Novel Thiotetraazapentalene Complexes from the Reaction of a Ruthenium Azide Complex with Alkyl Isothiocyanates

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Reactions of the ruthenium azide complex **1** with alkyl isothiocyanates give novel ruthenium thiotetraazapentalenedithione complexes **3a**–**c** containing a hypervalent sulfur atom. The ligand, bound through one sulfur atom, is derived from three isothiocyanate molecules and one nitrogen atom from an azide ion. The synthesis and structural determination of **3a**–**c**, as well as a possible mechanism for their formation is described.

Introduction

Isothiocyanates are known to undergo reactions with unsaturated substrates (including Diels−Alder reactions and nucleophilic additions) to provide heterocyclic derivatives.[1] The pathways for these conversions are controlled by the character of the substrates as well as by the type of reagent.[2−4] For example, addition to the C=S or C=N bond of the heteroallene moiety can occur, leading to polymerization,[5,6] whereas the reactions of acyl/thioacyl isothiocyanates often lead to the formation of 1,4-cycloadducts.[7] The organic chemistry of these isothiocyanate heteroallenes has been described in several reviews,[8,9] but reactions of isothiocyanates with metal complexes have not yet been comprehensively investigated. We reported previously the reactions of ruthenium acetylide complexes with isothiocyanate, which yielded ligands containing four- and six-membered heterocyclic rings.[10,11] Because the reaction of arylsulfonyl isothiocyanates with alkyl azides is known[12] to give 4-alkyl-5-arylsulfonylimino-1,2,3,4-thiatriazolines we were interested in studying the reactions of ruthenium azide complexes with isothiocyanates. Surprisingly, these reactions give ruthenium thiotetraazapentalene[13,14] complexes containing a hypervalent sulfur atom. It is known that thiotetraazapentalene can be prepared from the reaction of thiourea with isothiocyanate,[15,16] but metal-coordinated species are relatively rare. The synthesis and structural characterization of these novel thiotetraazapentalene ruthenium complexes **3a**−**c** are described below. The isolation of several minor products led to the elucidation of a possible mechanism.

Results and Discussion

The reaction of [Ru]N_3 (**1**, [Ru] = (η^5-C_5Me_5)(dppp)Ru, dppp = 1,3-bis(diphenylphosphanyl)propane) with a fivefold excess of $PhCH_2NCS$ in THF under nitrogen for one day gave **3a** in 40 % yield. This compound was identified as a ruthenium thiotetraazapentalene complex by single-crystal X-ray diffraction analysis. About 35 % of the unchanged azide was also isolated. Interestingly, the reaction of **1** with a tenfold excess of $PhCH_2NCS$ in THF gave $\{[Ru]NCS[Ru]\}^+NCS^-$ (**2**) as the major product in 55 % yield and complex **3a** in only 20 % yield (Scheme 1). Following removal of **2** and **3a**, two minor products, [Ru]SC(=NH)$NHCH_2Ph$ (**4**) and **5** (Scheme 2) could be separated from the reaction mixture by fractional crystallization in 5 % and 6 % yield respectively (based on **1**). The reaction of **1** with other alkyl isothiocyanates (EtNCS and MeNCS) in a fivefold excess resulted in the formation of the analogous ruthenium thiotetraazapentalene complexes **3b** and **3c** (Scheme 1) in comparable yields.

Varying the relative amounts of the reactants gave similar yields of the product, however no attempt was made to isolate the compounds analogous to **4** and **5** because of their low yields. Interestingly, the reaction of **1** with phenyl isothiocyanate yielded the monomeric complex [Ru]NCS (**6**) as the only isolable product.

The IR spectrum of **3a** displays absorption bands at 1174 and 699 cm^{-1}, assignable to the $\nu_{C=S}$ and ν_{C-S} stretches respectively.[17,18] In the ^{1}H NMR spectrum of **3a** at room

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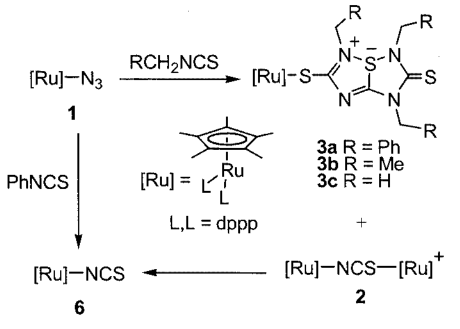
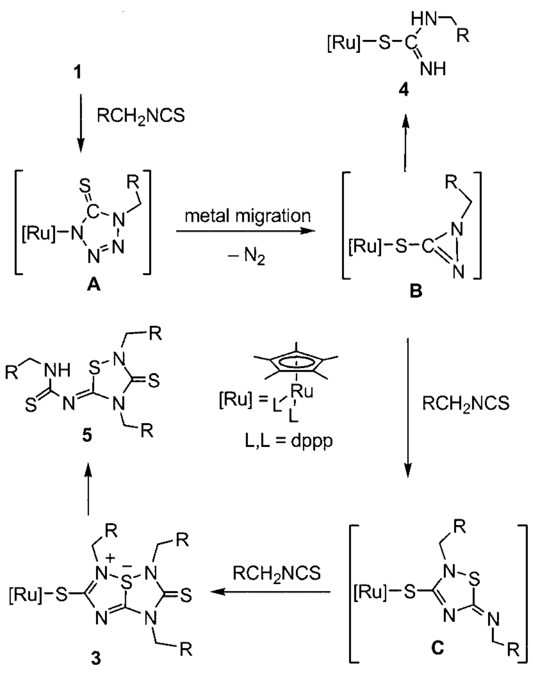


Scheme 1



Scheme 2

temperature (in addition to the singlet at δ = 1.51 ppm due to Cp*), there is a very broad resonance at δ = 5.07 ppm and two sharp singlet resonances at δ = 4.86 and 4.72 ppm, which are assignable to the three methylene groups. At 233 K, these resonances resolve into two AX patterns at δ = 5.57 and 3.93 ppm ($J_{H,H}$ = 16.09 Hz) and δ = 5.16 and 4.67 ppm ($J_{H,H}$ = 14.39 Hz), and an AB pattern at δ = 5.13 and 5.07 ppm ($J_{H,H}$ = 17.02 Hz). The ^{31}P NMR spectrum at room temperature displays a broad singlet resonance at δ = 37.54 ppm, which splits into two doublets at δ = 40.51 and 34.81 ppm with $J_{P,P}$ = 51.7 Hz at 233 K. This is possibly because of the hindered rotation of the Ru−S bond at low temperature.[12,19,20] Consistent with this structure, the FAB mass spectrum shows a parent peak at *m/z* = 1110.1. Single crystals of **3a** readily formed in a mixture of hexane and THF, enabling the structure of **3a** to be unambiguously determined by single-crystal X-ray diffraction analysis (Figure 1).

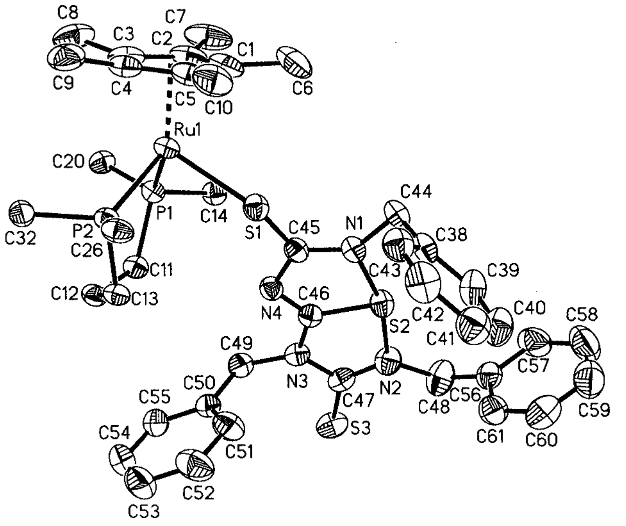


Figure 1. X-ray crystal structure of **3a** with thermal ellipsoids at the 30 % probability level; the four dppp phenyl groups and all of the hydrogen atoms have been omitted for clarity; selected bond lengths (Å): Ru(1)−S(1) 2.4427(8), S(1)−C(45) 1.739(3), C(45)−N(1) 1.305(4), C(45)−N(4) 1.370(4), C(47)−N(2) 1.296(5), C(47)−N(3) 1.406(4), C(46)−N(3) 1.370(4), C(46)−N(4) 1.314(4), S(2)−N(1) 1.884(3), S(2)−N(2) 1.969(3), C(46)−S(2) 1.722(3), C(47)−S(3) 1.683(3); selected bond angles (deg): C(45)−S(1)−Ru(1) 126.56(10), N(1)−S(2)−C(46) 81.80(14), S(2)−C(46)−N(4) 120.4(2), N(3)−C(46)−S(2) 116.6(2), C(46)−N(4)−C(45) 110.9(3), C(45)−N(1)−S(2) 113.1(2), N(2)−C(47)−N(3) 109.8(3), C(46)−N(3)−C(47) 116.1(3), C(46)−S(2)−N(2) 82.79(14), S(2)−N(2)−C(47) 114.7(2), N(1)−C(45)−S(1) 122.4(2), N(4)−C(45)−S(1) 123.7(2), N(2)−C(47)−S(3) 128.2(3), N(3)−C(47)−S(3) 122.1(3)

Thiatetraazapentalenes have been prepared from cyclic thioureas and two equivalents of RNCS.[15,16] A bis(thiatetraazapentalenedithione)copper(I) complex has also been reported, in which four sulfur atoms in the thiocarbonyl groups coordinate tetrahedrally to the copper atom, to form a one-dimensional coordination polymer.[21]

Even though complexes **2** and **6** have the same empirical formula, their spectra are quite distinctive. For example, in **2**, there are two singlets (with equal intensities) at δ = 37.93 and 35.38 ppm in the ^{31}P NMR spectrum and likewise at δ = 1.31 and 1.29 ppm in the ^{1}H NMR spectrum, attributable to the two Cp* groups. In contrast, there is a singlet at δ = 37.86 ppm in the ^{31}P NMR spectrum of **6** and a singlet at δ = 1.29 ppm in the ^{1}H NMR spectrum. The FAB mass spectrum of **2** also displays parent peaks at *m/z* = 1356.3, consistent with its formula. Generally, ruthenium isothiocyanate complexes form N-bound linkage isomers,[22−26] but many S-bound isothiocyanate ruthenium complexes are also known, one of which was recently characterized by single-crystal X-ray diffraction analysis.[27] Dinuclear Ru complexes bridged by isothiocyanate ligands are also known in the literature.[28,29]

Complex **4** was characterized by spectroscopic as well as elemental analysis. In the IR spectrum of **4**, two absorption bands at 1617 and 699 cm^{-1} (assignable to the $\nu_{C=N}$ and ν_{C-S} stretches respectively) were observed, with the $\nu_{C=S}$

being absent. In the ^{1}H NMR spectrum, the Cp* ligand appeared as a singlet at $\delta = 1.22$ ppm, a broad resonance at $\delta = 6.01$ ppm was attributed to the amine proton, and a broad resonance at $\delta = 4.08$ ppm was identified as belonging to the methylene protons of the benzyl group. These last two resonances showed $^{3}J_{H,H}$ coupling in the COSY spectrum. In addition, the broad resonance at $\delta = 4.32$ ppm was assigned to the =NH proton of the imine group. The room temperature ^{31}P NMR spectrum of **4** displays a singlet at $\delta = 37.09$ ppm. The crystal structure of **4** indicates that the isothiourea ligand is bound to the ruthenium metal through the sulfur atom (Figure 2).

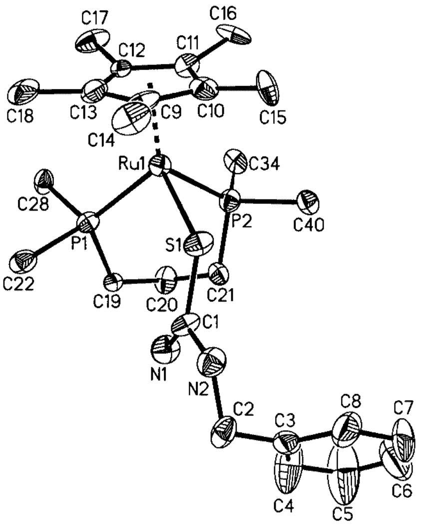


Figure 2. Structural drawing of **4** with thermal ellipsoids at the 30 % probability level; the four dppp phenyl groups and all of the hydrogen atoms have been omitted for clarity; selected bond lengths (Å): Ru(1)−S(1) 2.415(3), S(1)−C(1) 1.726(12), C(1)−N(1) 1.22(2), C(1)−N(2) 1.371(13); selected bond angles (deg): Ru(1)−S(1)−C(1) 126.0(4), S(1)−C(1)−N(1) 126.8(10), S(1)−C(1)−N(2) 112.4(9), N(1)−C(1)−N(2) 120.1(12)

The product **5** was identified by spectroscopic methods as being a five-membered 5-imino-1,2,4-thiadiazolidin-3-thione (Scheme 2).

In the IR spectrum of **5**, absorption bands at 1617, 1184 and 698 cm^{-1} were assigned to $\nu_{C=N}$, $\nu_{C=S}$ and ν_{C-S} stretches, respectively. The high resolution FAB mass spectrum of **5** has a parent peak at $m/z = 463.1807$, consistent with the molecular formula. Two isomers (*E* and *Z* forms) in a ratio of 3:2 were apparent from the NMR spectrum of **5**. The fact that the five-membered ring had opened was clear from the presence of a doublet at $\delta = 4.62$ ppm, assigned to one of the methylene groups from its coupling to the NH proton. The resonances for the other two methylene groups at $\delta = 5.18$ and 5.70 ppm remain as singlets. This indicates that the formation of **5** could result from cleavage of the dative N−S bond of **3a**, followed by cleavage of the Ru−S bond. Non metal-containing compounds with similar structures have been reported in the literature;[30] (*E*) and (*Z*) isomers arising from the imine bond are also known.

As mentioned in the literature,[12] it is common to observe the [3+2] cycloaddition of organic azides with the C=N bond of isothiocyanates. However, the thiatetraazapentalenes **3** incorporate three isothiocyanate molecules and only one nitrogen atom from the azide ligand. A possible mechanism for the formation of **3** is depicted in Scheme 2. Cycloaddition of the azide ligand of complex **1** with the C=N bond of the isothiocyanate to form **A** is followed by loss of nitrogen and migration of the ruthenium metal from nitrogen to sulfur to give **B**, which could provide the S-metalated isothiourea complex **4** as a minor product. Complex **B** could then undergo two successive [3+2] cycloadditions; the first with the C=S bond[31,32] of isothiocyanate (to give **C**), and the second with the C=N bond[33] of isothiocyanate, to afford **3**. Formation of **5** (R = Ph) might then be accounted for by loss of the metal from **3a**.

Conclusion

In summary, a novel metallated thiatetraazapentalene has been isolated from the reaction of a ruthenium azide with alkyl thioisocyanates. Formation of this product may proceed through a tandem process that involves three consecutive [3+2] cycloadditions with an alkyl thioisocyanate, a new method for the preparation of this type of compound. Isolation of the S-metalated isothiourea complex **4** and the 5-imino-[1,2,4]thiadiazolidine-3-thione **5** as minor products provides insight into a mechanism for the formation of **3**. Detailed mechanistic studies (including the use of ^{15}N-labeled azide as the starting material) are currently underway.

Experimental Section

Synthesis of 3a: A mixture of [Ru]N$_3$ **1** (0.45 g, 0.65 mmol) and PhCH$_2$NCS (0.90 mL, 10.3 mmol) in THF (30 mL) was heated at reflux for one day under nitrogen. The solvent was evaporated under reduced pressure and enough *n*-hexane added to cause precipitation of a yellow solid, which was isolated by filtration and washed with *n*-hexane to give {[Ru]NCS[Ru]}$^{+}$NCS^{-} **2** (0.13 g, 14 %). (Upon recrystallization, only the monomeric complex [Ru]NCS **6** was obtained.) Red crystals formed in the filtrate, which were isolated by filtration, washed with diethyl ether and *n*-hexane and dried under vacuum. This product was identified as **3a** (0.29 g, 40 %). Orange crystals formed in the remaining filtrate, which were isolated by filtration to provide **4** (0.03 g, 5 %). Finally, a white compound crystallized from the residual solution, identified as **5** (0.02 g, 6 %), in both the (*E*) and (*Z*) forms.

Data for 3a: $C_{61}H_{62}N_4P_2RuS_3$ (1110.27): calcd. C 65.98, H 5.63, N 5.05, S 8.66; found C 66.04, H 5.70, N 4.98, S 8.70. MS (FAB, ^{102}Ru): $m/z = 1110.1$ [M]$^{+}$, 649.1 [M − N(PhCH$_2$NCS)$_3$]$^{+}$. IR (KBr): $\tilde{\nu} = 1174$ (C=S), 699 (C−S) cm^{-1}. ^{1}H NMR ([D$_8$]THF): $\delta = 7.46-6.89$ (m, 20 H, Ph), 5.07 (br. s, 2 H, CH$_2$), 4.86 (s, 2 H, CH$_2$), 4.72 (s, 2 H, CH$_2$), 2.83−1.35 (m, 6 H, CH$_2$), 1.51 (s, 15 H, Cp*-CH$_3$) ppm. ^{31}P NMR ([D$_8$]THF): $\delta = 37.54$ (br. s) ppm.

X-ray Crystallographic Studies: Data was collected at room temperature from epoxy-coated crystals mounted on a glass fiber. All measurements were made on a CCD Smart diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied in each case. The relevant crystallographic data are presented in Table 1. The structure was solved by direct methods using the program SHELXTL (Sheldrick, 1997).[34] Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. CCDC-217188 (**3a**) and -217289 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **3a** and **4**

	3a	**4**
Empirical formula	$C_{61}H_{63}N_4P_2RuS_3$	$C_{48}H_{56}N_2P_2RuS$
Molecular mass	1111.34	856.02
T (K)	295(2)	295(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
a (Å)	11.55600(10)	13.3770(3)
b (Å)	18.0640(2)	18.4420(4)
c (Å)	13.33100(10)	20.4070(5)
α (°)	90	110.9660(10)
β (°)	97.5110(10)	90.8920(10)
γ (°)	90	111.2670(10)
V (Å^3)	2758.94(4)	4319.4(2)
Z	2	4
ρ(calcd.) (Mg/m^3)	1.338	1.316
F(000)	1158	1792
Data/parameters	12253/641	14753/982
GOF	1.112	0.990
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0372, 0.0902	0.0595, 0.1314
(all data)	0.0458, 0.1032	0.1736, 0.1992

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w(F_o^2)^2]^{1/2}$.

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