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Unusual chemical transformations of acetone thiosemicarbazone mediated by ruthenium: C–H bond activation, thiolation, and C–N bond cleavage†

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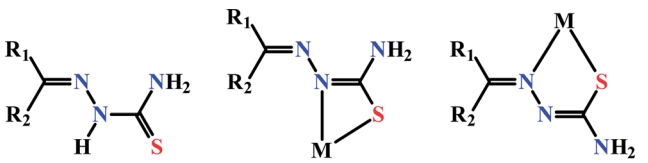
Upon reaction with $Ru(PPh_3)_3Cl_2$ in ethanol in the presence of triethylamine, acetone thiosemicarbazone undergoes several interesting chemical transformations, such as thiolation *via* methyl C–H bond activation, C–N bond cleavage, and conversion of the C=S fragment to C=O. Two complexes (**1** and **2**) were obtained from this reaction, both of which contained a modified thiosemicarbazone coordinated in SNS- or SNO-mode, two triphenylphosphines and a N-bound thiocyanate. The crystal structures of both the complexes have been determined. Theoretical and mass spectral studies have been carried out to probe the transformations. These complexes show intense absorptions in the visible and ultraviolet regions. Cyclic voltammetry on both the complexes show a reversible oxidation near 0.6 V *vs.* SCE, followed by an irreversible oxidation near 1.2 V *vs.* SCE. DFT calculations have been carried out to explain the electronic spectra, as well as the electrochemical observations.

Introduction

The chemistry of thiosemicarbazone complexes of transition metal ions has been receiving considerable attention, primarily because of the bioinorganic relevance of such complexes.[1] Systematic studies on the binding of thiosemicarbazones to selected transition metal ions are of considerable importance in this respect. However, we have been exploring the chemistry of transition metal complexes of thiosemicarbazones, mainly because of the variable binding modes displayed by these ligands in their complexes, and the present work has originated out of this exploration.[2] Through a series of studies we have observed that the coordination mode of thiosemicarbazones (depicted by **Htsc**, where H represents the dissociable acidic proton) is dictated, to a large extent, by the nature of the R_1 fragment. If R_1 is fairly large, like a phenyl group, then a four-membered chelate ring (**I**) is usually formed.[2r–u] However, when R_1 is reasonable small, such as a methyl group, the formation of a five-membered chelate ring (**II**) is usually observed.[2s]



Htsc **I** **II**

For the present study acetone thiosemicarbazone (**Hactsc**) was chosen as the ligand, and ruthenium as the metal center. It has been well demonstrated by our earlier studies that this particular ligand can readily bind to a metal center, *via* dissociation of the acidic proton, as an NS-donor forming a five-membered chelate ring (**III**).[2s] The source of ruthenium used was $Ru(PPh_3)_3Cl_2$, which is well known to undergo facile reactions with organic ligands having an acidic proton (denoted by **HL**), affording bis-complexes of type $Ru(PPh_3)_2L_2$.[3] The primary aim of the undertaken study was to synthesize a bis-thiosemicarbazone complex of ruthenium with triphenylphosphine as the ancillary ligand, and examine the binding mode of the thiosemicarbazone in the complex. During its interaction with $Ru(PPh_3)_3Cl_2$, acetone thiosemicarbazone was found to undergo several unusual chemical transformations, and the transformed species coordinated to the ruthenium center to afford two interesting complexes, **1** and **2**. Herein we

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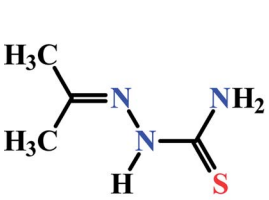
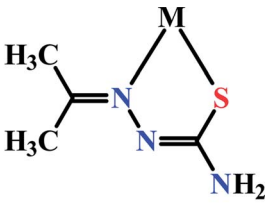
† Electronic supplementary information (ESI) available: Possible resonance structures in the SNS- and SNO-chelated ligands in **IV** and **V** (Fig. S1 and S2), contour plots of the HOMO and LUMO of complex **2** (Fig. S3) and cyclic voltammograms of complex **1** (Fig. S4). Atomic coordinates for the species depicted in Scheme 1 are available from M.G.R. upon request. CCDC 932348 and 932349. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra44329a

wish to report our findings on the formation and properties of these two complexes.



Hactsc

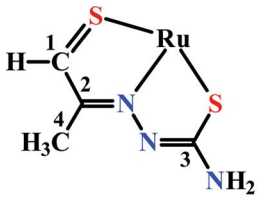


III

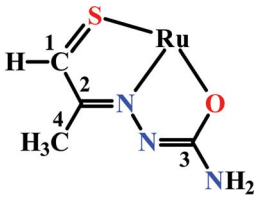
Results and discussion

Syntheses and structures

The reaction of acetone thiosemicarbazone (**Hactsc**) with $Ru(PPh_3)_3Cl_2$ in a 2 : 1 molar ratio was carried out in refluxing ethanol in the presence of triethylamine. This afforded two complexes, a green complex (**1**) and an orange complex (**2**), in decent yields. Preliminary characterization data (C, H, N analyses, IR spectroscopy and NMR spectroscopy) for these complexes clearly indicated that neither of them were a simple bis-complex of the expected type, *viz.* $Ru(PPh_3)_2(actsc)_2$. These characterization data also hinted that acetone thiosemicarbazone had probably undergone some unexpected chemical transformations during the course of the synthetic reaction. For an unambiguous characterization of these two complexes, with a particular reference to finding out the nature of the transformed acetone thiosemicarbazone in them, their structures were determined by X-ray crystallography. The structure of complex **1** is shown in Fig. 1 and selected bond parameters are given in Table 1. The structure revealed that acetone thiosemicarbazone had indeed gone through significant chemical transformations during the formation of this complex. For example, it had undergone thiolation at a terminal methyl-carbon *via* methyl C–H bond activation, and the modified thiosemicarbazone was coordinated to ruthenium as a monoanionic tridentate SNS-donor, forming two adjacent five-membered chelate rings (**IV**). Two triphenylphosphines were also coordinated to ruthenium, and they were mutually *trans*. The remaining sixth coordination site on the metal center was occupied by a thiocyanate ion, which was linked to ruthenium through the nitrogen. This thiocyanate ion seems to have originated from the chemical degradation of another molecule of acetone thiosemicarbazone *via* a C–N bond cleavage. It should be mentioned here that although a localized charge description of the mono-anionic SNS-coordinated ligand is presented in **IV**, actually the anionic ligand is resonance stabilized (Fig. S1, ESI†) and the observed bond parameters within the S–C–C–N–N–C–S fragment (Table 1) are consistent with the resonance-hybrid structure of this anionic ligand (Fig. S1, ESI†). It is relevant to mention here that although metal-mediated thiolation of aromatic carbon has been reported in the literature,[4] such thiolation of an alkyl carbon, as observed in our present study, appears to be unprecedented. It is also worth noting that the generation of a thiocyanate ion, *via* degradation of a thiosemicarbazone ligand is, to our knowledge, also unprecedented. Thus, the formation of complex **1**, as well as of complex **2** (*vide infra*), was associated with two novel transformations of acetone thiosemicarbazone.



IV



V

The structure of complex **2** (Fig. 2) was found to be very similar to that of complex **1**, where the ruthenium center was again coordinated to two triphenylphosphines, a thiocyanate (N-bound), and a modified acetone thiosemicarbazone. However, in the modified acetone thiosemicarbazone, in addition to thiolation of a terminal methyl-carbon as observed in complex **1**, the sulfur in the $-C(=S)NH_2$ fragment had been replaced by an oxygen atom, and the transformed ligand was coordinated to the metal center as a tridentate SNO-donor (**V**). The anionic SNO-coordinated ligand is also resonance stabilized (Fig. S2, ESI†), like the SNS-ligand in complex **1**, and the observed metrical parameters (Table 1) within the chelate **V** are in accordance with the resonance hybrid structure of this anion (Fig. S2, ESI†).

The formation of complexes **1** and **2**, involving several unusual chemical transformations of acetone thiosemicarbazone, is truly intriguing. Though it is not possible to provide an exact mechanism behind the formation of these two complexes, a few speculated steps, which seem probable, are shown in Schemes 1 and 2. The formation of complex **1** is

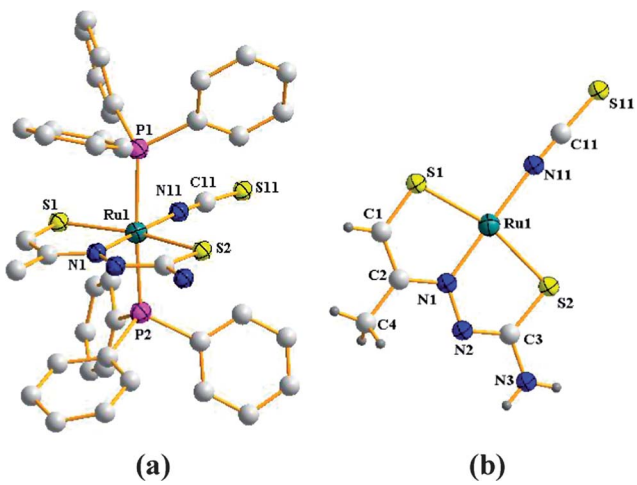


Fig. 1 (a) Molecular structure of complex **1** (hydrogen atoms are omitted for clarity) and (b) view of the equatorial plane.

Table 1 Selected bond distances and bond angles for complexes **1** and **2**

1			
Bond distances (Å)			
Ru(1)–S(1)	2.3321(17)	C(2)–N(1)	1.340(8)
Ru(1)–S(2)	2.3789(18)	N(1)–N(2)	1.355(7)
Ru(1)–N(1)	1.986(5)	N(2)–C(3)	1.327(9)
Ru(1)–N(11)	2.065(5)	C(3)–S(2)	1.716(7)
Ru(1)–P(1)	2.3772(17)	C(2)–C(4)	1.496(9)
Ru(1)–P(2)	2.3792(17)	N(11)–C(11)	1.166(8)
S(1)–C(1)	1.640(7)	C(11)–S(11)	1.613(6)
C(1)–C(2)	1.385(8)		
Bond angles (°)			
S(1)–Ru(1)–N(1)	81.91(13)	S(1)–Ru(1)–S(2)	164.08(6)
S(2)–Ru(1)–N(1)	82.18(13)	N(1)–Ru(1)–N(11)	178.90(17)
		P(1)–Ru(1)–P(2)	172.50(5)
2			
Bond distances (Å)			
Ru(1)–S(1)	2.299(2)	C(2)–N(1)	1.342(10)
Ru(1)–O(1)	2.170(4)	N(1)–N(2)	1.344(9)
Ru(1)–N(1)	1.966(6)	N(2)–C(3)	1.375(11)
Ru(1)–N(11)	2.050(6)	C(3)–O(1)	1.304(10)
Ru(1)–P(1)	2.383(2)	C(2)–C(4)	1.515(12)
Ru(1)–P(2)	2.376(2)	N(11)–C(11)	1.151(11)
S(1)–C(1)	1.681(8)	C(11)–S(11)	1.647(9)
C(1)–C(2)	1.349(11)		
Bond angles (°)			
S(1)–Ru(1)–N(1)	82.89(17)	S(1)–Ru(1)–O(1)	160.41(15)
O(1)–Ru(1)–N(1)	77.50(2)	N(1)–Ru(1)–N(11)	176.30(2)
		P(1)–Ru(1)–P(2)	171.20(8)

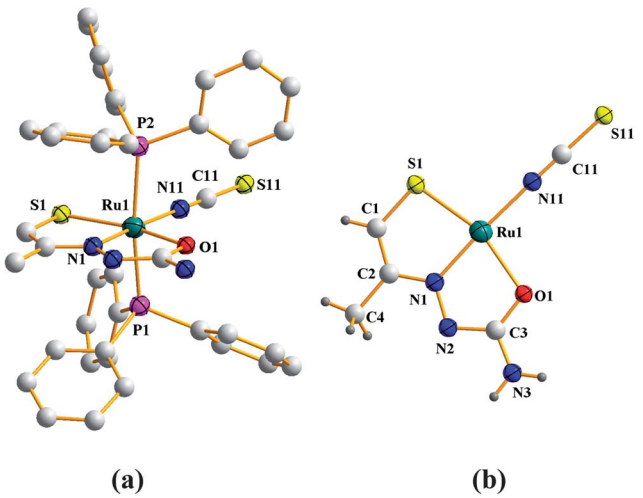
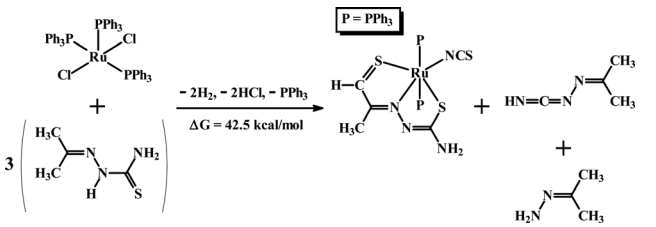
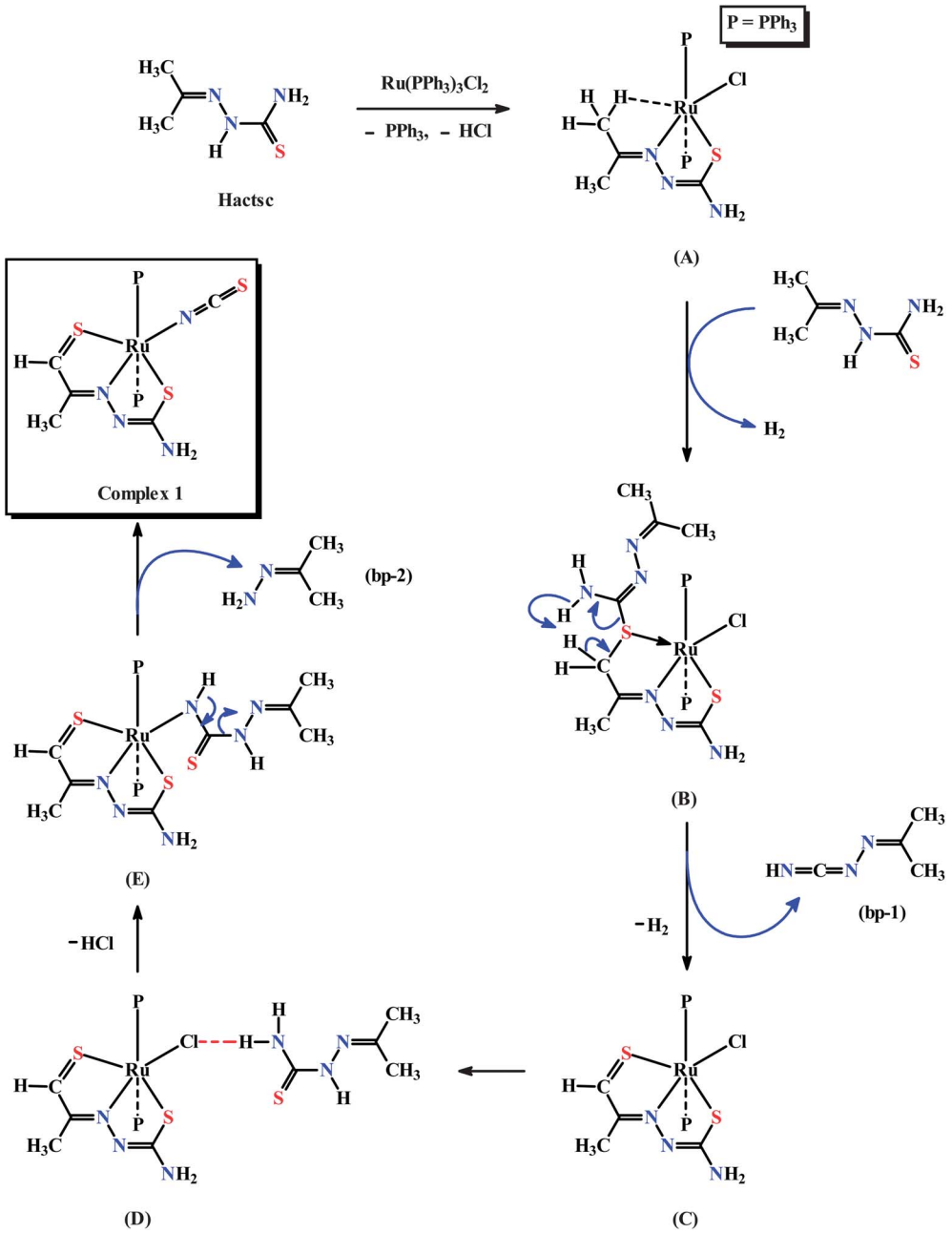


Fig. 2 (a) Molecular structure of complex **2** (hydrogen atoms are omitted for clarity) and (b) view of the equatorial plane.

believed to be initiated by the coordination of the thiosemicarbazone to ruthenium in the expected NS-fashion (**I**), with simultaneous elimination of PPh_3 and HCl to produce an intermediate, **A**; ONIOM calculations confirm this first step to be thermoneutral. In **A**, the metal center is formally five-coordinated, and hence it is a 16-electron species. Thus an agostic interaction between the metal center and a proximal methyl C–H, which is common in coordinatively unsaturated complexes of ruthenium(II),[5] seems inevitable. This makes the methyl-carbon electrophilic, and, as a consequence, it undergoes an interaction with the nucleophilic sulfur-center of another molecule of the thiosemicarbazone, leading to the formation of a new C–S bond, and thus a second intermediate, **B**, is generated. The electron-deficiency of the sulfur-center in **B**, developed due to its coordination to ruthenium(II), triggers some usual rearrangements, resulting in the cleavage of the C–S bond in the second thiosemicarbazone, and affords a third intermediate **C**, along with elimination of hydrogen and an organic by-product (**bp-1**). The thiocyanate ion in complex **1**, obviously provided by a third thiosemicarbazone, seems to result from an initial hydrogen-bonding interaction with the ruthenium-bound chloride in **C**, followed by elimination of HCl (from the adduct **D**) to generate **E**, and finally *via* elimination of another organic species (**bp-2**). The stoichiometrically balanced reaction for the sequence of events depicted in Scheme 1 is shown in eqn (1). DFT analysis (see the Experimental section for details) using a two-level ONIOM approach allowed us to determine the net free energy for the overall process, and we computed the conversion of $Ru(PPh_3)_3Cl_2$ to the thiocyanate complex **1** to be endergonic by 42.5 kcal mol^{-1}. The driving force for the formation of complex **1** traces its origin to the entropic contributions associated with this reaction. The computed entropy change for this process was *ca.* 140 eu, a number whose magnitude reflects the release of multiple molecules of H_2 and HCl and the accompanying organic by-products.



Attempts have also been made to identify the possible intermediates present during the formation of complex **1** by mass spectrometry.[6] The mass spectrum, recorded after the reaction had proceeded for 30 min, showed a weaker peak at m/z = 755 corresponding to intermediate **A** (for $[\mathbf{A} - Cl]^+$) and two much stronger peaks at m/z = 884 and 785 that are assignable to **B** (for $[\mathbf{B} - Cl]^+$) and **C** (for $[\mathbf{C} - Cl]^+$), respectively.[7] All these three peaks were detectable up to 1.5 h, after which the peak corresponding to **A** started loosing intensity more rapidly compared to the other two peaks, and a peak corresponding to complex **1** at m/z = 866 (for $[\mathbf{1} + Na^+]^+$) started growing.[8] No peaks corresponding to the hydrogen-bonded adduct **D** and the next intermediate **E** were identified, indicating their transient existence. Identification of the first organic by-product, *viz.*

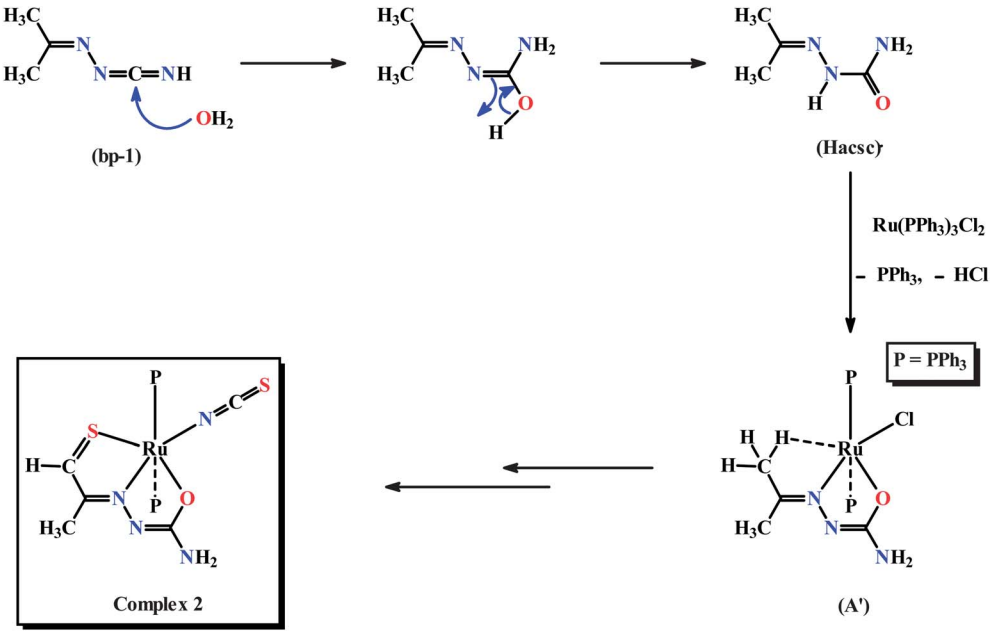


Scheme 1 Probable steps behind the formation of complex **1**.

bp-1, was also not possible, probably due to its rapid hydrolysis to form acetone semicarbazone (see Scheme 2). However, the second organic by-product, *viz.* **bp-2**, was identified in the reaction mixture by GC-MS. The mass spectral studies thus support most of the proposed steps behind the formation of complex **1**.

The formation of complex **2** (Scheme 2) is imagined to start with conversion of the first organic by-product (**bp-1**), generated during the synthesis of complex **1** (Scheme 1), to acetone semicarbazone (**Hacsc**) *via* its interaction with water present in the reaction medium. This newly formed semicarbazone then undergoes a reaction with $Ru(PPh_3)_3Cl_2$ similar to before, generating the first intermediate (**A′**), and the following sequences are believed to be similar to those in Scheme 1 to finally yield complex **2**. It is interesting to note that the observed changes to acetone thiosemicarbazone during the formation of complexes **1** and **2**, involved ruthenium-mediated C–S bond cleavage, as well as a new C–S bond formation, and such reactions are of crucial significance in synthetic organic chemistry,[9] biology,[10] and industry.[11]

The fact that there are three sulfur atoms in complex **1** and the only possible sulfur-provider within the reaction vessel was acetone thiosemicarbazone, clearly shows the involvement of three molecules of acetone thiosemicarbazone in the formation



Scheme 2 Probable steps behind the formation of complex **2**.

of one molecule of complex **1**. Though speculative, the same is indicated in Scheme 1. Similarly, for one molecule of complex **2**, two molecules of acetone thiosemicarbazone are necessary, as illustrated in Scheme 2. Thus, assuming equal probability for the formation of complexes **1** and **2**, five molecules of acetone thiosemicarbazone are required per two molecules of $Ru(PPh_3)_3Cl_2$. However the synthetic reaction, originally intended to prepare a bis-thiosemicarbazone complex, was carried out with only two moles of thiosemicarbazone per mole of the ruthenium starting material, which probably accounts for the relatively low yields of the complexes. This is further supported by the observation that the same reaction, when carried out with a 3 : 1 thiosemicarbazone–ruthenium ratio, yields the two complexes in much better yields (complex **1**: 39%; complex **2**: 32%).

Table 3 Composition of selected molecular orbitals in the complexes **1** and **2**

Complex	Contributing fragments	% Contribution of fragments to HOMO	LUMO
1	Ru	8.8	7.9
	SNS-ligand	41.9	82.9
	thiocyanate	49.3	6.9
	PPh_3	0	2.3
2	Ru	9.3	8.5
	SNO-ligand	42.8	81.7
	thiocyanate	47.9	7.7
	PPh_3	0	2.1

Spectral properties

Magnetic susceptibility measurements showed that both the complexes **1** and **2** were diamagnetic, which corresponds to the bivalent state of ruthenium (low-spin d^6, $S = 0$) in them. ^1H NMR spectra of the complexes showed broad signals between 7.35–7.73 ppm for the coordinated PPh_3 ligands, a sharp signal near 2.0 ppm for the methyl group in the coordinated acetone thiosemicarbazone derived ligand, and another sharp signal at 3.64 ppm for the NH_2 group. Only the signal for the proton in the H–C(=S)– fragment could not be detected, probably due to its overlap with the broad signals from PPh_3. Infrared spectra of the complexes **1** and **2** showed many bands of different intensities in the 400–4000 cm^{-1} region. No attempt was made to assign each individual band to a specific vibration. However, three strong bands were observed around 516, 692 and 744 cm^{-1} in both the complexes, indicating the presence of

Table 2 Electronic spectral and cyclic voltammetric data

Complex	Electronic spectral data,[a] λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)	Cyclic voltammetric data,[b] E, *V vs.* SCE
1	582 (3500), 438 (16 400), 272 (66 100)	0.63[c] (67),[d] 1.16[e]
2	538 (3300), 420 (11 500), 272 (43 100)	0.68[c] (70),[d] 1.22[e]

[a] In dichloromethane. [b] Solvent: acetonitrile, supporting electrolyte: TBHP, scan rate: 50 mV s^{-1}. [c] $E_{1/2}$ value ($E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively). [d] ΔE_p value (where $\Delta E_p = E_{pa} - E_{pc}$). [e] E_{pa} value.

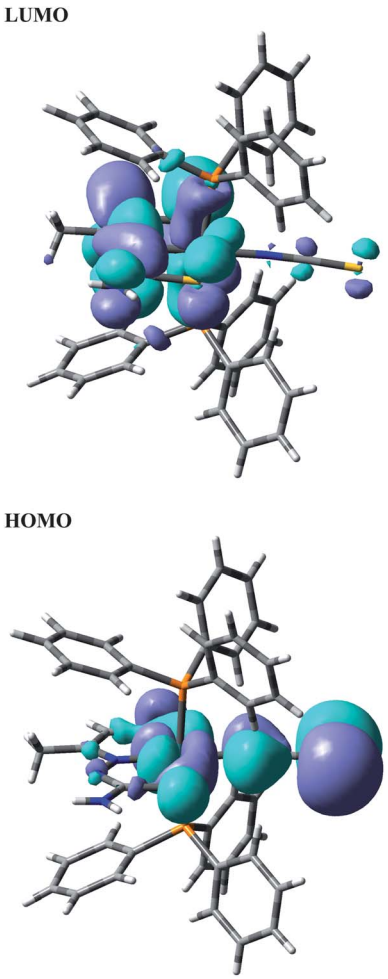


Fig. 3 Contour plots of the HOMO and LUMO in complex **1**.

coordinated PPh_3 ligands. A broad band near 2092 cm^{-1} was observed in both the complexes due to the presence of coordinated thiocyanate.

Complexes **1** and **2** were soluble in common organic solvents like methanol, ethanol, acetone, acetonitrile, dichloromethane, chloroform, *etc.*, producing green and orange solutions, respectively. Electronic spectra of the complexes were recorded in dichloromethane solutions. Each complex showed intense absorptions in the visible and ultraviolet regions (Table 2). The absorptions in the ultraviolet region are believed to be due to transitions within the orbitals of the SNS-/SNO-coordinated ligand. To have an understanding of the origin of the lowest-energy absorption, DFT calculations were performed on both the complexes. Compositions of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are given in Table 3. Contour plots of these orbitals for complex **1** are shown in Fig. 3, and those for complex **2** are shown in Fig. S3 (ESI†). In both the complexes, the HOMO had a maximum (~48%) contribution from the coordinated thiocyanate, a slightly lower (~42%) contribution from the coordinated SNS-/SNO-donor ligand, and a much lower (~9%) contribution from the metal center. The LUMO was found to be delocalized primarily (~82%) on the SNS-/SNO-donor ligand, with little contributions coming from the other fragments. The lowest energy absorption in both the complexes is hence assignable to a transition from a filled orbital having mixed (thiocyanate + SNS-/SNO-donor ligand) character, to a vacant orbital in the tridentate ligand.

Electrochemical properties

The electrochemical properties of the ruthenium complexes were studied by cyclic voltammetry in acetonitrile solutions (0.1 M TBHP). Each complex showed two oxidative responses on the positive side of SCE. Voltammetric data are given in Table 2 and a selected voltammogram is shown in Fig. S4 (ESI†). The first oxidation occurred near 0.6 V *vs.* SCE and it was reversible in nature, while the second oxidation, observed near 1.2 V *vs.* SCE, was found to be irreversible in nature. In view of the composition of the HOMO in all these complexes, the first oxidative response is assigned to the oxidation of the coordinated imine-ligand.

Conclusions

The present study thus shows that acetone thiosemicarbazone readily reacts with $Ru(PPh_3)_3Cl_2$, and by coordinating to the metal center it undergoes three major chemical changes, *viz.* thiolation *via* methyl C–H bond activation, C–N bond cleavage to generate the thiocyanate ion, and conversion of the C=S fragment to C=O to produce acetone semicarbazone. All these observed transformations, which are unusual as well as unprecedented, are believed to be initiated through an agostic interaction between the 16-electron metal center and a proximal methyl C–H. Our current research efforts remain centered on related bond-activation processes and these data will be published in due course.

Experimental

General procedures

Ruthenium trichloride, was purchased from Arora Matthey, Kolkata, India. $Ru(PPh_3)_3Cl_2$ was prepared by following a reported procedure.[12] Tetrabutylammonium hexaflurophosphate (TBHP), obtained from Aldrich, and AR grade acetonitrile, procured from Merck, India, were used for the electrochemical work. All other chemicals and solvents were reagent grade commercial materials and were used as received. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer. IR spectra were obtained on a Shimadzu FTIR-8300 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a Sherwood MK-1 balance. NMR spectra were recorded in $CDCl_3$ solutions on a Bruker Avance DPX 300 NMR spectrometer. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working

Table 4 Crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{41}H_{36}N_4S_3P_2Ru\cdot 0.5CH_3CN$	$C_{41}H_{36}N_4O_1S_2P_2Ru\cdot 0.5CH_3CN$
Formula weight	851.57	835.57
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.509(5)	12.436(5)
b/Å	12.844(5)	12.863(5)
c/Å	13.675(5)	13.394(5)
α/°	95.721(5)	94.291(5)
β/°	96.275(5)	94.205(5)
γ/°	104.012(5)	104.931(5)
V/Å^3	2100.3(14)	2054.9(14)
Z	2	2
D_{calcd}/mg m^{-3}	1.358	1.369
F(000)	875	867
Crystal size/mm	0.17 × 0.12 × 0.10	0.19 × 0.15 × 0.11
T/K	298	298
μ/mm^{-1}	0.633	0.599
Collected reflections	34 097	26 178
R_{int}	0.057	0.066
Independent reflections	9547	5733
$R1$[a]	0.0630	0.0611
w$R2$[b]	0.1944	0.1947
GOF[c]	1.20	1.05

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$. [c] $GOF = [\sum[w(F_0^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. GC-MS analyses were performed using a Perkin Elmer CLARUS 680 instrument. The nature of the HOMO and LUMO levels in complex **1** were investigated by DFT molecular orbital calculations using the Gaussian 03 (B3LYP/SDD-6-31G) package.[13] The different species in Scheme 1 were examined computationally using Morokuma's ONIOM method using the Gaussian 09 software suite.[14] All of the ruthenium-containing species were optimized *via* a two-level approach with the phenyl groups of the PPh_3 ligands treated as the lower of the two levels; all other compounds depicted in the scheme were optimized using *ab initio* DFT methods. For those species analyzed within the two-level treatment, we employed an ONIOM method that was defined by a B3LPY/PM6 composition. The phenyl groups (low level) were treated at the semi-empirical PM6 level of theory, while the remaining atoms (high level) were treated within the B3LYP framework. With respect to the high-level treatment of atoms, the ruthenium atoms were described by Stuttgart–Dresden effective core potentials (ecp) and a SDD basis set, while a 6-31G(d′) basis set was employed for the remaining atoms. All of the species in Scheme 1 furnished fully optimized ground-state structures based on positive eigenvalues obtained from the analytical Hessian. The computed frequencies were used to make zero-point and thermal corrections to the electronic energies.

Synthesis of acetone thiosemicarbazone (Hactsc). Acetone thiosemicarbazone was prepared by reacting equimolar amounts of thiosemicarbazide and acetone in a 1 : 1 ethanol–water mixture.[2s,15] Yield: 82%. Anal. calcd for $C_4H_9N_3S$: C 36.64; H 6.87; N 32.06. Found: C 36.61; H 6.90; N 32.03%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.90 (s, CH_3), 2.01 (s, CH_3), 6.46 and 7.22 (2s, NH_2), 8.59 (s, NH). IR (wave number, cm^{-1}): 3382, 2161, 1603, 1511, 1470, 1430, 1367, 1304, 1254, 1163, 1109, 1077, 1025, 866, 787, 727, 635, 581.

Synthesis of complexes 1 and 2. To a solution of acetone thiosemicarbazone (28 mg, 0.21 mmol) in ethanol (40 ml) was added triethylamine (25 mg, 0.25 mmol) followed by $Ru(PPh_3)_3Cl_2$ (100 mg, 0.10 mmol). The resulting mixture was then heated at reflux for 6 h to yield a dark brown solution. The solvent was then evaporated to give a solid mass, which was subjected to purification by thin layer chromatography on a silica plate. Using 1 : 1 acetonitrile–benzene as the eluant, a green band and an orange band separated, which were extracted with acetonitrile. Evaporation of these acetonitrile extracts gave green crystals of **1** and orange crystals of **2**.

*Complex **1**.* Yield: 24 mg (27% based on Ru-starting material). Anal. calcd for $C_{41}H_{36}N_4S_3P_2Ru$: C 58.36; H 4.27; N 6.64. Found: C 58.27; H 4.25; N 6.65%. MS (ESI), positive mode: $[\mathbf{1} + Na^+]^+$ 866. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.00 (s, 3H), 3.64 (s, 2H), 7.37–7.73 (2PPh_3 + 1H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 16.7 (C_4), 127.9–133.8 (PPh_3), 161.7 (SCN), 181.7 (C_3), 190.7 (C_2), 206.9 (C_1). ^{31}P NMR ($CDCl_3$, 25 °C): δ 28.6. IR (wave number, cm^{-1}): 2922, 2855, 2092, 1731, 1431, 1263, 1160, 961, 813, 744, 715, 692, 516.

*Complex **2**.* Yield: 18 mg (21% based on Ru-starting material). Anal. calcd for $C_{41}H_{38}N_4O_1S_2P_2Ru$: C 59.48; H 4.35; N 6.77.

Found: C 59.55; H 4.37; N 6.76%. MS (ESI), positive mode: [**2** + Na^+]$^+$ 850. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.01 (s, 3H), 3.64 (s, 2H), 7.35–7.51 (2PPh_3 + 1H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 15.3 (C_4), 128.0–134.1 (PPh_3), 161.1 (SCN), 177.7 (C_3), 191.1 (C_2), 207.0 (C_1). ^{31}P NMR ($CDCl_3$, 25 °C): δ 30.2. IR (wave number, cm^{-1}): 2919, 2850, 2093, 1735, 1436, 1269, 1160, 960, 813, 743, 715, 694, 517.

Crystallography

Single crystals of complexes **1** and **2** were grown by the slow evaporation of solvent from acetonitrile solutions of the respective complexes. Selected crystal data and data collection parameters are given in Table 4. Data on the crystals were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). X-ray data reductions, structure solutions and refinements were done using SHELXS-97 and SHELXL-97 programs.[16] The structures were solved by direct methods.

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6 For the mass spectral study, aliquots of 0.1 ml were taken from the reaction bed after certain time intervals and the aliquots were frozen immediately in liquid nitrogen. These samples were brought to room temperature prior to mass spectral analysis and the spectra were recorded as soon as possible.

7 The mass spectrum also shows a much weaker peak at $m/z = 739$, corresponding to the intermediate $\mathbf{A}'$ (for $[\mathbf{A}' - \mathrm{Cl}]^+$) shown in Scheme 2.

8 A peak corresponding to complex **2** at $m/z = 850$ (for $[\mathbf{2} + \mathrm{Na}^+]^+$) also started showing up.

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