Room Temperature Activation of an Aliphatic C–H Bond: Synthesis and Structure of the Ruthenium Clusters $[(\mu_2\text{-H})Ru_3(CO)_8(\mu_3\text{-S})(\eta^2\text{-}CH_2CMe_2NHCNHBu^t)]$ and $[(\mu_2\text{-H})Ru_3(CO)_9\{\mu_3\text{-S-}Ru(CO)_3(\eta^2\text{-}CH_2CMe_2NHCNHBu^t)\}]$

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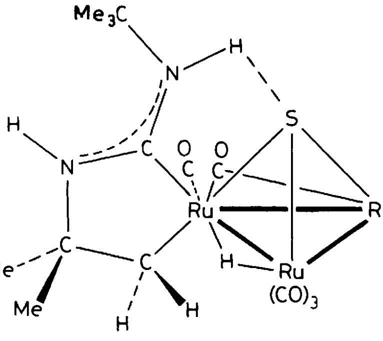
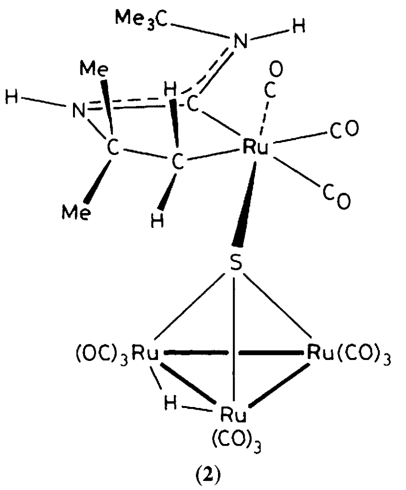
The thiourea derivative $(Me_3CNH)_2CS$ reacts with $[Ru_3(CO)_{12}]$ in tetrahydrofuran with C=S bond cleavage and oxidative addition of the non-activated C–H bond of a peripheral methyl group; the reaction proceeds in the dark at room temperature.

The activation of aliphatic C–H bonds by metal complexes is one of the research topics in co-ordination chemistry.[1] As such reactions proceed photolytically in most cases, only a few examples of thermal activation are known. Tetramethylsilane and methane react thermally with C–H activation at bis(pentamethylcyclopentadienyl) complexes of lutetium[2] and thorium,[3] they also add oxidatively to the thermally generated fragment bis(dicyclohexylphosphino)ethane-platinum;[4] toluene undergoes an analogous reaction with the dehydrobenzene complex $(PPh_3)_4Ru(C_6H_4)$.[5] Activation processes of aliphatic C–H bonds which do not require elevated temperatures are particularly rare. In the complexes $Ta(OSiBu^t_3)_3$[6] and $TaCl_3(OC_6H_3Bu^t_2)_2$, a methyl group can already undergo an intramolecular oxidative addition to the metal atom at 20 °C; in the latter case, however, the reaction occurs only in the presence of lithium phenyl[7] or sodium amalgam.[8]

We report here the activation of the aliphatic C–H bond of a peripheric methyl group of *N,N'*-di(t-butyl)thiourea also proceeding at room temperature. From a solution of $(Me_3CNH)_2CS$ and $Ru_3(CO)_{12}$ in tetrahydrofuran (THF), stirred in the dark at 20 °C for several days, the clusters (**1**) and (**2**) can be isolated.† The reaction is not accelerated by UV irradiation. In this reaction the thiourea is formally cleaved into a sulphur fragment and a diaminocarbene fragment, which are both co-ordinated to ruthenium. Furthermore, a hydrogen atom of a t-butyl group is transferred with co-ordination of the CH_2 unit to the Ru_3 metal framework.



(**1**)



(**2**)

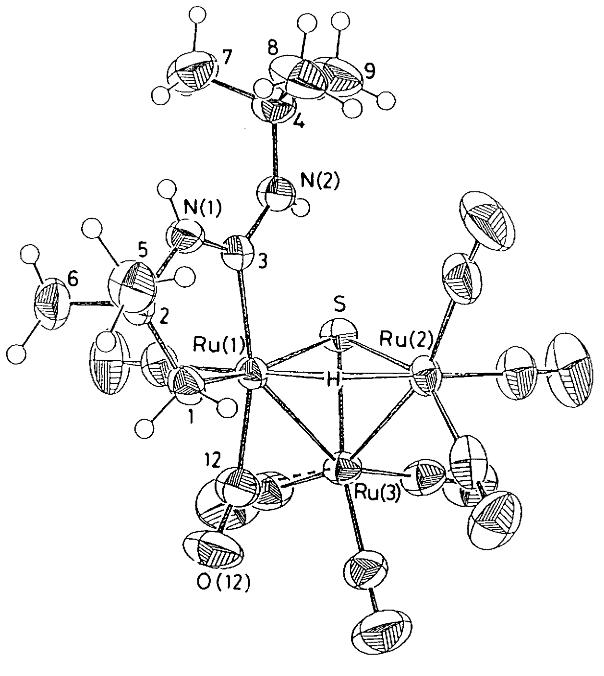


Figure 1. Molecular structure of (**1**) (ORTEP plot, thermal ellipsoids, 50% propability), selected bond distances (Å) and bond angles (°): Ru(1)–Ru(2) 2.929(1), Ru(2)–Ru(3) 2.736(1), Ru(1)–Ru(3) 2.836(1), Ru(1)–S 2.404(1), Ru(2)–S 2.373(1), Ru(3)–S 2.339(1), Ru(1)–C(12) 1.930(4), Ru(3)–C(12) 2.549(4), S–H[N(2)] 2.541(1), Ru–Ru(1)–C(1) 2.171(4), Ru(1)–C(3) 2.108(3), C(3)–N(1) 1.313(5), C(3)–N(2) 1.326(5); Ru(1)–C(12)–O(12) 159.3(4), N(1)–C(3)–N(2) 120.4(3), Ru(1)–C(3)–N(1) 116.6(3), Ru(1)–C(3)–N(2) 123.0(3).

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† A solution of $Ru_3(CO)_{12}$ (0.58 mmol) and $(Me_3CNH)_2CS$ (0.50 mmol) in THF (50 ml) is stirred at 20 °C under nitrogen for 14 days. After evaporation of the solvent the residue is dissolved in CH_2Cl_2 (5 ml) and separated by preparative TLC (Al_2O_3, CH_2Cl_2/cyclohexane 6:5). The products, (**1**) and (**2**), are extracted with CH_2Cl_2 from the second and the third bands, with yields of 11 and 4%, respectively. UV irradiation during the reaction increases the yield of (**2**) (11%) at the expense of (**1**) (0%).

Compounds (**1**) and (**2**) are obtained after chromatographic separation as slightly air-sensitive yellow–orange crystals.‡ Both clusters contain a metallacyclic moiety with the dihapto-$CH_2CMe_2NHCNHBu^t$ ligand bonded to a ruthenium atom by both the methylene carbon atom and the diamino carbon atom. In (**1**) this ligand is co-ordinated to the trinuclear framework of the cluster, and in (**2**) it is bound to another sulphur-bound ruthenium atom. The single-crystal *X*-ray structure analyses gave the molecular structures depicted in Figures 1 and 2.§

In both cases, the Ru–C(1) distance corresponds to a metal–carbon single bond [(**1**) 2.171(4); (**2**) 2.155(6) Å];† the Ru–C(3) distance is insignificantly shorter despite the carbenoid character. In both compounds, the carbon atom C(3) is sp^2-hybridised, as reflected in a planar co-ordination sphere; the C–N distances reveal a partial double-bond character [(**1**) 1.313(5), 1.326(5); (**2**) 1.314(7), 1.339(5) Å]. In mononuclear diaminocarbene ruthenium complexes, which are accessible from tetra-aminoethylenes, slightly shorter Ru–C and slightly longer C–N bonds have been found. In $[(PEt_3)_2Ru(CN_2C_{16}H_{17})(CO)Cl]$[9] the Ru–C distance is 1.989 Å and the C–N bonds have been determined to be 1.34 and 1.35 Å. For both (**1**) and (**2**), the hydride ligand bridges Ru(1)–Ru(2). The sulphur ligand capping the Ru_3 framework forms a hydrogen bridge with the H atom on N(2) in (**1**) [S–H 2.541(1) Å], while in (**2**) it is co-ordinated to a $Ru(CO)_3(\eta^2\text{-}CH_2CMe_2NHCNHBu^t)$ unit. With respect to the Ru_3 skeleton, the S atom in (**1**) functions as a four-electron donor. In (**2**), however, it functions as a five-electron donor; the $Ru(CO)_3(\eta^2CH_2CMe_2NHCNHBu^t)$ moiety uses the S atom as a one-electron donor.

The clusters (**1**) and (**2**) are not interconvertible; obviously, they are formed independently of one another. Their formation from $Ru_3(CO)_{12}$ and $(Me_3CNH)CS$ demonstrates the remarkable capability of the trinuclear ruthenium framework to abstract non-activated hydrogen atoms from aliphatic C–H bonds.

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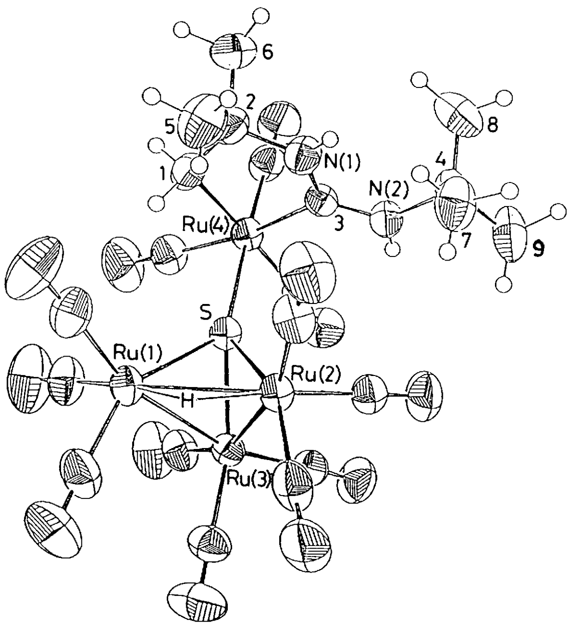

Figure 2. Molecular structure of (**2**) (ORTEP plot, thermal ellipsoids, 50% probability), selected bond distances (Å) and bond angles (°): Ru(1)–Ru(2) 2.8935(6), Ru(2)–Ru(3) 2.750(1), Ru(1)–Ru(3) 2.757(1), Ru(1)–S 2.349(1), Ru(2)–S 2.344(1), Ru(3)–S 2.330(1), Ru(4)–S 2.448(1), Ru(4)–C(1) 2.155(6), Ru(4)–C(3) 2.087(4), C(3)–N(1) 1.314(7), C(3)–N(2) 1.339(5); N(1)–C(3)–N(2) 119.9(4), N(1)–C(3)–Ru(4) 115.9(3), N(2)–C(3)–Ru(4) 124.2(3), Ru(1)–S–Ru(4) 137.79(5), Ru(2)–S–Ru(4) 137.17(4), Ru(3)–S(1)–Ru(4) 133.51(5).

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‡ Satisfactory elemental analyses were obtained for the compounds described. *Selected spectroscopic data* for: (**1**): IR ν_{co} (cyclohexane) 2081s, 2047vs, 2014s, 2006vs, 1981m, 1936w, 1853w cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.72 (s, br., NH), 5.88 (s, br., NH), 2.53 (d, CH), 2.44 (dd, CH), 1.50 (s, Me), 1.37 (s, Me), 1.33 (s, CMe_3), −18.18 (d, Ru_2H). For (**2**): IR ν_{CO} (cyclohexane) 2135w, 2098s, 2073m, 2049vs, 2022vs, 2011m, 1999vs, 1984m, 1961w, 1943w cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19 (s, br., NH), 5.49 (s, br., NH), 2.27 (d, CH), 1.63 (d, CH), 1.54 (s, Me), 1.42 (s, CMe_3), 1.36 (s, Me), −18.69 (s, Ru_2H).

§ *Crystal data* for (**1**): space group $P2_1/c$, $a = 9.165(1)$, $b = 19.839(2)$, $c = 14.042(1)$ Å, $\beta = 101.57(1)°$, $U = 2501.3$ Å^3, $Z = 4$, $D_x = 1.943$ g cm^{-3}, $\mu = 17.4$ cm^{-1}. $\theta_{max.} = 25°$; 4364 unique reflections, 3918 with $F_o > 4\sigma(F_o)$, weighted anisotropic full-matrix least-squares refinement gave $R = 0.031$ and $R_w = 0.033$ with $w^{-1} = \sigma^2(F_o) + 0.00108(F_o^2)$. For (**2**): space group $P\bar{1}$, $a = 9.190(1)$, $b = 11.553(2)$, $c = 16.044(2)$ Å, $\alpha = 100.88(1)$, $\beta = 90.03(1)$, $\gamma = 110.60(1)°$, $U = 1561.7$ Å^3, $Z = 2$, $D_x = 1.975$ g cm^{-3}, $\mu = 18.3$ cm^{-1}. $\theta_{max.} = 27.5°$; 5437 unique reflections, 4310 with $F_o > 4\sigma(F_o)$. Empirical correction of absorption[10] and weighted anisotropic full-matrix least-squares refinement gave $R = 0.029$ and $R_w = 0.029$ with $w^{-1} = \sigma^2(F_o) + 0.00040(F_o^2)$. Data measured with Mo-$K_\alpha$ radiation (Stoe-Siemens AED2 four-circle diffractometer, graphite monochromator, $\lambda = 0.71073$ Å, room temperature). Structures solved using SHELXS-86,[11] refined with SHELX-76.[12] Complex neutral atom scattering factors not included in SHELX-76 were taken from ref. 13. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.