals.[7b] The ^{1}H NMR spectra of **2** and **3** in CDCl$_3$ show two sets of methyl resonance signals, indicating that the two-up one-down conformation is maintained in solution. In **2**, the Ru−S(equato-

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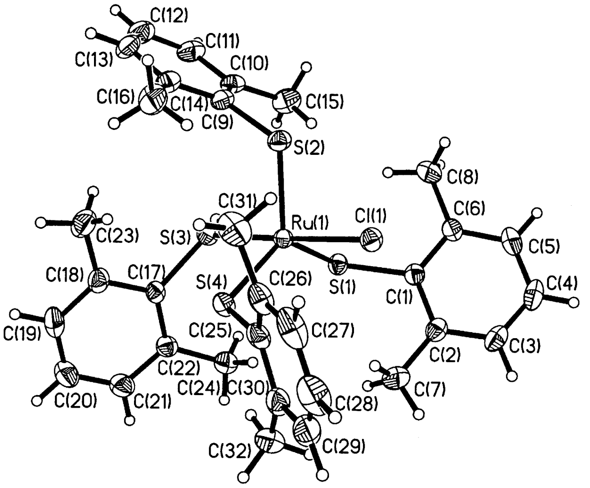

Figure 1. Molecular structure of the anion $[Ru(Sxylyl)_4Cl]^-$. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.1946(11), Ru(1)−S(2) = 2.2003(12), Ru(1)−S(3) = 2.3986(10), Ru(1)−S(4) = 2.2161(12), Ru(1)−Cl(1) = 2.4369(10); S(1)−Ru(1)−S(2) = 117.59(5), S(1)−Ru(1)−S(4) = 123.11(5), S(2)−Ru(1)−S(4) = 119.18(5), S(1)−Ru(1)−S(3) = 84.23(5), S(2)−Ru(1)−S(3) = 95.24(4), S(4)−Ru(1)−S(3) = 87.44(4), S(1)−Ru(1)−Cl(1) = 93.13(4), S(2)−Ru(1)−Cl(1) = 83.97(4), S(4)−Ru(1)−Cl(1) = 95.90(4), S(3)−Ru(1)−Cl(1) = 176.53(5).

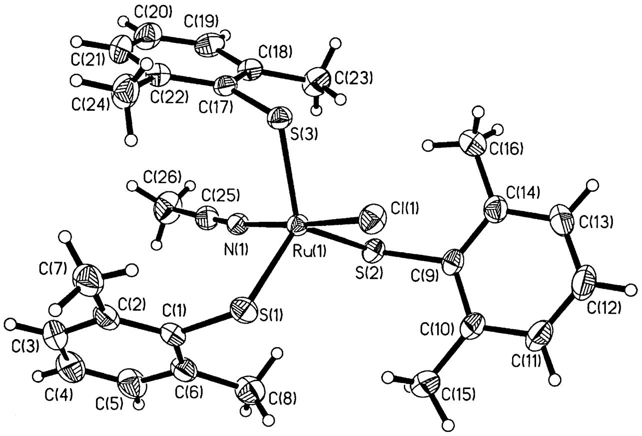

Figure 2. Molecular structure of $[Ru(Sxylyl)_3(MeCN)Cl]$ (**3**). Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2072(8), Ru(1)−S(2) = 2.1984(8), Ru(1)−S(3) = 2.2012(8), Ru(1)−N(1) = 2.037(2), Ru(1)−Cl(1) = 2.3643(8); N(1)−Ru(1)−S(2) = 86.25(7), N(1)−Ru(1)−S(3) = 92.33(7), S(2)−Ru(1)−S(3) = 119.00(3), N(1)−Ru(1)−S(1) = 94.51(7), S(2)−Ru(1)−S(1) = 116.87(3), S(3)−Ru(1)−S(1) = 124.01(3), N(1)−Ru(1)−Cl(1) = 176.04(7), S(2)−Ru(1)−Cl(1) = 96.64(3), S(3)−Ru(1)−Cl(1) = 83.91(3), S(1)−Ru(1)−Cl(1) = 86.61(3).

rial) bond distances (average of 2.2037 Å) are shorter than the Ru−S(axial) distance (2.3986(10) Å), indicative of Ru−S(equatorial) π bonding. The average Ru−S (2.2022 Å) and Ru−N (2.037(2) Å) distances in **3** are comparable to those in $[Ru(SAr)_4(MeCN)]$ (Ar = 2,3,5,6-tetramethylphenyl) (2.209 and 2.096(5) Å, respectively[7a]). The Ru−Cl distance in **2** (2.4369(10) Å) is slightly longer than that in **3** (2.3643(8) Å), indicative of the trans influence of the thiolate ligand.

Treatment of **2** with PhC≡CH in CH_2Cl_2 resulted in the formation of $[Et_4N][Ru(Sxylyl)_3(C{\equiv}CPh)Cl]$ (**4**), which shows $\nu_{C\equiv C}$ at 2052 cm^{-1} in the IR spectrum. No reactions were found between **2** and alkylacetylenes such as $Me_3SiC{\equiv}CH$ or *t*-BuC≡CH. Reaction of **3** with 4-tolylacetylene in the presence of Et_3N afforded $[Et_3NH][Ru(Sxylyl)_3(C{\equiv}Ctol)Cl]$ (**5**), which has been characterized by X-ray crystallography (Figure 3). Similarly, the Os analogue $[Et_3NH][Os(Sxylyl)_3(C{\equiv}CPh)Cl]$ (**6**) was prepared from $[Os(Sxylyl)_3(MeCN)Cl]$[14] and PhC≡CH in the presence of Et_3N. It may be noted that structurally characterized Ru(IV) σ-acetylides are rather rare.[14] The structure of the anion $[Ru(Sxylyl)_3(C{\equiv}Ctol)Cl]^-$ consists of the trigonal {$Ru(Sxylyl)_3$} core with the chloride and acetylide at the axial positions. The average Ru−S distance (2.1980 Å) in **5** is similar to that in **3**. The Ru−Cl distance (2.5131(13) Å) in **5** is longer than those in **2** and **3**, indicative of the order of trans influence $PhC{\equiv}C^- > xylylS^- > MeCN$. The ethynyl moiety is almost linear ($Ru{-}C_\alpha{-}C_\beta$ = 177.8(4)°). The $Ru{-}C_\alpha$ distance of 1.991(5) Å is similar to that in $[Cp^*RuH(C{\equiv}CCO_2Me)(dippe)][BPh_4]$ (2.04(2) Å; dippe = 1,2-bis(diisopropylphosphino)ethane).[15]

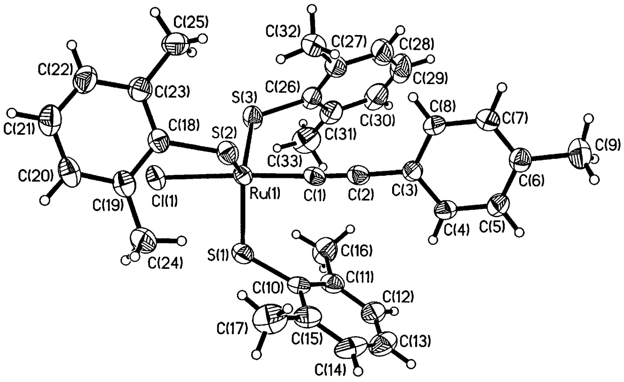

Figure 3. Molecular structure of the anion $[Ru(Sxylyl)_3(C{\equiv}Ctol)Cl]^-$. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.1999(12), Ru(1)−S(2) = 2.1938(12), Ru(1)−S(3) = 2.2003(12), Ru(1)−C(1) = 1.991(5), Ru(1)−Cl(1) = 2.5131(13), C(1)−C(2) = 1.180(7); C(1)−Ru(1)−S(2) = 85.12(12), C(1)−Ru(1)−S(1) = 93.10(12), S(2)−Ru(1)−S(1) = 119.10(5), C(1)−Ru(1)−S(3) = 94.01(12), S(2)−Ru(1)−S(3) = 117.78(5), S(1)−Ru(1)−S(3) = 123.06(6), C(1)−Ru(1)−Cl(1) = 177.00(12), S(2)−Ru(1)−Cl(1) = 97.51(4), S(1)−Ru(1)−Cl(1) = 84.37(5), S(3)−Ru(1)−Cl(1) = 86.05(4), C(2)−C(1)−Ru(1) = 177.8(4).

Treatment of **4** with 1 equiv of *t*-BuNC led to the formation of a yellowish green solid, characterized as $[Ru(Sxylyl)_3(t\text{-}BuNC)Cl]$ (**7**). When an excess of *t*-BuNC (>4 equiv) was used, **4** was reduced to the Ru(II) complex *trans*-$[Ru(t\text{-}BuNC)_4(Sxylyl)_2]$ (**8**). Complex **8** could also be synthesized directly from **1** and excess *t*-BuNC. The reaction mixture of **4** and *t*-BuNC was found to contain 1,4-diphenylbutadiyne, identified by ^{13}C NMR and IR analyses, suggesting that coupling of the acetylide ligands had occurred. The molecular structure of complex **8** is shown in Figure 4. The geometry around Ru is pseudo-octahedral with two mutually trans *t*-BuNC ligands. The Ru−S bond lengths (average 2.4493 Å) in **8** are obviously longer than those in **2**, **3**, and **5**, indicative of the absence of Ru−S π bonding. The average Ru−C distances in **8** of 1.9965 Å are similar to those in related Ru(II) isocyanide

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[14] $[Os(Sxylyl)_3(MeCN)Cl]$ was prepared by the reaction of $[NH_4]_2[OsCl_6]$ with 2,6-dimethylthiophenol in the presence of Et_3N in EtOH/MeCN and purified by column chromatography (yield 46%).

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Table 1. Crystallographic Data and Experimental Details for 2·CH_2Cl_2, 3, 5, and 8·$2H_2O$

	2·CH_2Cl_2	**3**	**5**	**8**·$2H_2O$
formula	$C_{41}H_{58}Cl_3NRuS_4$	$C_{26}H_{30}ClNRuS_3$	$C_{39}H_{50}ClNRuS_3$	$C_{36}H_{58}N_4O_2RuS_2$
fw	900.54	589.21	765.50	744.05
a, Å	13.4154(8)	11.0214(8)	11.3258(7)	9.2197(7)
b, Å	15.7625(9)	15.219(1)	15.619(1)	9.9086(7)
c, Å	21.157(1)	16.421(1)	22.317(2)	12.3324(9)
α, deg				108.901(1)
β, deg		102.148(1)	98.347(1)	100.538(1)
γ, deg				97.534(1)
V, Å^3	4473.8(4)	2692.6(3)	3906.0(4)	1025.7(1)
Z	4	4	4	1
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P1$
ρ_{calcd}, g cm^{-3}	1.337	1.453	1.302	1.205
T, K	293(2)	293(2)	293(2)	293(2)
μ, mm^{-1}	0.745	0.929	0.657	0.516
$F(000)$	1880	1208	1600	394
no. of rflns measd	26478	15677	22488	5940
no. of indep rflns	10115	6079	8642	5114
R_{int}	0.0475	0.0311	0.0387	0.0098
R1,[a] wR2[b] ($I > 2.0\sigma(I)$)	0.0385, 0.0853	0.0335, 0.0742	0.0528, 0.1475	0.0368, 0.1026
R1, wR2 (all data)	0.0817, 0.1030	0.0610, 0.0829	0.0911, 0.1883	0.0371, 0.1035
GOF[c] on F^2	0.762	0.946	0.896	1.050

[a] $R1 = (\sum|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = [(\sum w(F_o^2 - F_c^2)^2/\sum w|F_o^2|^2]^{1/2}$. [c] $GOF = [(\sum w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

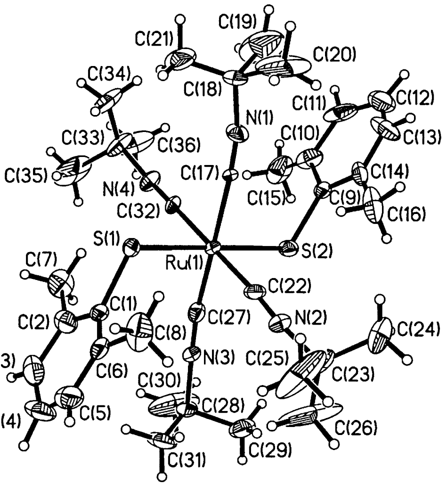

Figure 4. Molecular structure of *trans*-[Ru(*t*-BuNC)$_4$(Sxylyl)$_2$] (**8**). Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.4558(7), Ru(1)−S(2) = 2.4427(9), Ru(1)−C(17) = 2.054(2), Ru(1)−C(22) = 1.987(4), Ru(1)−C(27) = 1.917(4), Ru(1)−C(32) = 2.028(3); C(27)−Ru(1)−C(22) = 84.77(16), C(27)−Ru(1)−C(32) = 95.24(16), C(22)−Ru(1)−C(32) = 179.45(15), C(27)−Ru(1)−C(17) = 179.70(16), C(22)−Ru(1)−C(17) = 95.43(13), C(32)−Ru(1)−C(17) = 84.56(12), C(27)−Ru(1)−S(2) = 85.22(10), C(22)−Ru(1)−S(2) = 87.42(10), C(32)−Ru(1)−S(2) = 92.03(9), C(17)−Ru(1)−S(2) = 95.01(7), C(27)−Ru(1)−S(1) = 94.31(10), C(22)−Ru(1)−S(1) = 92.56(10), C(32)−Ru(1)−S(1) = 87.99(9), C(17)−Ru(1)−S(1) = 85.46(7), S(2)−Ru(1)−S(1) = 179.54(4).

complexes: e.g., *trans*-[Ru{N(*i*-$Pr_2PS)_2\}_2$(*t*-BuNC)$_2$] (1.990(3) Å)[16] and *trans*-[Ru($S_2CNEt_2)_2$(*t*-BuNC)$_2$] (1.997(2) Å).[17]

In summary, the first σ-acetylide complexes of Ru(IV) and Os(IV) thiolates [M(Sxylyl)$_3$(C≡CPh)Cl]$^-$ have been synthesized from [M(Sxylyl)$_3$(MeCN)Cl] (M = Ru, Os) and PhC≡CH in the presence of Et_3N. [Ru(Sxylyl)$_3$(C≡CPh)Cl]$^-$ was reduced by *t*-BuNC to give *trans*-[Ru(*t*-BuNC)$_4$(Sxylyl)$_2$]. A preliminary study showed that [M(Sxylyl)$_3$(C≡CPh)Cl]$^-$ is capable of catalyzing ring-opening metathesis polymerization of norbornene. The investigation into the catalytic activity of these σ-acetylide complexes is under way.

Experimental Section

General Considerations. Solvents were purified by standard procedures and distilled prior to use. All manipulations were carried out under nitrogen using standard Schlenk techniques. [Et_4N][$RuCl_4(MeCN)_2$] was prepared according to a literature method.[18] 2,6-Dimethylthiophenol (xylylSH) and *t*-BuNC were purchased from Aldrich. ^1H NMR spectra were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, and mass spectra were obtained on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd, Surrey, U.K.

Preparations of [Ru(Sxylyl)$_4$(MeCN)] (1) and [Et_4N][Ru(Sxylyl)$_4$Cl] (2). This was synthesized by a modification of the literature method. To a slurry of [Et_4N][$RuCl_4(MeCN)_2$] (511 mg, 1.25 mmol) in MeOH/MeCN (2:1, 50 mL) were added 2,6-dimethylthiophenol (863 mg, 6.25 mmol) and NaOMe (338 mg, 6.25 mmol), and the mixture was heated at reflux for 8 h and then cooled at room temperature. After removal of solvents under vacuum, the brown crude product was washed with hexane and Et_2O and then was extracted with $CHCl_3$. Et_2O was layered on the concentrated extract, and the mixture was cooled to −10 °C, giving **1** as dark brown crystals (457 mg, 53%). Further recrystallization of the dark residue from CH_2Cl_2/EtOH/Et_2O afforded green-brown crystals of **2** (366 mg, 26%). Complex **2** could also be purified by column chromatography (silica gel) using CH_2Cl_2/acetone (2:1, v/v) as eluant. Data for **1** are as follows. ^1H NMR ($CDCl_3$): δ 7.34 (t, 1H, H_p), 7.29 (t, 1H, H_p), 7.22 (t, 2H, H_p), 7.15 (d, 2H, H_m), 7.08 (d, 2H, H_m), 6.99 (d, 4H, H_o), 2.21 (s, 18H, Me), 2.09 (s, 6H, Me), 1.98 (s, 3H, MeCN). MS (FAB): *m/z* 692 ($M^+ + 1$), 650 ([Ru(Sxylyl)$_4$] + 1), 512 ([Ru(Sxylyl)$_3$]), 375 ([Ru(Sxylyl)$_2$]). Anal. Calcd for $C_{34}H_{39}NRuS_4$: C, 59.10; H, 5.69; N, 2.03. Found: C, 58.76; H, 5.61; N, 2.01. Data for **2** are as follows. ^1H NMR ($CDCl_3$): δ 7.32 (t, 1H, H_p), 7.27 (t, 1H, H_p), 7.21 (t, 2H, H_p), 7.13 (d, 2H, H_m), 7.05 (d, 2H, H_m), 6.98 (d, 4H, H_m), 3.31 (dt, 8H, $CH_3C\mathit{H}_2$),

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2.19 (s, 18H, Me), 2.01 (s, 6H, Me), 1.32 (t, 12H, $C\mathit{H}_3CH_2$). MS (FAB): *m*/*z* 685 ($M^+ - Et_4N + 1$), 650 ([Ru(Sxylyl)$_4$] + 1), 512 ([Ru(Sxylyl)$_3$]), 373 ([Ru(Sxylyl)$_2$] − 1). Anal. Calcd for $C_{40}H_{56}ClNS_4Ru{\cdot}CH_2Cl_2{\cdot}H_2O$: C, 53.62; H, 6.54; N, 1.53. Found: C, 52.84; H, 7.21; N, 1.73.

Preparation of [Ru(Sxylyl)$_3$Cl(MeCN)] (3). This was prepared according to a literature method.[7d] To **1** (200 mg, 0.29 mmol) in THF (25 mL) was added HCl (2.32 mL of a 1.5 M solution in Et_2O), and the mixture was stirred overnight at room temperature. The solvent was pumped off, and the residue was washed with hexane and Et_2O. Recrystallization from CH_2Cl_2/Et_2O afforded a brown crystalline solid (162 mg, 96%). ^1H NMR ($CDCl_3$): δ 7.32 (t, 1H, H_p), 7.20 (t, 2H, H_p), 7.12 (d, 2H, H_m), 7.03 (d, 4H, H_m), 2.24 (s, 12H, Me), 2.11 (s, 6H, Me), 2.03 (s, 3H, MeCN). MS (FAB): *m*/*z* 589 ($M^+ + 1$), 553 ($M^+ - Cl + 1$), 547 ($M^+ - MeCN + 1$), 512 ([Ru(Sxylyl)$_3$]), 373 ([Ru(Sxylyl)$_2$] − 1). Anal. Calcd for $C_{26}H_{30}ClNRuS_3$: C, 53.00; H, 5.13; N, 2.38. Found: C, 52.24; H, 5.08; N, 2.32.

Preparation of [Et$_4$N][Ru(Sxylyl)$_3$Cl(C≡CPh)] (4). A mixture of **2** (150 mg, 0.185 mmol) and phenylacetylene (94 mg, 0.92 mmol) in CH_2Cl_2 (30 mL) were stirred overnight at room temperature. During this time, the solution changed from brown to dark green. The solvent was pumped off, and the residue was washed with hexane and Et_2O. Recrystallization from CH_2Cl_2/Et_2O gave dark green crystals of **4** (yield 72 mg, 58%). ^1H NMR ($CDCl_3$): δ 7.31 (t, 1H, H_p), 7.21 (t, 2H, H_p), 7.12 (d, 2H, H_m), 7.05 (d, 4H, H_m), 6.67−7.00 (m, 5H, Ph), 3.34 (dt, 8H, $CH_3C\mathit{H}_2$), 2.32 (s, 12H, Me), 2.24 (s, 6H, Me), 1.31 (t, 12H, $C\mathit{H}_3CH_2$). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2052. MS (FAB): *m*/*z* 650 (M^+ - Et_4N), 614 ([Ru(Sxylyl)$_3$(C≡CPh)]), 476 ([Ru(Sxylyl)$_2$(C≡CPh)]), 373 ([Ru(Sxylyl)$_2$] − 1). Anal. Calcd for $C_{39}H_{52}ClNRuS_3$: C, 61.02; H, 6.83; N, 1.82. Found: C, 60.52; H, 6.73; N, 1.79.

Preparation of [Et$_3$NH][Ru(Sxylyl)$_3$(C≡Ctol)] (5). To a mixture of **3** (120 mg, 0.204 mmol) and 4-tolylacetylene (107 mg, 0.95 mmol) in CH_2Cl_2 (30 mL) was added Et_3N (ca. 0.1 mL), and the mixture was stirred for ca. 2 h until the color of the mixture changed from brown to dark green. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to give dark green crystals (yield 132 mg, 85%). ^1H NMR ($CDCl_3$): δ 7.30 (t, 1H, H_p), 7.21 (t, 2H, H_p), 7.12 (d, 2H, H_m), 7.05 (d, 4H, H_m), 6.84 (d, 2H, H_o), 6.14 (d, 2H, H_m), 4.82 (s br, 1H, N*H*), 3.33 (dt, 8H, $CH_3C\mathit{H}_2$), 2.31 (s, 12H, $C\mathit{H}_3$), 2.23 (s, 6H, $C\mathit{H}_3$), 2.16 (s, 3H, $C\mathit{H}_3$), 1.33 (t, 9H, $C\mathit{H}_3CH_2$). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2094. MS (FAB): *m*/*z* 628 ($M^+ - Cl$), 491 ($M^+ - Cl - Sxylyl - 1$). Anal. Calcd for $C_{41}H_{56}NClS_3Ru$: C, 61.90; H, 7.10; N, 1.76. Found: C, 61.13; H, 6.92; N, 1.73.

Preparation of [Et$_3$NH][Os(Sxylyl)$_3$Cl(C≡CPh)] (6). To a mixture of the compound [Os(Sxylyl)$_3$(MeCN)Cl][14] (135 mg, 0.20 mmol) and phenylacetylene (100 mg, 0.99 mmol) in CH_2Cl_2 (30 mL) was added Et_3N (ca. 0.1 mL), and this mixture was stirred at room temperature for 4 h. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to afford dark green crystals (84 mg, 71%). ^1H NMR ($CDCl_3$): δ 7.36 (t, 1H, H_p), 7.22 (t, 2H, H_p), 7.14 (d, 2H, H_m), 7.05 (d, 4H, H_m), 6.63−6.98 (m, 5H, Ph), 4.82 (s br., 1H, N*H*), 3.34 (dt, 6H, $CH_3C\mathit{H}_2$), 2.36 (s, 12H, Me), 2.22 (s, 6H, Me), 1.35 (t, 9H, $C\mathit{H}_3CH_2$). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2092. MS (FAB): *m*/*z* 704 ([Os(Sxylyl)$_3$(C≡CPh)]), 567 ([Os(SR)$_2$(C≡CPh)] − 1), 462 ([Os(SR)$_2$] + 1). Anal. Calcd for $C_{38}H_{47}ClNS_3Os{\cdot}H_2O$: C, 53.23; H, 5.70; N, 1.63. Found: C, 52.82; H, 5.51; N, 1.63.

Preparation of [Ru(Sxylyl)$_3$Cl(*t*-BuNC)] (7). To a solution of **4** (100 mg, 0.145 mmol) in CH_2Cl_2 (20 mL) was added 1 equiv of *t*-BuNC (12 μL, 0.145 mmol), and the mixture was stirred at room temperature for 2 h, during which time there was a color change from brown to yellowish brown. The solvent was pumped off, and the residue was washed with hexane. Recrystallization from CH_2Cl_2/hexane afforded a yellow solid (91 mg, 86%). ^1H NMR ($CDCl_3$): δ 7.35 (t, 1H, H_p), 7.21 (t, 2H, H_p), 7.12 (d, 2H, H_m), 7.01 (d, 4H, H_m), 2.27 (s, 12H, Me), 2.15 (s, 6H, Me), 1.34 (s, 9H, *t*-Bu). IR (KBr, cm^{-1}): ν(N≡C) 2106. MS (FAB): *m*/*z* 596 ($M^+ - Cl + 1$), 512 ($M^+ - t$-BuNC + 1), 459 ([Ru(Sxylyl)$_2$(*t*-BuNC)] + 1).

Preparation of *trans*-[Ru(*t*-BuNC)$_4$(Sxylyl)$_2$] (8). To a solution of **4** (100 mg, 0.145 mmol) in CH_2Cl_2 (20 mL) was added 4 equiv of *t*-BuNC (48 μL, 0.58 mmol). The mixture was stirred at room temperature for 30 min and gradually turned yellow. After removal of the solvent under vacuum, the residue was extracted with hexane. Concentration and cooling at −20 °C afforded yellow crystals (61 mg, 56%). ^1H NMR ($CDCl_3$): δ 6.76 (t, 2H, H_p), 6.90 (d, 4H, H_m), 2.58 (s, 12H, Me), 1.33 (s, 36H, *t*-Bu). IR (KBr, cm^{-1}): 2074 ν(N≡C). MS (FAB): *m*/*z* 708 ($M^+ + 1$), 625 ($M^+ - t$-BuNC + 1), 571 ($M^+ -$ Sxylyl + 1). Anal. Calcd for $C_{36}H_{54}N_4RuS_2$: C, 61.07; H, 7.69; N, 7.91. Found: C, 59.84; H, 7.36; N, 7.50.

X-ray Structure Determination of 2·CH$_2$Cl$_2$, 3, 5, and 8·2H$_2$O. The crystal data for **2**·CH_2Cl_2, **3**, **5**, and **8**·$2H_2O$ are summarized in Table 1. The crystals were mounted on a glass fiber using epoxy resin. Data were collected on a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at room temperature. Structural determinations were made using the SHELXTL package of programs.[19] All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms.

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Supporting Information Available: Tables of final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles of **2**·CH_2Cl_2, **3**, **5**, and **8**·$2H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Sheldrick, G. M. *SHELXTL Reference Manual*, version 5.1; Siemens Energy and Automation: Madison, WI, 1997.