Ruthenium Thiolate Complexes

A Half-Sandwich Ruthenium(II) Complex Containing a Coordinatively Unsaturated 2,6-Dimesitylphenyl Thiolate Ligand**

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Transition-metal complexes with low-coordination numbers are a class of highly reactive substances which are important as key intermediates in catalytic reactions. A number of coordinatively unsaturated transition-metal complexes have been reported, most of which contain bulky alkyl, alkoxy, amide, and phospane ligands.[1] Bulky thiolates are also attractive ligands in this regard. The S-donor ligands are

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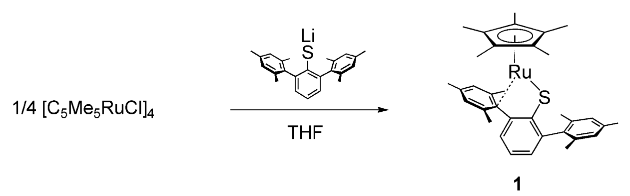
soft in character, can donate π electrons to a metal atom, and show high affinity for a wide variety of transition metals. Although thiolate ligands tend to produce multinuclear structures by linking metal atoms, some sterically demanding thiolates are effective in stabilizing low-coordinate, monomeric complexes.[2] One such ligand is 2,6-dimesitylphenyl thiolate (SDmp).[2b] The mesityl group can modulate the stereoelectronic properties of transition-metal centers by its bulk and by possible weak coordination of a mesityl group, which thereby generates hemilabile reaction sites. Herein we report the synthesis of a half-sandwich ruthenium(II) complex of SDmp, lability of the ligand in the coordination sphere, and reactivity of the complex.

The reaction of $[(Cp^*RuCl)_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[3] with 4 equivalents of LiSDmp in THF afforded a dark blue solution, from which mononuclear ruthenium(II) complex $[Cp^*Ru(SDmp)]$ (**1**) was isolated in 83 % yield (Scheme 1).[4]



Scheme 1. Synthesis of **1**.

Complex **1** is air- and moisture-sensitive, and is soluble in common organic solvents. In the ^{1}H NMR spectrum taken at room temperature, the *o*- and *p*-methyl protons of the SDmp ligand gave rise to four ^{1}H resonances with an intensity ratio of 3:3:6:6,[4] and these signals do not show notable line broadening even at 80 °C. Thus, the two mesityl groups of SDmp in **1** are chemically inequivalent in solution.

The molecular structure of **1** is shown in Figure 1.[5] An interesting structural feature is the interaction between Ru and the *ipso*-carbon atom C7 of one mesityl group.[6] Without this interaction **1** would formally be a 14-electron complex,[7] and the electron deficiency of the ruthenium promotes the bonding interaction with the nearby *ipso*-carbon atom. This bonding mode may be analogous to that in the Wheland intermediate of Friedel–Crafts reactions.[8] Thus, the Ru^{II} atom forms a five-membered ruthenacycle with the SDmp sulfur and *ipso*-carbon atoms. This coordination geometry of SDmp appears to be retained in solution according to ^{1}H and ^{13}C NMR data. The molecule has a crystallographic mirror plane, which bisects SDmp and Cp*, and the ruthenacycle and the central arene ring of SDmp are crystallographically coplanar. Due to the Ru−C7 bonding, the mesityl ring bends away from the metal atom, and the C2-C7-C8-C9 dihedral angle is 144.3(2)°. Furthermore, the C7−C8 bond is clearly elongated (1.432(3) Å) relative to the other C−C distances (1.395 (3) and 1.387(3) Å) in the mesityl ring. While the Ru−C7 distance of 2.278(3) Å is long relative to reported $Ru{-}C_{alkyl}$ bond lengths (2.08–2.18 Å),[9] it is comparable to $Ru{-}C_{olefin}$ distances (2.14–2.27 Å).[9] This indicates a strong $Ru{-}C_{ipso}$ interaction in **1**, in accordance with the structural rigidity of **1** in solution. The Ru−S distance of 2.294(1) Å is shorter than those of electronically saturated Ru^{II} thiolate complexes (2.38–2.47 Å),[10] because π backdonation of electrons from an occupied sulfur p_π orbital occurs to ease the electron deficiency of the metal center.

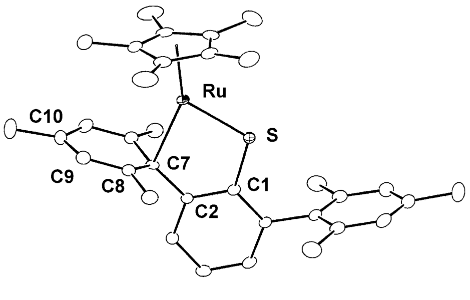
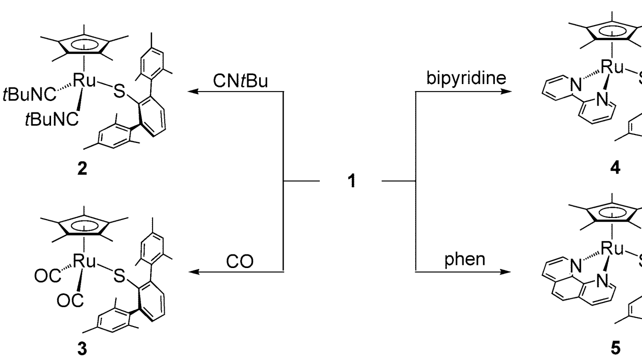


Figure 1. Molecular structure of **1** with thermal ellipsoids at 50 % probability level. Selected bond lengths [Å] and angles [°]: Ru−S 2.294(1), Ru−C7 2.278(3), S−C1 1.756(3), C2−C7 1.491(4), C7−C8 1.432(3), C8−C9 1.395(3), C9−C10 1.387(3); Ru-C7-C2 113.7(2) Ru-C7-C8 88.3(1), C2-C7-C8 119.0(1), S-C1-C2 116.9(2).

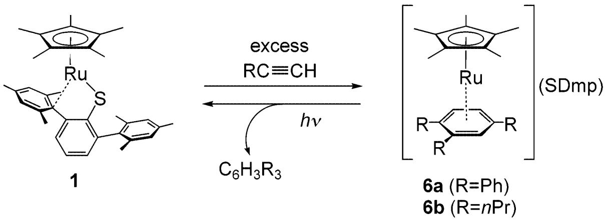
Coordinative unsaturation of **1** and lability of the *ipso*-carbon atom in the coordination sphere of ruthenium were manifested in facile reactions of **1** with CN*t*Bu, CO, bipyridine, and phenanthroline. Analytically pure 18-electron complexes $[Cp^*Ru(SDmp)(L_2)]$ [$L_2 = (CNtBu)_2$ (**2**), $(CO)_2$ (**3**), bipy (**4**), phen (**5**)] were isolated therefrom in good yields (Scheme 2).[4] The molecular structures of **2**–**5** were determined by X-ray analysis.[11] These complexes have a common three-legged piano-stool geometry in which the SDmp ligand is bound to Ru through the sulfur atom. Due to the electron-rich nature of Ru in **2**–**5**, there is no π back-donation from SDmp, and the Ru−S bonds are long (2.427(1)–2.4313(8) Å), while steric congestion makes the Ru-S-C angles large (112.0(1)° for **3**, ca. 124.8(2)° for **5**). In the ^{1}H NMR spectra, the two mesityl groups are now equivalent. For complexes **3** and **4**, the IR bands for ν_{CO} and ν_{CN} were observed at 2008 and 1957 cm^{-1} (CO), and 2112 and 2052 cm^{-1} (CN*t*Bu), respectively. Complex **1** does not react with bulky phosphanes such as PPh_3 and $P(c\text{-}C_6H_{11})_3$.



Scheme 2. Reactivity of **1** with various ligands.

When **1** was treated with an excess of phenylacetylene or 1-pentyne, cyclotrimerization of the alkyne took place, and ruthenium(II) sandwich complexes with Cp* and trisubstituted benzene ligands $[Cp^*Ru(\eta^6\text{-}1,2,4\text{-}R_3C_6H_3)](SDmp)$

(R = Ph, **6a**; *n*Pr, **6b**) were isolated as yellow crystals in 31–58 % yield (Scheme 3).[4] Since the X-ray crystal structures of **6a** and **6b** are similar, only the structure of **6a** is shown in Figure 2.[11] The regioselective formation of 1,2,4-trisubstituted benzenes was also proved by the ^{1}H NMR spectra, which showed vicinal spin coupling between the aromatic protons at C5 and C6. The observed regioselectivity of the cyclotrimerization of the alkynes points to a 2,5-disubstituted ruthenacyclopentadiene intermediate in the reaction, as shown in Scheme 4.[12] The subsequent insertion of an alkyne molecule into the Ru–C bond would be followed by oxidative C–C coupling to give 1,2,4-trisubstituted benzene. Intriguingly, the SDmp ligand exists as a discrete counteranion in the crystal structures of **6a** and **6b**. The dissociation of SDmp might preceed alkyne insertion into the Ru–C bond of a ruthenacyclopentadiene. Transition-metal complexes with uncoordinated thiolate anions are rare because of high affinity of sulfur for a wide variety of transition metals.[13] The bulkiness of Dmp and delocalization of the anionic charge over the aromatic rings probably stabilize the coordination-free form of SDmp. Complex **1** does not react with disubstituted alkynes such as phenylpropyne and diphenylacetylene, and this indicates that formation of the ruthenacycle is hampered by the substituents.



Scheme 3. Cyclotrimerization of the alkyne on treatment with **1**.

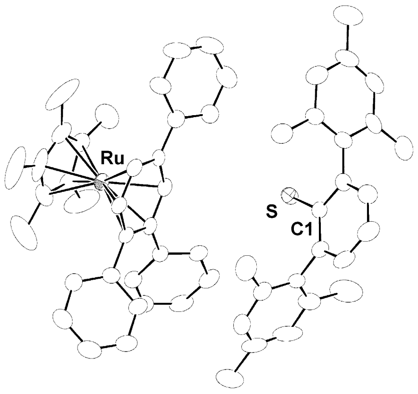
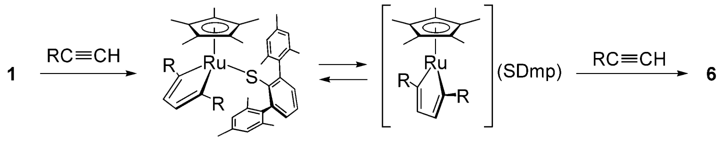


Figure 2. Molecular structure of **6a** with thermal ellipsoids at 50% probability level. Selected bond lengths [Å]: Ru–Cp* 1.814(3), Ru–$C_6H_3Ph_3$ 1.705(3), S–C1 1.748(6).



Scheme 4. Synthesis of **6** from **1**.

The trisubstituted benzene ligands of **6a** and **6b** were liberated under UV irradiation, and the counteranion SDmp was bound to Ru, regenerating **1**.[4] Therefore, cyclotrimerization of alkynes could in principle be catalyzed by **1**, whereby the reversible dissociation/association of SDmp may assist the reactions. Dissociation of cystein sulfur from active metal sites in certain metalloproteins and its recombination are thought to be important for enzymatic functions.[14] Successful isolation of **1** and **6a** and **6b** and their interconversion provides the first well-characterized examples of reversible coordination of thiolate sulfur atoms at a transition metal center. These findings offer the possibility of assessing the unique role of reversible thiolate coordination in catalytic/enzymatic reactions. At the moment, however, the catalytic cycle for trimerization of alkynes promoted by **1** has not been achieved, because some side reactions occur upon irradiation of **1** in the presence of alkynes.

In summary, we have isolated an electron-deficient ruthenium(II) complex **1** carrying the bulky thiolate SDmp. This complex was shown to serve as a precursor of coordinatively unsaturated species in two ways: by the lability of the coordinated *ipso*-carbon atom, and by reversible dissociation/association of the SDmp ligand. Further investigations on reactivity of **1** associated with the unique coodination properties of SDmp are currently underway.

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Keywords: cyclization · electron-deficient compounds · ruthenium · S ligands

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[4] For experimental details, see Supporting Information.

[5] a) X-ray diffraction was performed on a Rigaku AFC7R equipped with a rotating anode and a MSC/ADSC Quantum 1 CCD detector. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at the calculated positions. Crystal data for **1**: orthorhombic, *Pnma*, $a = 21.46(1)$, $b = 8.9893(7)$, $c = 15.157(2)$ Å, $V = 2923(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.322$ g cm^{-1}; 3555

reflections ($5.5 \leq 2\theta \leq 55°$), 2909 observed reflections with $F > 3\sigma(F)$, 187 parameters; $R = 0.033$, $Rw = 0.047$; b) CCDC-226919 to 226925 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[11] Diffraction measurements were made on a Rigaku AFC7R equipped with a rotating anode and a MSC/ADSC Quantum 1 CCD detector (**2**) or on a Rigaku RASA-7 Quantum system equipped with a rotating anode and a Mercury CCD detector (**3**, **4**, **5**·$0.5\,C_4H_8O$, **6a**, and **6b**·$0.5\,C_7H_8$). All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, except for the THF molecule in **5**·$0.5\,C_4H_8O$ (refined isotropically), and hydrogen atoms were fixed at calculated positions. Crystal data for **2**: monoclinic, $C2/c$, $a = 26.188(1)$, $b = 21.126(3)$, $c = 17.1937(3)$ Å, $\beta = 120.5609(4)$, $V = 8190.9(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.283\ \mathrm{g\,cm^{-1}}$; 8541 reflections ($5.5 \leq 2\theta \leq 55°$), 6992 observed reflections with $F > 3\sigma(F)$, 423 parameters; $R = 0.046$, $Rw = 0.058$. Crystal data for **3**: orthorhombic, $Fdd2$, $a = 20.109(6)$, $b = 60.26(2)$, $c = 10.312(3)$ Å, $V = 12495(6)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.356\ \mathrm{g\,cm^{-1}}$; 24070 reflections ($5.5 \leq 2\theta \leq 55°$), 6776 observed reflections with $F > 0\sigma(F)$, 360 parameters; $R = 0.053$, $Rw = 0.081$. Crystal data for **4**: orthorhombic, $P2_12_12_1$, $a = 11.2974(9)$, $b = 15.943(1)$, $c = 20.790(1)$ Å, $V = 3744.7(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.309\ \mathrm{g\,cm^{-1}}$; 4578 reflections ($5.5 \leq 2\ \theta \leq 55°$), 4028 observed reflections with $F > 3\sigma(F)$, 434 parameters; $R = 0.062$, $Rw = 0.103$. Crystal data for **5**·$0.5\,C_4H_8O$: monoclinic, $P2_1/a$, $a = 20.891(1)$, $b = 12.3594(6)$, $c = 29.942(2)$ Å, $\beta = 96.407(3)$, $V = 7682.5(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.380\ \mathrm{g\,cm^{-1}}$; 16327 reflections ($5.5 \leq 2\theta \leq 55°$), 10877 observed reflections with $F > 2\sigma(F)$, 908 parameters; $R = 0.064$, $Rw = 0.091$. Crystal data for **6a**: monoclinic, $P2_1/c$, $a = 10.975(5)$, $b = 28.57(1)$, $c = 17.434(7)$ Å, $\beta = 95.815(7)$, $V = 5438(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.085\ \mathrm{g\,cm^{-1}}$; 12174 reflections ($5.5 \leq 2\theta \leq 55°$), 7041 observed reflections with $F > 3\sigma(F)$, 541 parameters; $R = 0.061$, $Rw = 0.098$. Crystal data for **6b**·$0.5\,C_7H_8$: triclinic, $P\bar{1}$, $a = 11.69(2)$, $b = 12.51(2)$, $c = 17.95(3)$ Å, $\alpha = 106.52(3)$, $\beta = 100.14(2)$, $\gamma = 108.41(1)$, $V = 2284(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.230\ \mathrm{g\,cm^{-1}}$; 9654 reflections ($5.5 \leq 2\theta \leq 55°$), 6967 observed reflections with $F > 3\sigma(F)$, 505 parameters; $R = 0.066$, $Rw = 0.087$.

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