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LETTER

Tris(*N*,*N*′-diphenylthioureato)-chromium(III)

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The reaction of the hexacarbonyls $M(CO)_6$ ($M = Cr$, Mo, W) with thioureas $SC(NR^1R^2)_2$ has been extensively studied by various groups: the photochemical [1–5] and thermal [5] pathways are reported to yield the monosubstituted derivatives $M(CO)_5[SC(NR^1R^2)_2]$. In contrast, we recently observed that the thermal reaction of $Cr(CO)_6$ with *N*,*N*′-diphenylthiourea leads, with complete decarbonylation of the chromium, to the new complex $Cr[SC(NPh)(NHPh)]_3$ (**1**), the synthesis and structure of which is reported here.

Experimental

Preparation of 1

A solution of 110 mg (0.5 mmol) $Cr(CO)_6$ and 365 mg (1.6 mmol) $SC(NHPh)_2$ in 30 ml THF was heated in a thick-walled high-pressure Schlenk tube to 140 °C for 15 h. After evaporation of the solvent the residue was dissolved in 5 ml CH_2Cl_2 and separated by preparative TLC (Al_2O_3, CH_2Cl_2/cyclohexane 3:7). The product was extracted from the blue band with CH_2Cl_2 (yield 133 mg, 36%). Single crystals of **1** suitable for X-ray crystallography were obtained from a CH_2Cl_2–cyclohexane mixture by slow evaporation at room temperature. *Anal.* Calc. for $C_{39}H_{33}N_6CrS_3$: C, 63.85; H, 4.50; N, 11.46. Found: C, 62.73; H, 4.75; N, 11.80%. IR spectrum (KBr pellet) of **1**: ν(NH) 3351; ν(CN) 1593 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 10.56 (s, br, 3H, 3 N*H*), 7.38 (m, 30H, 6 C_6H_5) ppm. In an alternative synthetic route 210 mg (0.5 mmol) $Cr(CO)_5[SC(NHPh)_2]$ and 228 mg (1 mmol) $SC(NHPh)_2$ in 30 ml THF were heated for 24 h under reflux. The dark green solution, worked up as described above, gave 92 mg (25%) of **1**.

Preparation of 2

A suspension of 174 mg (0.5 mmol) $W(CO)_6$ and 94 mg (0.5 mmol) $SC(NH^tBu)_2$ in 30 ml pentane was irradiated for 8 h with vigorous stirring. After decantation of the solvent, the residue was dissolved in 5 ml THF and separated by preparative TLC (Al_2O_3, CH_2Cl_2). The products $W(CO)_5[SC(NH^tBu)_2]$ (yield 56 mg, 22%) and $W(CO)_4[SC(NH^tBu)_2]_2$ (**2**) (yield 49 mg, 29%) were extracted with THF from the first and the second band, respectively. *Anal.* Calc. for $C_{22}H_{40}N_4O_4S_2W$: C, 39.29; H, 6.00; N, 8.33. Found: C, 39.14; H, 6.07; N, 8.09%. IR spectrum (CH_2Cl_2) of **2**: ν(CO) 2001w, 1931vw, 1864vs, 1822s; ν(NH) (KBr) 3437m, 3267m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 5.72 (s, 4H, N*H*), 1.44 (s, 36H, CH_3) ppm.

X-ray data collection, structure solution and refinement of 1

Intensity data were collected on a Stoe-Siemens AED 2 diffractometer. All calculations were performed using the NRCVAX program package [6]. Direct methods were used to find the heavy atom positions. The positions of the remaining non-hydrogen atoms were taken from difference maps. The hydrogen atoms were taken from the last difference map and refined isotropically. All non-hydrogen atoms were refined anisotropically, using weighted full matrix least-squares. Crystal data, details of data collection and structure refinement are given in Table 1, see also 'Supplementary material'.

TABLE 1. Crystal data, details of data collection and structure refinement for *fac*-$Cr[SC(NPh)(NHPh)]_3$ (**1**)

Formula	$CrC_{39}H_{33}N_6S_3$
Molecular weight	733.9
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.085(1)
b (Å)	15.634(1)
c (Å)	20.266(1)
β (°)	106.34(1)
V (Å^3)	3666.3
Z	4
D_{calc} (g/cm^3)	1.330
μ(Mo Kα) (cm^{-1})	4.3
Scan method	ω/θ
Maximum 2θ (°)	50
No. reflections measured	6440
No. unique data with $(I) > 2.5\sigma(I)$	3882
No. parameters refined	574
R_F[a]	0.031
R_w[b]	0.038

[a] $R_F = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]^{1/2}$, $w^{-1} = \sigma^2(F_o) + 0.0002(F_o^2)$.

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Results and discussion

The thermal decomposition of $Cr(CO)_6$ in the presence of an excess of diphenylthiourea gives in a first step the well-known compound $Cr(CO)_5[SC(NHPh)_2]$ [1], which decarbonylates on further heating to yield *fac*-$Cr[SC(NPh)(NHPh)]_3$ (**1**).

$$Cr(CO)_6 \xrightarrow[-CO]{+SC(NHPh)_2} Cr(CO)_5[SC(NHPh)_2] \xrightarrow[-5CO,\ -3/2H_2]{+2SC(NHPh)_2}$$

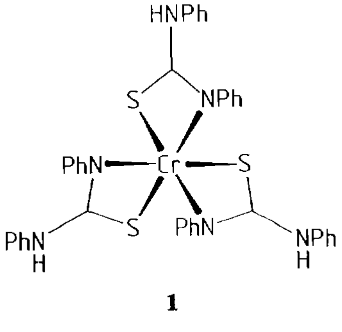
$$Cr[SC(NPh)(NHPh)]_3$$

1

In **1** the three *N,N'*-diphenylthioureato ligands are coordinated in a bidentate fashion through the sulfur and one of the nitrogen atoms. The bidentate ligands are arranged facially with respect to the three sulfur or the three nitrogen atoms. The coordination geometry of the complex is a distorted trigonal antiprismatic. The ligands are arranged in a propeller-like manner; the mean angle between the plane of the sulfur atoms and the planes defined by the chromium atom and the coordinated atoms of one ligand being 59° (Fig. 1).

Due to the formation of four-membered Cr–S–C–N cycles, the angles S–Cr–N have a mean value of 69.1(1)°. The formation of the four-membered rings (mean distances: Cr–S 2.4246(5), Cr–N 2.030(1), S–C 1.733(2), C–N 1.310(2) Å) results in a large deviation of the S–C–N angles (mean value 112.9(1)°). The C–N distances of the non-coordinated nitrogen atoms (mean value 1.350(2) Å) are significantly longer than those of the coordinated ones. With exception of the phenyl group attached to N(2), all other phenyl groups are arranged nearly perpendicular to the thioureato ligands to which they are connected.

In contrast to the thiourea complexes, only a few complexes with thioureato ligands have been reported so far. In $Rh(Cl)(\eta^5\text{-}C_5Me_5)[NPhCSN(p\text{-}C_6H_4\text{-}Me)CHN(p\text{-}C_6H_4\text{-}Me)]$ a thioureato moiety is formed by insertion of an isothiocyanate into a rhodium–nitrogen bond [8]. The cyclic thiourea 4,6-dimethylpyrimidine reacts with $Co(ClO_4)_2$ to give the cobalt complex *fac*-$Co[SCNC(Me)CHC(Me)N]_3$ [9], which has the same coordination geometry as **1**.



1

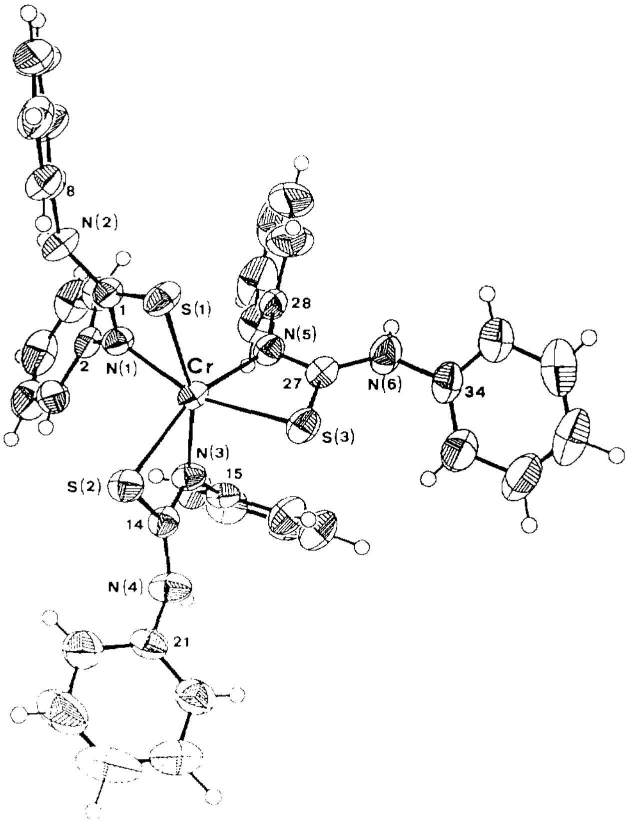


Fig. 1. ORTEP plot [7] (50% probability) of *fac*-$Cr[SC(NPh)(NHPh)]_3$ (**1**). Important bond lengths (Å) and angles (°): Cr–S(1) 2.4165(8), Cr–S(2) 2.4256(9), Cr–S(3) 2.4318(8), Cr–N(1) 2.0323(21), Cr–N(3) 2.0318(22), Cr–N(5) 2.0268(23), S(1)–C(1) 1.733(3), S(2)–C(14) 1.737(3), S(3)–C(27) 1.728(3), N(1)–C(1) 1.312(3), N(1)–C(2) 1.426(3), N(2)–C(1) 1.355(3), N(2)–C(8) 1.421(4), N(3)–C(14) 1.309(4), N(4)–C(14) 1.347(4), N(5)–C(27) 1.308(3), N(6)–C(27) 1.348(4), S(1)–Cr–S(2) 100.03(3), S(1)–Cr–S(3) 99.48(3), S(1)–Cr–N(1) 69.16(6), S(2)–Cr–S(3) 96.15(3), S(2)–Cr–N(3) 69.16(7), S(3)–Cr–N(5) 68.84(6), Cr–S(1)–C(1) 76.67(9), Cr–S(2)–C(14) 75.24(10), Cr–S(3)–C(27) 76.31(10), Cr–N(1)–C(1) 101.47(17), Cr–N(3)–C(14) 99.86(17), Cr–N(5)–C(27) 101.88(18), S(1)–C(1)–N(1) 112.69(19), S(2)–C(14)–N(3) 112.94(20), S(3)–C(27)–N(5) 112.97(21).

The analogous reaction of $W(CO)_6$ with $SC(NHPh)_2$ does not lead to the tungsten analogue of **1** but gives the known thiourea complex $W(CO)_5[SC(NHPh)_2]$ [1]. With the tert-butyl derivative $SC(NH^tBu)_2$ the reaction with $W(CO)_6$ yields, under photolytic conditions, the known mono-substituted thiourea complex $W(CO)_5[SC(NH^tBu)_2]$ [2], along with a new compound which turned out to be the new disubstituted thiourea complex *cis*-$W(CO)_4[SC(NH^tBu)_2]_2$ (**2**). The *cis*-arrangement of the two sulfur atoms bonded to the tungsten atom can be concluded from the ν(CO) pattern in the IR spectrum [5].

Supplementary material

Further data (atomic fractional coordinates, etc.) can be obtained on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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