Communications

Nitrosyl Displacement Reactions, C–H Activation, and M–H–C Interactions in Ruthenium Thiolate Compounds

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Summary: $[Ru(NO)(SR)_4]^-$ complexes with sterically hindered thiolate ligands react thermally to give products with NO ligand displacement, cyclometalation, and agostic hydrogen interaction.

Coordinatively unsaturated metal–sulfur centers located on the surfaces and edges of metal sulfide crystallites have been frequently proposed to be the active sites of metal sulfide heterogeneous catalysts.[1] We have been studying the reactivity of coordinatively unsaturated ruthenium thiolate complexes as simple models for these centers.[2] RuS_2 is a very active catalyst for the industrially important hydrodesulfurization reaction.[1b]

Complexes that contain the $[Ru(SR)_4(NO)]^-$ anion have been prepared from the reaction of $K_2Ru(NO)Cl_5$ with a series of aromatic thiolate anions that are substituted in the 2- and 6-positions with methyl or isopropyl groups.[3,4] The $[Ru(SR)_4(NO)]^-$ (SR = S-2,3,5,6-Me_4C_6H, S-2,6-$Me_2C_6H_3$, S-2,4,6-*i*-$Pr_3C_6H_2$) compounds are unusual in several regards: (1) their NO stretching frequencies (1720–1740 cm^{-1}) are quite low for compounds with a $[RuNO]^6$ electron configuration;[5] (2) they are five- rather than six-coordinate (the rule for $[RuNO]^6$ compounds);[5a] (3) they show unusual reactivity patterns that are dependent on the steric nature of the thiolate ligands.

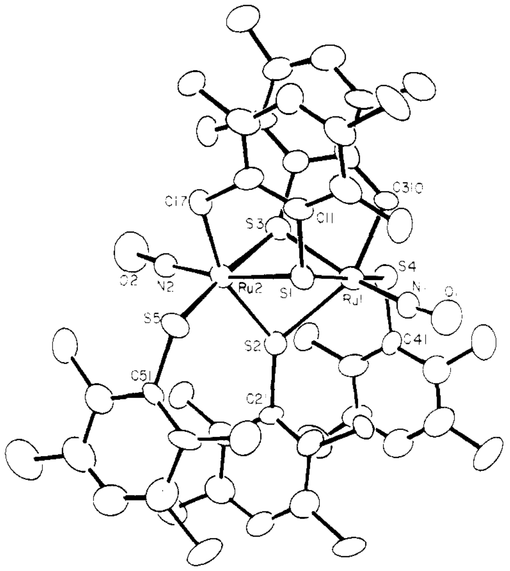

Figure 1. ORTEP structure of $[(\overline{Ru(\mu\text{-S-2-C}}H_2\text{-3,5,6-}Me_3C_6H)(S\text{-2,3,5,6-}Me_4C_6H)(NO))_2(\mu\text{-S-2,3,5,6-}Me_4C_6H)]^-$. Selected bond distances (Å) and angles (deg): Ru1–S1, 2.440 (3); Ru1–S2, 2.574 (2); Ru1–S3, 2.388 (3); Ru1–S4, 2.385; Ru1–N, 1.707 (9); Ru1–C310, 2.118 (9); Ru2–S1, 2.384 (3); Ru2–S2, 2.499 (3), Ru2–S3, 2.457 (3); N1–O, 1.17 (1), Ru1–N1–O1, 172.8 (9).

The reaction of $K_2[Ru(NO)Cl_5]$ with Li(S-2,4,6-*i*-$Pr_3C_6H_2$) gives [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(MeOH)] in addition to the [Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4]^-$ compound.[4b] The isolated [Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4]^-$ complex is readily converted into [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(MeOH)] by refluxing in MeOH for 3 h (90% yield). [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$L] (L = DMSO, CH_3CN) complexes are obtained in analogous reactions.[2] ^1H NMR spectroscopy has shown that these NO displacement reactions proceed with quantitative conversion.[6] The mild conditions required for this NO displacement reaction appear to be unprecedented for a $[RuNO]^6$ center; the RuNO coordination mode has been noted for its ability to persist during substitution and oxidation–reduction reactions.[5] The redox stability of the $[Ru^{IV}(SR)_4L]$ products is a likely driving force for the displacement reaction.[2]

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[3] 2,4,6-Triisopropylbenzenethiolate = [S-2,4,6-*i*-$Pr_3C_6H_2]^-$; 2,6-diisopropylbenzenethiolate = [S-2,6-*i*-$Pr_2C_6H_3]^-$; 2,3,5,6-tetramethylbenzenethiolate = [S-2,3,5,6-$Me_4C_6H]^-$; 2,6-dimethylbenzenethiolate = [S-2,6-$Me_2C_6H_3]^-$.

[4] (a) Preparation of [(*n*-Bu)$_4$N][Ru(S-2,6-$Me_2C_6H_3)_4$(NO)]: $K_2Ru(NO)Cl_5$ (0.45 g, 1.16 mmol) and 5 equiv of Li(S-2,6-$Me_2C_6H_3$ were refluxed under N_2 for 8 h in 25 mL of MeOH. The addition of Bu_4NBr to the dark red solution at room temperature gave dark red crystals in 70% yield: IR (Nujol) 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (8 H, d), 6.84 (4 H, t), 3.45 (8 H, t), 2.33 (24 H, s), 1.82 (8 H, m), 1.46 (8 H, m), 1.01 (12 H, t); electronic spectrum (acetone) 652 nm (ϵ 878 M^{-1} cm^{-1}), 460 (6900), 383 (10 400 sh), 320 (42 700). Elemental Anal. Found (Calcd): C, 62.39 (62.50); H, 7.92 (7.87); N, 3.01 (3.04); S, 13.98 (13.90); O, 1.97 (1.73). (b) In an analogous fashion, [$Me_3NCH_2C_6H_5$][Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4$] is obtained in 45% yield by addition of [$Me_3NCH_2C_6H_5$]Cl to the reaction mixture: IR (Nujol) 1735 cm^{-1}; ^1H NMR (MeOH-d_4) δ 7.53 (5 H, m), 6.84 (8 H, s), 4.47 (2 H, s), 3.72 (8 H, sept), 3.05 (9 H, s), 2.75 (4 H, sept), 1.17 (24 H, d), 1.07 (48 H, d). Elemental Anal. Found (Calcd): C, 68.75 (67.71); H, 8.63 (8.90); N, 2.09 (2.29); S, 10.68 (10.49). When the filtrate was allowed to stand at room temperature for 4 days, [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(MeOH)] crystallized in 35% yield. This product was characterized by its unit cell and its ^1H NMR (see supplementary material) and by its conversion upon addition of CH_3CN to [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(CH_3CN)] which was previously characterized by X-ray crystallography.[2a]

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[6] The fate of the NO group is under investigation.

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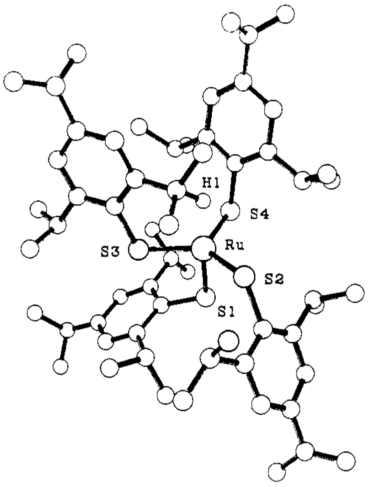

Figure 2. Computer-drawn structural diagram of [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$]. Selected bond distances (Å) and angles (deg): Ru–S1, 2.328 (2); Ru–S2, 2.222 (2); Ru–S3, 2.199 (2); Ru–S4, 2.185 (2); Ru–H1, 2.33 (6); H1–C36A, 0.97 (6); Ru–H1–C36A, 134 (5); S1–Ru–S2, 97.49 (7); S1–Ru–S3, 92.47 (7); S1–Ru–S4, 89.67 (7); S2–Ru–S3, 125.11 (7); S2–Ru–S4, 116.07 (7); S3–Ru–S4, 117.84 (7).

A different reactivity pattern is displayed by the less sterically encumbered *o*-dimethylbenzenethiolate ligands. Upon standing for several days at room temperature in MeOH, $[Ru(SR)_4(NO)]^-$ (SR = S-2,3,5,6-Me_4C_6H or S-2,6-$Me_2C_6H_3$) undergoes a cyclometalation reaction in which there is C–H bond activation of an ortho methyl group of a thiolate ligand.[7] The dimeric product, in which there is no displacement of the nitrosyl ligand, was characterized by X-ray crystallography (Figure 1).[7] The $[RuNO]^6$ electron configuration is preserved for each metal center. There is no Ru–Ru bonding since the Ru–Ru distance is 3.347 (1) Å. A likely mechanism for formation of this dimer would involve oxidative addition of an ortho C–H bond at the vacant sixth coordination site of $[Ru(SR)_4(NO)]^-$ followed by reductive elimination of RSH and then dimerization. In contrast to the reaction in MeOH, $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4(NO)]^-$ reacts in CH_3CN at room temperature over a period of a day to give $[Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4(CH_3CN)]$ in 80% isolated yield.[2a]

The MeOH ligand in Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(MeOH) can be easily replaced by a wide variety of donors including CO, *t*-BuNC, and CH_3CN.[2] In fact, the coordinated MeOH can be removed simply by heating the solid compound under vacuum (10^{-1} Torr) at 30 °C for 24 h. The X-ray crystal structure of [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$] (Figure 2) revealed the complex to be pentacoordinate despite the lack of a coordinated exogenous small molecule.[8] In addition to the four thiolates the ruthenium is also coordinated to the methine C–H of an ortho isopropyl group. The coordination geometry is trigonal-bipyramidal with the agostic hydrogen occupying an axial position. This is the first example of an agostic interaction in a metal–sulfur system.[9] The structure of [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$] can be contrasted to the structures of [Fe(S-2,4,6-*i*-$Pr_3C_6H_2)_4]^-$ and [Mo(S-2,4,6-*i*-$Pr_3C_6H_2)_4$] which are tetrahedral with normal nonbonding distances between the metals and the ortho-substituents.[10,11]

It is interesting to note that the benzylic proton rather than a methyl hydrogen of the isopropyl group is involved in the M–H–C interaction. In contrast, cyclometalation of 2,6-R_2-phenoxide complexes of the early transition metals occurs for R = *tert*-butyl but not for R = Me.[12] It has not been determined whether activation of the benzylic proton or a $CH(CH_3)_2$ hydrogen is the primary step in the recently observed dehydrogenation of an ortho isopropyl group in a Rh complex of S-2,6-*i*-$Pr_2C_6H_3$.[13]

M-H-C interaction and H–C bond activation, reactivity pathways important for many organometallic compounds, have been demonstrated in a metal–sulfur compound. This metal-centered reactivity can be contrasted to many organic transformations in metal-sulfur systems which take place at the sulfur ligands.[14]

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Registry No. $K_2Ru(NO)Cl_5$, 14854-54-7; Li(S-2,4,6-*i*-$Pr_3C_6H_2$), 107847-82-5; j[Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$(MeOH)], 112319-86-5; [Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4]^-$, 112319-87-6; [(*n*-Bu)$_4$N][Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4$], 112319-88-7; [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4CH_3CN$], 85479-95-4; [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$DMSO], 112319-89-8; [Ru(S-2,3,5,6-$Me_4C_6H)_4(NO)]^-$, 112319-90-1; [Ru(S-2,6-$Me_2C_6H_3)_4(NO)]^-$, 112319-91-2; [(*n*-Bu)$_4$N][(Ru(*μ*-S-2-CH_2-3,5,6-Me_3C_6H)(S-2,3,5,6-Me_4C_6H)(NO))$_2$·(*μ*-S-2,3,5,6-Me_4C_6H)], 112319-98-9; [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$]·$^1/_2$(*n*-hexane), 112319-93-4; [(*n*-Bu)$_4$N][Ru(S-2,6-$Me_2C_6H_3)_4$(NO)], 112319-94-5; Li(S-2,6-$Me_2C_6H_3$), 112319-95-6; [$Me_3NCH_2C_6H_5$][Ru(NO)(S-2,4,6-*i*-$Pr_3C_6H_2)_4$], 112319-96-7; [$Me_3NCH_2C_6H_5$]Cl, 56-93-9; [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$], 112319-92-3.

Supplementary Material Available: ^{1}H NMR spectra and electronic spectra and tables of crystal data fractional atomic coordinates, and thermal parameters (17 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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(7) [(*n*-Bu)$_4$N][$Ru_2(SC_{10}H_{13})_3(SC_{10}H_{12})_2(NO)_2$] crystallized in 60% yield over several days from a MeOH solution of [(*n*-Bu)$_4$N][Ru(NO)(S-2,3,5,6-$Me_4C_6H)_4$]. Recrystallization from DMF/*i*-PrOH gave a triclinic crystal with space group $P\bar{1}$ with a = 14.535 (4) Å, b = 19.972 (8) Å, c = 12.234 (3) Å, α = 93.50 (3)°, β = 101.64 (2)°, γ = 89.12 (3)°, V = 3472 (3) Å^3, Z = 2. Final least-squares refinement of all the non-hydrogen atoms gave $R = 0.060$ and $R_w = 0.077$ for 3788 reflections with $|F_o| > 3\sigma(|F_o|)$. Spectral data: IR (Nujol) 1780, 1763 cm^{-1}; electronic spectrum ($HCCl_3$) 461 nm (ϵ 4230, sh), 350 (29 700), 300 (30 800); ^{1}H NMR ($CDCl_3$) δ 6.68 (1 H, s), 6.54 (2 H, s), 6.26 (2 H, s), 3.08 (8 H, m), 2.89 (2 H, s), 2.84 (2 H, s), 2.77 (6 H, s), 2.25 (12 H, s), 2.13 (6 H, s), 1.59 (12 H, s), 1.43 (8 H, m), 1.28 (8 H, q, J = 7.2 Hz), 0.86 (12 H, t, J = 7.2 Hz).

(8) [$Ru(SC_{15}H_{23})_4$]·$^1/_2$(*n*-hexane) crystallized from hot hexanes in the triclinic space group $P\bar{1}$ with a = 14.980 (6) Å, b = 20.452 (15) Å, c = 10.490 (4) Å, α = 90.29 (4)° β = 94.08 (3)°, γ = 73.63 (5)°, V = 3075 Å^3, and Z = 2. The agostic hydrogen was located in a Fourier map. Final least-squares refinement of the non-hydrogen atoms and the agostic hydrogen gave $R = 0.063$ and $R_w = 0.074$ for 4739 reflections with $|F_o| > 3\sigma(|F_o|)$. The ^{1}H NMR of [Ru(S-2,4,6-*i*-$Pr_3C_6H_2)_4$] is given in the supplementary material.

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(15) **Note Added in Proof.** The chemistry of [Ru(NO)(1,2-benzenedithiolate)$_2]^-$ has recently been described: Sellman, D.; Binker, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1987**, *42B*, 341.