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Reactivity of double thioureas towards metal complexes.

Synthesis and crystal structure

of $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9]_2\{\text{SC}(\text{NPh})\text{N}(\text{Et})(\text{CH}_2)_2\text{NH}(\text{PhN})\text{CS}\}]^*$

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Abstract

By reaction of PhNCS with $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ (2:1 molar ratio), a substituted dithiourea has been obtained which affords a new functionalized xerogel (XGditu) by hydrolysis and polycondensation with $(\text{EtO})_4\text{Si}$. This material is able to bind metal species, giving systems of potential interest in catalysis. In order to ascertain the nature of the tethered metal species, the non-siloxanized dithiourea $\text{PhNHC}(\text{S})\text{N}(\text{Et})(\text{CH}_2)_2\text{NHC}(\text{S})\text{NPh}$ (2) has been prepared. It reacts with $[\text{Ru}_3(\text{CO})_{12}]$ to give the complex $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9]_2\{\text{SC}(\text{NPh})\text{N}(\text{Et})(\text{CH}_2)_2\text{NH}(\text{PhN})\text{CS}\}$ (4), which contains two distinct hydrido carbonyl clusters bound to the two deprotonated thiourea groups.

1. Introduction

Recently we produced new thiourea-functionalized silica xerogels by hydrolysis and co-condensation of $\text{Si}(\text{OR})_4$ (fourfold cross-linking) and the suitable functionalized siloxane $\text{L-Si}(\text{OR})_3$. Thioureas are of notable interest in catalysis owing to the specific catalytic properties of the thiourea/ PdX_2 complexes, which were found to be efficient in catalyzing carbonylation of alkynes [1] and in inducing ring-closure processes of diynes [2].

The use in catalysis of sol-gel [3] materials is attracting increasing interest. Both anchored transition metal complexes with catalytic activity [4] and supported small metal particles [5] can be conveniently prepared by the sol-gel process. In the former case, a donor-functionalized support is required. A phosphine [4a,b,6] anchored to silica is the most common binding function,

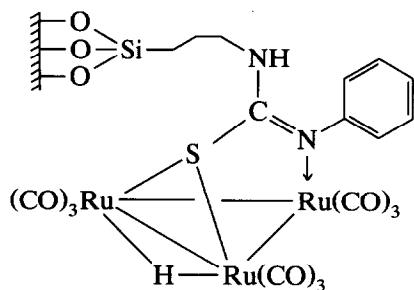
but nitrogen [4d] and sulphur [7] donors are also suitable surface modifiers.

We have found that a new thiourea-functionalized sol-gel material (XGtu), derived from $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NPh}$, easily binds palladium(II) and metal carbonyl species by coordinative interactions. In the case of palladium, treatment with dihydrogen afforded well-dispersed nanometresized metal particles with high, selective hydrogenating activity [8].

In an effort to explore the coordinating capability of this functionalized material and the production of new catalytic systems, we allowed the xerogel to react with $[\text{Ru}_3(\text{CO})_{12}]$, obtaining a tethered metal carbonyl cluster. This surface organometallic species has the same CO stretching pattern as the model compound $[(\mu\text{-H})\text{Ru}_3(\mu_3\text{-SC}(\text{NHP})\text{NPh})(\text{CO})_9]$ (1), obtained from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with *N*-phenyl-*N'*-propylthiourea, whose molecular structure has been fully elucidated by X-ray diffraction [9]. The structure displays a triangular metal cluster and contains the intact, even if *N*-deprotonated, thiourea interacting with all three ruthenium atoms. Similar complexes have been obtained with symmetrically substituted thioureas [10]. The IR spectroscopic data suggest that the same ruthenium

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* Dedicated to Professor Gian Paolo Chiusoli, illustrious colleague and dear friend of the authors, in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.



Scheme 1.

mium cluster is tethered to the xerogel surface as depicted by Scheme 1.

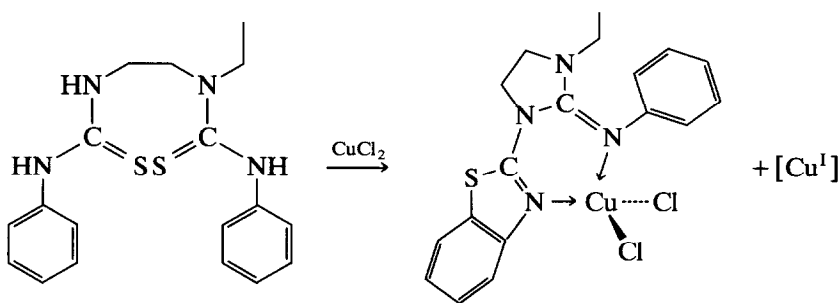
In an extension of this work, we have attempted the synthesis of a new dithiourethane-functionalized xerogel (XGditu) from the siloxanized dithiourethane ligand $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{N}(\text{C}(\text{S})\text{NHPh}(\text{CH}_2)_2\text{NHC}(\text{S})\text{NHPh})$, in order to obtain multifunctional systems, possibly able to bind two different metals such as palladium and copper.

At the same time, we have produced the non-siloxanized dithiourethane $\text{PhNHC}(\text{S})\text{N}(\text{Et})(\text{CH}_2)_2\text{NHC}(\text{S})\text{NHPh}$ (**2**) (as a molecular model for the surface binding function) and allowed it to react with CuCl_2 . The reaction (depicted in Scheme 2) is quite clean and affords a copper(I) species as well as the unexpected copper(II) complex $[\text{CuCl}_2\{(\text{C}_7\text{H}_4\text{NS})\text{N}(\text{CH}_2)_2\text{N}(\text{Et})\text{C}=\text{NPh}\}]$ (**3**), containing a cyclization derivative of **2** as chelating ligand [11].

These results stimulated us to examine the reactivity of the new xerogel XGditu and of **2** towards different metal species and this paper deals chiefly with the synthesis and the crystal structure of the title compound $\{(\mu\text{-H})\text{Ru}_3(\text{CO})_9\}_2\{\text{SC}(\text{NPh})\text{N}(\text{Et})(\text{CH}_2)_2\text{NH}(\text{PhNCS})\}$ (**4**) obtained by reaction of **2** with $[\text{Ru}_3(\text{CO})_{12}]$.

2. Experimental details

All the organic reagents, copper(II) and palladium-



Scheme 2.

(II) acetates, palladium(II) chloride and $[\text{Ru}_3(\text{CO})_{12}]$ were pure commercial products. The solvents were reagent grade and were dried and distilled by standard techniques before use. All manipulation of siloxanized reagents (prior to the sol-gel process) were carried out under dry dinitrogen by means of standard Schlenk tube techniques.

Elemental analyses were performed with a Carlo Erba automated analyzer (C, H, N, S) and with a Philips ICP emission spectrometer. IR spectra were recorded on a Nicolet 5PC FT spectrometer; ^1H and ^{13}C NMR spectra were obtained with Bruker AC100 and CXP200 instruments; mass spectra were recorded on a Finnigan 1020 mass spectrometer at 70 eV ionizing voltage.

2.1. Preparations

2.1.1. Dithiourethane xerogel (XGditu)

$(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ was allowed to react with PhNCS (1:2 molar ratio) in absolute ethanol. After refluxing for 15 min, the solvent was removed under reduced pressure, affording quantitatively the siloxanized thiourethane $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{N}(\text{C}(\text{S})\text{NHPh}(\text{CH}_2)_2\text{NHC}(\text{S})\text{NHPh})$ as a colourless oily product; IR: 1596m, 1538vs, 1497s, 1248s, 1193s, 1081vs, 761m, 706m cm^{-1} . MS: m/z 372(65), 358(30), 340(20), 135(100), 93(70), 77(80)%. It was mixed with $\text{Si}(\text{OEt})_4$, EtOH, and H_2O (1:8:8:4 volume ratio), at room temperature, under vigorous stirring. A few drops of acetic acid were added and stirring was stopped after 2 h. Homogeneous gelification occurred in 4–5 days, affording an opalescent colourless solid, which was crushed, washed and dried *in vacuo*. Anal. Found: C, 15.0; H, 1.2; N, 1.6; S, 1.4%. IR: 1599w, 1547w, 1077vs, 956mw, 795mw, 694w cm^{-1} ; surface area (BET) 120 $\text{m}^2 \text{g}^{-1}$.

2.1.2. Anchoring palladium

XGditu was suspended by stirring in a water solution containing $\text{K}_2[\text{PdCl}_4]$ in a large molar excess with respect to the thiourethane groups. In 30 min at room temperature, the gel turned deep brown. It was fil-

tered, washed with water, ethanol and ether, and dried *in vacuo*. By metal analysis, carried out after acidic digestion, the S/Pd atomic ratio was found to be 1.6:1.

2.1.3. Anchoring palladium and copper

XGditu was suspended by stirring in an acetonitrile solution containing palladium(II) acetate in large excess. After 2 h the brown gel was filtered and washed with ethanol and diethyl ether. Further, it was suspended in a water solution containing an excess of copper(II) acetate, affording a deep brown powder, which was washed as previously and dried *in vacuo*. The Pd/Cu atomic ratio was found to be 5:1.

2.1.4. Anchoring $[Ru_3(CO)_{12}]$

The functionalized silica xerogel, XGditu, was added to a solution of $[Ru_3(CO)_{12}]$ in isopropanol, under a N_2 atmosphere. The stirred solution was refluxed for 30 min. The brownish yellow suspended solid was filtered, washed and dried *in vacuo*. FT-IR (KBr): 2084, 2058, 2027, 1998, 1976 cm^{-1} .

2.1.5. $PhNHC(S)N(Et)(CH_2)_2NHC(S)NPh$ (2)

The dithiourea was prepared by reaction of $EtNH(CH_2)_2NH_2$ with $PhNCS$ (1:2 molar ratio) in absolute ethanol. After heating for 15 min under reflux, colourless crystals of **1** were obtained by slow evaporation of the solvent in a few hours (80% yield); these were analyzed by FTIR, 1H , ^{13}C NMR and mass spectroscopy. 1H NMR ($CDCl_3$, TMS): δ 1.33 (t, 3H, CH_3 , $J = 7$ Hz); 3.87 (q, 2H, CH_2 , $J = 7$ Hz); 3.96 (m, 4H, CH_2); 6.71 (br s, 1H, NH); 7.1–7.5 (m, 5H, Ph); 7.86 (br s, 1H, HNPh); 8.37 (br s, 1H, HNPh) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 12.5 (CH_3); 41.4 (CH_2); 46.0 (CH_2); 47.9 (CH_2); 123.7, 124.7, 126.3, 127.8, 128.7, 138.5, 140.6 (Ph); 180.2 (CS); 180.6 (CS) ppm. MS: m/z 358(75), 324(10), 224(20), 153(90), 135(100), 93(70), 77(80)%. IR: 1596ms, 1557s, 1533s, 1496vs, 1359vs, 1315ms, 1249ms, 765ms cm^{-1} .

2.1.6. Reaction of **2** with $K_2[PdCl_4]$

The double thiourea **2** (ditu) was allowed to react with $K_2[PdCl_4]$ (1:1 molar ratio) in a water/ethanol mixture at room temperature. An orange product quickly precipitated, which was filtered, washed and dried *in vacuo* (70% yield). Anal. Found: C, 33.2; H, 3.8; N, 10.1; S, 9.3. $C_{18}H_{22}Cl_2N_4PdS_2$, $[Pd(ditu)Cl_2]$ calcd.: C, 33.7; H, 3.5; N, 8.7; S, 10.0%. IR: 1555s, 1495vs, 1240ms, 759ms cm^{-1} .

2.1.7. $\{[(\mu-H)Ru_3(CO)_9]\}_2\{SC(NPh)N(Et)(CH_2)_2NH(PhN)CS\}$ (**4**)

The dithiourea **2** (0.2 g) was added to a solution of $[Ru_3(CO)_{12}]$ (0.3 g) in hexane (75 cm^3) under dinitro-

TABLE 1. Summary of crystallographic data for complex **4**

Formula	$C_{36}H_{22}N_4O_{18}Ru_6S_2 \cdot CH_2Cl_2$
Mol. wt.	1554.06
Crystal system	Monoclinic
Space group	$P2_1/n$
Radiation (λ , Å)	Niobium-filtered Mo $K\alpha$ (0.71073)
a (Å)	19.360(9)
b (Å)	16.940(6)
c (Å)	16.132(6)
β (°)	103.94(2)
V (Å ³)	5135(4)
Z	4
D_{calcd} (g cm^{-3})	2.010
$F(000)$	2992
Crystal size (mm ³)	0.18 × 0.22 × 0.28
μ (Mo $K\alpha$) (cm ⁻¹)	19.41
Diffractometer	Siemens AED
2θ range (°)	6–50
Reflections measured	$\pm h, k, l$
Unique total data	9369
Unique observed data [$I > 2\sigma(I)$]	3973
R	0.0484
R_w	0.0534

gen. The solution was stirred under reflux for 90 min, then filtered and dried *in vacuo*. TLC on silica gel (eluent, hexane/acetone 2:1) yielded 0.15 g (43% yield) of **4** (red band), unreacted $[Ru_3(CO)_{12}]$ and a minor amount of a green unidentified compound. Anal. Found: C, 28.8; H, 1.4; N, 3.9; S, 4.2. $C_{36}H_{22}N_4O_{18}Ru_6S_2$ calcd.: C, 29.4; H, 1.5; N, 3.8; S, 4.4%. 1H NMR (100 MHz, 295 K, $CDCl_3$): δ -12.91 (s, 1H, μ -H); δ -13.29 (s, 1H, μ -H); 0.97 (t, 3H, CH_3 , $J = 7$ Hz); 2.86 (q 2H, CH_2 , $J = 7$ Hz); 3.15 (m, 4H, CH_2); 4.26 (t, 1H, NH, $J = 5$ Hz); 6.7–7.5 (m, 10H, Ph) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 13.7 (CH_3); 43.7 (CH_2); 50.8 (CH_2); 52.5 (CH_2); 122.2 (2C); 122.6 (2C); 126.0, 127.3, 129.8 (2C); 131.1 (2C); 148.4, 152.7 (Ph); 179.8 (CS); 181.1 (CS); 196.6 (v br, 16C, CO); 202.0 (2 C, CO) ppm. FT-IR (KBr): ν (CO) 2083s, 2059s, 2050s, 2027vs, 1999s, 1977vs, 1951sh cm^{-1} .

2.2. X-Ray data collection, structure determination and refinement for $\{[(\mu-H)Ru_3(CO)_9]\}_2\{SC(NPh)N(Et)(CH_2)_2NH(PhN)CS\} \cdot CH_2Cl_2$ (**4** · CH_2Cl_2)

Suitable deep orange crystals for the X-ray analysis were obtained by recrystallization in CH_2Cl_2 . The crystallographic data are summarized in Table 1. Data were collected at room temperature (22°C) on a Siemens AED diffractometer, using the niobium-filtered Mo $K\alpha$ radiation and the θ – 2θ scan type. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.65)^\circ$ to $(\theta + 0.65 + 0.346 \tan \theta)^\circ$. One standard reflection was

TABLE 2. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex 4

	<i>x</i>	<i>y</i>	<i>z</i>
Ru(1)	2922(1)	−402(1)	2321(1)
Ru(2)	2113(1)	659(1)	1180(1)
Ru(3)	1450(1)	−573(1)	1905(1)
Ru(4)	−919(1)	1952(1)	1766(1)
Ru(5)	−1671(1)	897(1)	2592(1)
Ru(6)	−1587(1)	2490(1)	2999(1)
S(1)	1541(2)	782(2)	2343(2)
S(2)	−408(2)	1087(2)	2915(2)
O(1)	3337(9)	−1787(9)	3531(11)
O(2)	4435(7)	120(7)	2362(9)
O(3)	2970(8)	−1447(7)	849(9)
O(4)	1073(8)	1777(9)	5(10)
O(5)	3237(7)	1865(7)	1856(8)
O(6)	2790(8)	183(9)	−252(7)
O(7)	1636(8)	−1258(9)	3675(8)
O(8)	1516(9)	−2174(8)	1103(9)
O(9)	−174(8)	−524(9)	1401(11)
O(10)	−2464(7)	2589(11)	4331(10)
O(11)	−1243(9)	4248(8)	2886(11)
O(12)	−2919(7)	2760(9)	1657(8)
O(13)	−1928(7)	2960(7)	454(7)
O(14)	201(7)	3215(8)	2305(8)
O(15)	−262(8)	1132(11)	462(8)
O(16)	−1651(8)	−829(8)	2050(12)
O(17)	−1805(8)	655(9)	4422(8)
O(18)	−3255(7)	952(9)	1884(12)
N(1)	2811(5)	379(6)	3318(6)
N(2)	2134(6)	1278(7)	3896(7)
N(3)	−594(5)	2250(5)	3936(6)
N(4)	378(5)	1418(6)	4470(6)
C(1)	3167(10)	−1272(10)	3095(12)
C(2)	3863(10)	−40(9)	2378(10)
C(3)	2920(9)	−1054(9)	1390(12)
C(4)	1433(9)	1369(10)	447(10)
C(5)	2824(8)	1407(10)	1592(10)
C(6)	2548(10)	330(10)	273(10)
C(7)	1563(10)	−1020(11)	2995(12)
C(8)	1494(10)	−1545(12)	1387(11)
C(9)	417(9)	−524(10)	1581(11)
C(10)	−2121(8)	2544(10)	3865(11)
C(11)	−1356(9)	3604(10)	2969(11)
C(12)	−2420(8)	2628(9)	2144(10)
C(13)	−1542(8)	2579(10)	962(9)
C(14)	−228(8)	2754(10)	2103(10)
C(15)	−512(10)	1396(11)	935(10)
C(16)	−1623(9)	−171(9)	2243(10)
C(17)	−1768(9)	740(10)	3728(13)
C(18)	−2675(9)	937(11)	2160(11)
C(19)	2234(7)	803(8)	3282(9)
C(20)	−186(6)	1665(7)	3878(7)
C(21)	1472(6)	1635(7)	4001(9)
C(22)	990(6)	1045(7)	4244(9)
C(23)	461(7)	1539(8)	5396(7)
C(24)	99(14)	951(15)	5786(11)
C(25)	3345(6)	455(7)	4093(8)
C(26)	3919(6)	963(7)	4133(8)
C(27)	4457(6)	1016(7)	4881(8)
C(28)	4421(6)	561(7)	5590(8)
C(29)	3847(6)	52(7)	5550(8)
C(30)	3309(6)	−1(7)	4801(8)

TABLE 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>
C(31)	−342(6)	2880(7)	4540(7)
C(32)	253(7)	3320(8)	4468(8)
C(33)	485(8)	3936(9)	5047(9)
C(34)	123(8)	4107(10)	5639(10)
C(35)	−456(9)	3692(10)	5713(11)
C(36)	−673(8)	3073(9)	5161(9)
C(37)	845(19)	2595(21)	7627(22)
Cl(1)	−164(7)	2433(8)	7678(7)
Cl(2)	1028(9)	3290(9)	8486(11)

monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analyzed following Lehmann and Larsen [12]. Intensities were corrected for Lorentz and polarization effects; no correction for absorption was necessary. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by blocked-matrix least-squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of the carbon atoms of the two phenyl groups and the atoms of the dichloromethane found as solvation molecule. All hydrogen atoms (except the hydride hydrogens clearly localized in the final ΔF map and refined isotropically) were placed at their geometrically calculated positions and refined “riding” on the corresponding atoms. In the final cycles of refinement, a weighting scheme, $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence, the g value was 0.0323. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from [13]. All calculations were carried out on the Gould powernode 6040 of the Centro di Studio per la Strutturistica Diffattometrica del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [14]. The final atomic coordinates for the non-hydrogen atoms are given in Table 2. Additional data (atomic coordinates of the hydrogen atoms, thermal parameters) are available from the authors on request.

3. Results and discussion

By reaction of PhNCS with $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ (2:1 molar ratio), the siloxanized dithiourea $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{N}[\text{C}(\text{S})\text{NHPh}(\text{CH}_2)_2\text{NHC}(\text{S})\text{NHPh}]$ can be obtained. It produces a new functionalized xerogel (XGditu) by hydrolysis and polycondensation with $\text{Si}(\text{EtO})_4$.

Preliminary results show that this material is able to bind palladium and copper complexes affording

TABLE 3. Selected bond distances (Å) and angles (deg) for complex 4

Ru(1)–Ru(2)	2.772(2)	Ru(5)–Ru(6)	2.773(2)
Ru(1)–Ru(3)	2.781(2)	Ru(4)–Ru(6)	2.774(2)
Ru(2)–Ru(3)	2.844(2)	Ru(4)–Ru(5)	2.832(2)
Ru(2)–S(1)	2.406(4)	Ru(4)–S(2)	2.383(3)
Ru(3)–S(1)	2.396(4)	Ru(5)–S(2)	2.396(3)
Ru(1)–N(1)	2.132(10)	Ru(6)–N(3)	2.179(9)
Ru(1)–C(1)	1.916(18)	Ru(4)–C(13)	1.875(14)
Ru(1)–C(2)	1.903(19)	Ru(4)–C(14)	1.891(16)
Ru(1)–C(3)	1.864(18)	Ru(4)–C(15)	1.955(19)
Ru(2)–C(4)	1.957(15)	Ru(5)–C(16)	1.902(15)
Ru(2)–C(5)	1.872(15)	Ru(5)–C(17)	1.906(22)
Ru(2)–C(6)	1.938(19)	Ru(5)–C(18)	1.901(16)
Ru(3)–C(7)	1.879(19)	Ru(6)–C(10)	1.930(19)
Ru(3)–C(8)	1.857(19)	Ru(6)–C(11)	1.942(18)
Ru(3)–C(9)	1.943(18)	Ru(6)–C(12)	1.867(14)
C(19)–S(1)	1.766(13)	C(20)–S(2)	1.799(11)
C(19)–N(1)	1.318(18)	C(20)–N(3)	1.284(15)
C(19)–N(2)	1.326(19)	C(20)–N(4)	1.332(13)
N(2)–C(21)	1.463(18)	N(3)–C(31)	1.449(15)
N(1)–C(25)	1.422(14)	N(4)–C(23)	1.477(15)
C(21)–C(22)	1.483(19)	N(4)–C(22)	1.466(17)
C(23)–C(24)	1.446(30)		
Ru(2)–Ru(1)–Ru(3)	61.6(1)	Ru(4)–Ru(6)–Ru(5)	61.4(1)
Ru(1)–Ru(2)–Ru(3)	59.3(1)	Ru(4)–Ru(5)–Ru(6)	59.3(1)
Ru(1)–Ru(3)–Ru(2)	59.0(1)	Ru(5)–Ru(4)–Ru(6)	59.3(1)
Ru(2)–S(1)–Ru(3)	72.6(1)	Ru(4)–S(2)–Ru(5)	72.7(1)
Ru(2)–S(1)–C(19)	105.8(5)	Ru(4)–S(2)–C(20)	107.7(4)
Ru(3)–S(1)–C(19)	105.0(5)	Ru(5)–S(2)–C(20)	106.3(4)
Ru(1)–N(1)–C(19)	122.9(9)	Ru(6)–N(3)–C(20)	123.3(8)
Ru(1)–N(1)–C(25)	122.4(8)	Ru(6)–N(3)–C(31)	115.2(7)
C(19)–N(1)–C(25)	114.7(11)	C(20)–N(3)–C(31)	120.3(10)
S(1)–C(19)–N(1)	119.2(10)	S(2)–C(20)–N(3)	117.3(8)
S(1)–C(19)–N(2)	115.7(11)	S(2)–C(20)–N(4)	115.6(8)
N(1)–C(19)–N(2)	125.0(13)	N(3)–C(20)–N(4)	127.0(10)
C(19)–N(2)–C(21)	128.8(12)	C(20)–N(4)–C(22)	121.9(10)
N(2)–C(21)–C(22)	112.1(11)	C(20)–N(4)–C(23)	123.5(10)
N(4)–C(22)–C(21)	111.9(10)	C(22)–N(4)–C(23)	114.4(10)

bimetallic anchored systems of potential interest in catalysis. In the case of the anchoring reaction of palladium alone, the S/Pd atomic ratio (1.6:1) suggests that different complexes are present on the xerogel surface in spite of the unique species, [Pd(ditu)Cl₂], obtained with the model dithiourea 2.

Moreover, [Ru₃(CO)₁₂] reacts with XGditu to give a tethered metal carbonyl cluster, which shows almost the same CO stretching pattern of the model compound obtained from 2. Indeed, the reaction of [Ru₃(CO)₁₂] with the double thiourea 2 is quite clean and produces a usable amount of {(μ-H)Ru₃(CO)₉}₂{SC(NPh)N(Et)(CH₂)₂NH(PhN)CS} (4) in moderate yield. Its ¹H and ¹³C NMR spectra are consistent with the molecular structure found in the solid state and compare well with those obtained for complex 1 containing a mono-thiourea ligand [9].

Unlike the reaction of 2 with copper(II) chloride [11], the two thiourea groups can react independently with the Ru₃ triangles, affording the complex 4.

A view of the structure of 4, fully elucidated by an X-ray study, is depicted in Fig. 1 together with the atomic labelling scheme; selected bond distances and angles are given in Table 3.

In the structure of 4, the two thiourea moieties of 2 bind through the sulphur and the deprotonated N(Ph) atoms to two different hydrido carbonyl (μ-H)Ru₃(CO)₉ groups, in which each Ru atom of the isosceles metal triangles is bound to three terminal carbonyls. Each thiourea moiety interacts with all three Ru atoms, being bonded through the N(Ph) atom to one Ru atom and through the sulphur atom (acting as a symmetrical bridge) to the other two Ru atoms. The two S-bridges form dihedral angles of 101.2(1)° and

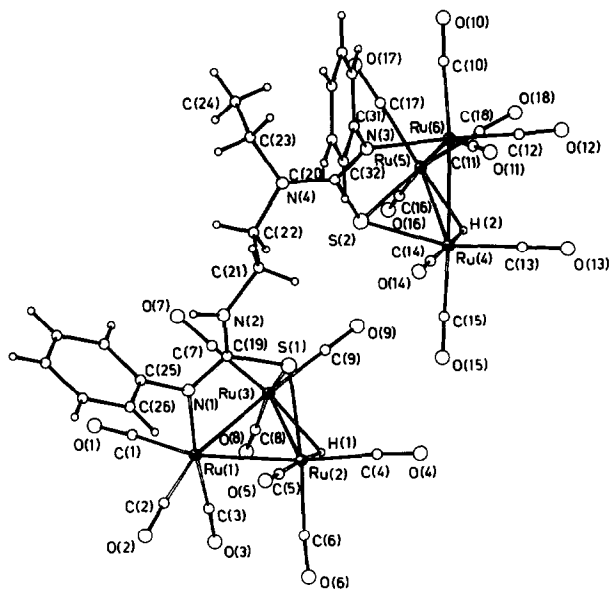


Fig. 1. View of the molecular structure of $((\mu\text{-H})\text{Ru}_3(\text{CO})_9)_2[\text{SC}(\text{NPh})\text{N}(\text{Et})(\text{CH}_2)_2\text{NH}(\text{PhN})\text{CS}]$ (**4**) together with the atomic numbering scheme.

$100.3(1)^\circ$, respectively, with the cluster triangle. A hydride bridge spans the longest edge of the cluster, which also contains a sulphur bridge.

For the thiourea moieties, the S–C bond distances (1.766(13) and 1.799(11) Å) are much longer than those found in **2** (1.668(7) and 1.694(7) Å) [11] and are consistent with a remarkable decrease of double bond character with respect to the free dithiourea. On the contrary, the values of the N–C bonds, in the range 1.284(15)–1.332(13) Å, indicate an increased multiple bond character, especially for those N–C bonds involving the deprotonated N atoms, as compared to free dithiourea, in the range 1.334(9)–1.360(9) Å. The two thiourea moieties are almost coplanar (the dihedral angle is $13.7(3)^\circ$), as in **2** where this situation is determined by an intramolecular N–H–S hydrogen bond.

The bonding of the two thiourea moieties to the two $(\mu\text{-H})\text{Ru}_3(\text{CO})_9$ fragments in **4** is strictly comparable to that found for the *N*-phenyl-*N*'-propylthiourea to the same fragment in the complex $[(\mu\text{-H})\text{Ru}_3\{\mu_3\text{-SC}(\text{NHP})\text{NPh}(\text{CO})_9\}]$ (**1**) [9]. In **1**, the Ru–Ru distances are 2.782(1), 2.779(1) and 2.844(1) Å, Ru–N is 2.160(6) Å, and Ru–S are 2.404(2) and 2.412(2) Å. The symmetric S-bridge makes a dihedral angle of $100.8(1)^\circ$ with the metal cluster. In the thiourea moiety, the S–C

and the two N–C bond distances are 1.786(6) Å, 1.285(9) and 1.351(10) Å respectively, the shorter N–C bond involving the deprotonated N atom.

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