Addition of Cr(CO)$_5$ to the M(η^2-S$_2$) moiety of Cp$_2$M(S$_2$)H (Cp′ = ^{t}BuC$_5$H$_4$: M = Ta; Cp^x = C$_5$Me$_4$Et: M = Nb) and crystal structures of Cp′$_2$TaS$_2$H · [Cr(CO)$_5$]$_n$ (n = 1, 2)

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Abstract

Reaction of Cp′$_2$TaS$_2$H (Cp′ = ^{t}BuC$_5$H$_4$) or Cp$^x_2$NbS$_2$H (Cp^x = C$_5$Me$_4$Et) with an excess of Cr(CO)$_5$THF gives the adducts Cp′$_2$TaS$_2$H · Cr(CO)$_5$ **1**, Cp′$_2$TaS$_2$H · 2Cr(CO)$_5$ **2**, and Cp$^x_2$NbS$_2$H · Cr(CO)$_5$ **3** respectively. **1** and **2** are separated by fractional crystallisation. The crystal structures show the Cr(CO)$_5$ fragment in **1** to be coordinated to the 'outer' sulfur, and in **2** both Cr(CO)$_5$ fragments are coordinated to each sulfur of the S$_2$ ligand in a trans fashion. In all cases approximate sp^3 hybridisation of the S atoms is observed. The new compounds are thermally labile and give CO-free, trinuclear compounds of the type Cp$_4$M$_2$S$_4$Cr upon heating their solutions.

Keywords: Chromium; Molybdenum; Disulfide ligand; X-ray structure; Niobium

1. Introduction

Disulfide ligands show an impressive variety of coordination possibilities [1] in polynuclear transition metal complexes in that they predominantly bridge homonuclear building blocks. A particular case of mononuclear complexes are metallocene disulfides in which only the η^2 coordination mode is possible [2]. When early transition metals are involved in these types of compounds the presence of additional 'functional' groups, e.g. CO in (C$_5$Me$_5$)$_2$Zr(S$_2$)CO [3] or H in Cp$^{(')}_2$M(S$_2$)H (M = Nb, Ta) [4–6] is required which may enhance the reactivity. A typical reaction of the η^2-S$_2{}^{2-}$ ligand is the oxidative insertion of other metal fragments to produce polynuclear sulfide clusters [7]. However, the potential of forming polymetallic compounds by simple addition of unsaturated complex fragments seems to be unexplored. This refers in particular to the coordination of M′(CO)$_5$ fragments (M′ = Cr, Mo, W) which has

already been realised for monosulfide ligands regardless of their coordination mode [8]. In this paper we report on the synthesis of new heterobimetallic compounds in which both metal centers are linked by a disulfide bridge by the addition of Cr(CO)$_5$ to the M(η^2-S$_2$) moiety of Cp$_2$M(S$_2$)H (Cp′ = ^{t}BuC$_5$H$_4$: M = Ta; Cp^x = C$_5$Me$_4$Et: M = Nb). First results on their reactivity are also given.

2. Results and discussion

2.1. Synthesis and characterisation of Cp′$_2$TaS$_2$H · Cr(CO)$_5$ 1 and Cp′$_2$TaS$_2$H · 2Cr(CO)$_5$ 2

Cp′$_2$TaS$_2$H reacts with a slight excess of Cr(CO)$_5$-THF to give a mixture of two compounds (Eq. (1)). This is prepurified by column chromatography, whereas isolation of the individual compounds Cp′$_2$TaS$_2$H · Cr(CO)$_5$ **1** and Cp′$_2$TaS$_2$H · 2Cr(CO)$_5$ **2** occurs by fractional crystallisation at −20 °C. The overall yield for both compounds is 84%, the ratio **1:2** is ca. 6:1. Toluene

solutions of pure **2** slowly form **1**, e.g. after 3 h at room temperature the ratio **1:2** is ca. 1:1.

$$Cp'_2Ta \underset{H}{\overset{S}{<}} \big\backslash_{S} \quad \xrightarrow{Cr(CO)_5THF} \quad Cp'_2Ta \underset{H}{\overset{S}{<}} \big\backslash_{S}^{\nearrow Cr(CO)_5}$$

1

$$+ \quad Cp'_2Ta \underset{H}{\overset{S}{<}} \big\backslash_{S}^{\nwarrow Cr(CO)_5}_{\searrow Cr(CO)_5} \qquad (1)$$

2
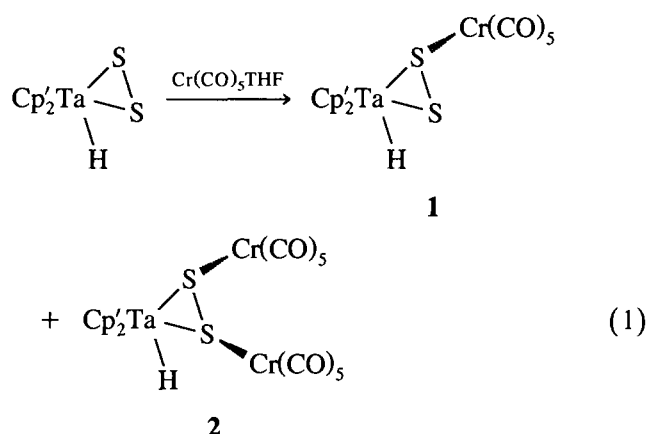
The IR spectra of **1** and **2** exhibit the typical absorption pattern for the coordinated $Cr(CO)_5$ moiety. In the case of **2** the peak at 2060 cm^{-1} splits into two peaks of equal intensity, indicating the presence of two $Cr(CO)_5$ groups in slightly different surroundings. The ^1H NMR spectra of **1** and **2** show only one peak for the ^tBu protons what suggests equivalent Cp' ligands. However, as shown by the X-ray crystal diffraction studies (see below), the orientation of the $Cr(CO)_5$ fragment in **1** should give rise to two different resonances. The fact that the signals remain invariant down to $-60\ °C$ may be explained by a pseudo inversion at the sp^3 sulfur. It should be noted that the attack of CH_3^+ at the S_2^{2-} ligand of Cp'_2TaS_2H also gives rise to the formation of a chiral sulfur site which in this case could be unequivocally inferred from the ^1H NMR data [4].

The X-ray structure analysis of **1** shows that its structure may be derived from that of its precursor complex Cp'_2TaS_2H [5] by coordination of the $Cr(CO)_5$ fragment at the lateral sulfur S(1) (Tables 1 and 2; Fig. 1). The angle Ta–S(1)–Cr (136.0(1)°) seems to be affected by repulsive interactions between the CO groups and the Cp' hydrogens. The crystal structure of **2** exhibits two $Cr(CO)_5$ groups coordinated in a trans con-

Table 1
Selected bond lengths (Å) and angles (deg) for $Cp'_2TaS_2H \cdot Cr(CO)_5$ (**1**)

Ta(1)–S(1)	2.558(4)
Ta(1)–S(2)	2.447(4)
S(1)–S(2)	2.055(5)
S(1)–Cr(1)	2.466(4)
S(1)–Ta(1)–S(2)	48.4(1)
Ta(1)–S(1)–S(2)	63.0(1)
Ta(1)–S(1)–Cr(1)	136.0(1)
S(2)–S(1)–Cr(1)	115.6(2)
Ta(1)–S(2)–S(1)	68.6(1)
S(1)–Cr(1)–C(21)	88.9(4)
S(1)–Cr(1)–C(22)	96.1(4)
S(1)–Cr(1)–C(23)	176.6(4)

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $Cp'_2TaS_2H \cdot Cr(CO)_5$ (**1**)

Atom	x	y	z	U_{eq}[a]
Ta(1)	3603(1)	3608(1)	3934(1)	34(1)
Cr(1)	4088(1)	456(2)	2206(1)	43(1)
S(1)	3581(1)	1821(3)	2828(2)	43(1)
S(2)	3553(1)	3392(3)	2130(2)	47(1)
O(21)	3677(3)	564(10)	166(7)	91(5)
O(22)	4535(3)	−65(8)	4179(7)	79(4)
O(23)	4659(3)	−1289(8)	1399(7)	78(4)
O(24)	4688(3)	2321(9)	1631(7)	82(4)
O(25)	3473(3)	−1410(9)	2578(8)	98(5)
C(1)	4078(4)	4499(9)	5104(8)	42(4)
C(2)	4222(3)	4804(10)	4169(9)	40(4)
C(3)	4334(4)	3803(13)	3694(10)	67(6)
C(4)	4272(5)	2881(3)	4377(15)	98(8)
C(5)	4110(5)	3313(12)	5226(11)	73(6)
C(6)	4330(4)	6003(13)	3851(10)	61(6)
C(7)	4260(5)	6154(14)	2731(10)	117(9)
C(8)	4080(5)	6919(11)	4382(11)	90(7)
C(9)	4779(4)	6192(13)	4140(11)	108(8)
C(11)	3124(4)	4375(12)	5075(10)	61(6)
C(12)	2911(4)	4414(11)	4138(9)	44(5)
C(13)	2874(4)	3246(11)	3860(11)	62(6)
C(14)	3054(5)	2546(12)	4611(13)	79(7)
C(15)	3202(5)	3275(14)	5350(11)	79(7)
C(16)	2685(4)	5421(13)	3692(12)	71(6)
C(17)	2883(5)	6516(14)	3882(19)	209(17)
C(18)	2266(4)	5466(13)	4095(11)	91(7)
C(19)	2650(6)	5311(19)	2571(12)	188(14)
C(21)	3830(4)	575(12)	945(10)	58(5)
C(22)	4362(4)	168(10)	3452(10)	46(5)
C(23)	4440(4)	−611(11)	1718(9)	51(5)
C(24)	4460(3)	1643(11)	1845(9)	47(5)
C(25)	3709(4)	−684(12)	2473(10)	57(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

figuration (Tables 3 and 4; Fig. 2). As in **1** and Cp'_2TaS_2H, the H atom could not be localised. It is striking that in both these compounds the central sulfur S(2) is located very close to the plane defined by the
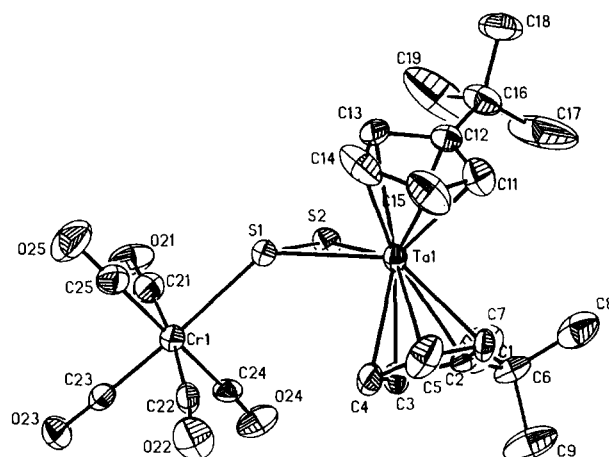

Fig. 1. ORTEP plot of **1**. The H atom bound to Ta cannot be localised exactly and is therefore omitted.

Table 3

Selected bond lengths (Å) and angles (deg) for Cp′$_2$TaS$_2$H · 2Cr(CO)$_5$ (2)

Ta(1)–S(1)	2.529(4)
Ta(1)–S(2)	2.502(4)
Cr(1)–S(1)	2.456(4)
Cr(2)–S(2)	2.439(4)
S(1)–S(2)	2.049(4)
S(1)–Ta(1)–S(2)	48.0(1)
C(31)–Cr(1)–S(1)	89.8(4)
C(32)–Cr(1)–S(1)	84.7(4)
C(33)–Cr(1)–S(1)	88.4(4)
C(34)–Cr(1)–S(1)	101.2(4)
C(35)–Cr(1)–S(1)	172.1(6)
C(36)–Cr(2)–S(2)	171.6(4)
Ta(1)–S(1)–Cr(1)	133.5(2)
Ta(1)–S(1)–S(2)	65.3(1)
Cr(1)–S(1)–S(2)	115.5(1)
Ta(1)–S(2)–Cr(2)	133.4(1)
Ta(1)–S(2)–S(1)	66.7(1)
Cr(2)–S(2)–S(1)	116.2(2)

gravity centers of both Cp rings and Ta. In **2**, S(1) and S(2) are −1.31 and +0.70 Å outside this plane. The angles Ta–Cr–S are in the range of 133° for both Cr(CO)$_5$ groups. A comparison of the other bond parameters of the cores of **1**, **2**, and Cp′$_2$TaS$_2$H shows that they are quite similar with the exception of the S–S bonds. These are significantly shortened by 0.11 (**1**) and 0.12 (**2**) Å as a consequence of the coordination.

2.2. Synthesis and reactivity of Cp$^x_2$NbS$_2$H · Cr(CO)$_5$ **3**

The reaction of Cp$^x_2$NbS$_2$H with two equivalents of Cr(CO)$_5$THF gives exclusively the red monoadduct **3** in moderate yield. C,H analyses are in agreement with the
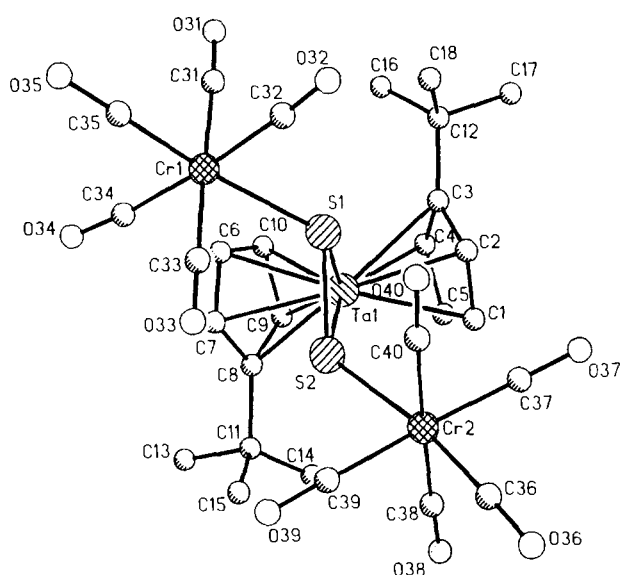

Fig. 2. Crystal structure of **2**. The H atom bound to Ta cannot be localised exactly and is therefore omitted.

composition Cp$^x_2$NbS$_2$H · Cr(CO)$_5$ and the IR spectrum exhibits ν(CO) absorptions typical of the Cr(CO)$_5$ moiety. The field desorption spectrum contains, instead of the expected parent ion of **3**, mass peaks of Cp$^x_2$NbS$_2$H and of Cp$^x_4$Nb$_2$S$_4$Cr (see below) in nearly equal amounts. The ^{1}H NMR spectrum shows, as for its precursor Cp$^x_2$NbS$_2$H [7], four resonances for the ring methyl groups. This means that on the NMR time scale both Cp^x ligands are equivalent. Owing to the sterically

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for Cp′$_2$TaS$_2$H · 2Cr(CO)$_5$ (2)

Atom	x	y	z	U_{eq} [a]
Ta(1)	979(1)	1831(1)	2301(1)	58(1)
Cr(1)	−2071(2)	−302(2)	3610(1)	54(1)
C(31)	−396(14)	−1434(11)	3899(8)	69(7)
O(31)	564(10)	−2129(9)	4113(6)	105(6)
C(32)	−1995(14)	−1242(12)	2783(8)	68(7)
O(32)	−2007(12)	−1812(9)	2328(7)	109(7)
C(33)	−3658(13)	805(12)	3294(7)	62(7)
O(33)	−4675(9)	1507(9)	3098(5)	88(5)
C(34)	−2299(12)	563(10)	4500(7)	55(6)
O(34)	−2519(9)	1020(8)	5085(5)	81(5)
C(35)	−3193(14)	−1080(12)	4397(9)	77(8)
O(35)	−3887(11)	1580(9)	4916(6)	125(7)
Cr(2)	−2446(2)	2991(2)	790(1)	70(1)
C(36)	−3438(16)	3544(13)	−63(9)	104(9)
O(36)	−4105(14)	3922(10)	−593(7)	159(8)
C(37)	−837(16)	2342(15)	−27(9)	99(9)
O(37)	83(12)	1901(13)	−555(7)	154(9)
C(38)	−2047(18)	4350(15)	600(10)	102(10)
O(38)	−1760(18)	5234(11)	448(9)	178(10)
C(39)	−4179(15)	3633(13)	1557(9)	91(8)
O(39)	−5314(11)	3980(10)	2000(7)	128(7)
C(40)	−2830(15)	1542(13)	961(8)	78(8)
O(40)	−2975(11)	636(10)	1043(7)	106(6)
S(1)	−605(3)	616(3)	2399(2)	49(1)
S(2)	−1487(3)	2402(3)	2073(2)	53(1)
C(1)	1910(12)	2116(13)	759(7)	67(7)
C(2)	1993(12)	988(12)	985(7)	56(6)
C(3)	2987(12)	371(11)	1501(7)	54(6)
C(4)	3468(11)	1250(12)	1628(7)	58(6)
C(5)	2801(13)	2317(11)	1205(8)	65(7)
C(6)	534(13)	1455(12)	3829(7)	63(7)
C(7)	−420(12)	2498(11)	3657(6)	49(6)
C(8)	312(14)	3319(11)	3255(7)	62(7)
C(9)	1786(12)	2686(12)	3153(7)	62(7)
C(10)	1951(12)	1504(11)	3524(7)	62(6)
C(11)	−346(15)	4669(12)	3069(10)	82(8)
C(13)	−497(19)	5136(14)	3918(11)	165(14)
C(14)	605(16)	5230(12)	2368(11)	181(13)
C(15)	−1813(14)	5046(12)	2918(10)	117(10)
C(12)	3635(14)	−936(12)	1705(8)	66(7)
C(16)	4145(17)	−1278(12)	2526(9)	140(12)
C(17)	4954(12)	−1356(11)	988(8)	97(8)
C(18)	2648(14)	−1627(11)	1774(9)	98(8)
C(41)	5124(21)	3977(16)	4888(14)	133(6)
C(42)	4283(21)	5925(18)	4561(14)	155(7)
C(43)	3847(38)	5395(37)	3910(23)	126(14)
C(44)	4302(31)	4615(30)	4298(19)	224(12)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

more demanding Cp^x ligands, when compared with 1, the pseudo inversion at sulfur in 3 may be assumed to proceed much easier. In agreement with this assumption, 3 loses the Cr(CO)$_5$ fragment easier than 1 under mass spectroscopic conditions.

Complex 3 decomposes nearly quantitatively in boiling toluene to give the CO-free complex 4, which analyses as Cp$^x_4$Nb$_2$S$_4$Cr (Eq. (2)). The IR spectrum of 4 is of little diagnostic value and the ^{1}H NMR spectrum exhibits two resonances for the ring methyls. The compound belongs to the class of bis(niobocene)tetrathiometalates, which contains a tetrahedral MS$_4$ core. It is more directly accessible by the reaction of Cp$^{(')}_2$NbS$_2$H with binary metal carbonyls [9], but now it is evident that compounds of type 3 are intermediates on this route.

3

    (2)

4
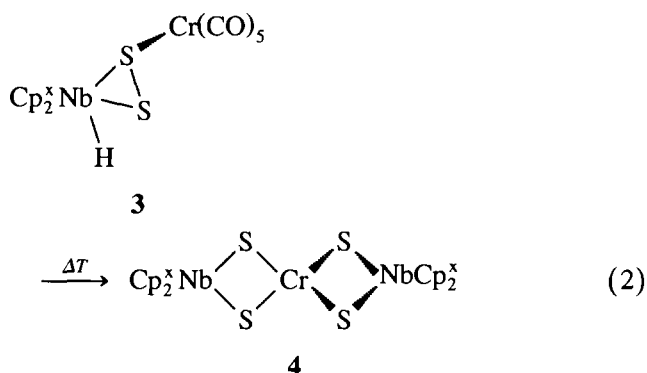
Analogous behavior has been described for solutions of 1 and 2 which develop into green Cp$'_4$Ta$_2$S$_4$Cr upon heating in toluene [10].

3. Experimental section

Experimental and spectroscopic techniques are the same as reported in Ref. [4]. Cp$'_2$TaS$_2$H [5] and Cp$^x_2$NbS$_2$H [6] were prepared by literature methods.

3.1. Reaction of Cp'$_2$TaS$_2$H with Cr(CO)$_5$THF

A solution of 247 mg (0.94 mmol) of Cr(CO)$_5$THF in 20 ml THF (prepared by irradiation of Cr(CO)$_6$ [11]) was added dropwise to a stirred solution of 380 mg (0.78 mmol) of Cp'$_2$TaS$_2$H in 30 ml of THF. The resulting brown reaction mixture was stirred for 1 h and then the solvent was removed under vacuum. The residual solid was chromatographed on silica gel (column 20 × 2 cm). With toluene an orange band was eluted containing 1 and 2. After evaporation of the solvent the mixture was dissolved in about 40 ml of toluene. After 1 day at −20 °C orange crystals of 2 were isolated (13% yield). The concentrated solution gave orange crystals of 1 at −20 °C (71% yield).

1: Anal. Found: C, 40.72; H, 3.78. C$_{23}$H$_{27}$CrO$_5$S$_2$Ta (680.5). Calc.: C, 40.59; H, 4.00%. FD mass spec-

troscopy (MS) (from toluene): 680.0. ^{1}H NMR (C$_6$D$_6$): 1.10 (s, 18), 3.14 (s, 1), 3.67 (m, 2), 4.23 (m, 2), 4.31 (m, 2), 5.87 (m, 2) ppm. IR (THF): ν_{CO} 2060 s, 1935 vs, 1900 s cm^{-1}.

2: Anal. Found: C, 41.17; H, 3.29. C$_{28}$H$_{27}$Cr$_2$O$_{10}$S$_2$Ta (872.6). Calc.: C, 41.19; H, 3.28% (calculated with 0.5 toluene). FD-MS (from toluene): 871.9. ^{1}H NMR (C$_6$D$_6$): 1.03 (s, 18), 3.98 (m, 2), 4.09 (s, 1), 4.35 (m, 2), 5.09 (m, 2), 5.36 (m, 2) ppm. IR (KBr): ν_{CO} 2064 s, 2057 s, 1916 vs cm^{-1}.

3.2. Preparation of Cp$^x_2$NbS$_2$H · Cr(CO)$_5$ 3

A solution of 456 mg (1.0 mmol) of Cp$^x_2$NbS$_2$H and 527 mg (2.0 mmol) of Cr(CO)$_5$THF [11] in 50 ml of THF was stirred for 2 h at room temperature in the dark, while the color turned from orange to red. After evaporation of the solvent the residue was diluted in 20 ml of toluene and transferred onto SiO$_2$ (column 20 × 3 cm). With toluene 175 mg (27%) of dark red 3 were isolated.

3: Anal. Found: C, 50.66; H, 5.87. C$_{27}$H$_{35}$CrNbO$_5$S$_2$ (648.1). Calc.: C, 50.00; H, 5.43%. FD-MS (from toluene): 456.0 (calc. 456.2 for C$_{22}$H$_{35}$NbS$_2$). ^{1}H NMR (C$_6$D$_6$): 0.71 (t, 6; $^3J_{HH}$ = 7.5 Hz), 0.82 (s, 1), 1.50 (s, 6), 1.52 (s, 6), 1.53 (s, 6), 1.58 (s, 6), 2.04 (m, 4) ppm. IR (KBr): ν_{CO} 2055 s, 1945 vs, 1884 s cm^{-1}.

3.3. Thermolysis of Cp$^x_2$NbS$_2$H · Cr(CO)$_5$ 3

A solution of 139 mg (0.21 mmol) of 3 in 50 ml of toluene was refluxed for 18 h. The concentrated solution was chromatographed on SiO$_2$ (column 20 × 3 cm). With toluene a red band containing 90 mg (44%) of Cp$^x_4$Nb$_2$S$_4$Cr 4 was isolated.

4: Anal. Found: C, 54.93; H, 7.13. C$_{44}$H$_{68}$CrNb$_2$S$_4$ (963.2). Calc.: C, 54.87; H, 7.12%. FD-MS (from toluene): 963.1. ^{1}H NMR (C$_6$D$_6$): 0.91 (t, 12; $^3J_{HH}$ = 7.5 Hz), 1.80 (s, 24), 1.89 (s, 24), 2.34 (q, 8; $^3J_{HH}$ = 7.5 Hz) ppm.

3.4. Crystallographic data

3.4.1. Cp'$_2$TaS$_2$H · Cr(CO)$_5$ 1
Red needles (0.10 × 0.17 × 0.85 mm^3), monoclinic C2h/6, C2/c (15); cell: a 32.54(3), b 11.63(1), c 13.500(8) Å, β 92.54°; V 5103.9 Å^3, Z = 8; empirical absorption correction: 6 reflections 6.0 < 2Θ < 36.0°. Transmission factor (min/max) 0.66/1.00, μ 4.84 mm^{-1}. F(000) 2664, d(calc) = 1.77 g cm^{-3}; Syntex R3. Mo K α radiation, graphite monochromator, 6989 unique observed reflections; 3791 independent reflections (I > 2.5σ(I)). Structure solution by means of Patterson and Fourier methods. R = 0.069, R$_w$ = 0.052; residual electron density (max/min) 2.0/− 2.40 e Å^{-3}, shift/esd (max) 0.004, GOOF = 1.66.

3.4.2. $Cp'_2TaS_2H \cdot 2Cr(CO)_5 \cdot 0.5C_7H_8$ **2**

Red plates ($0.15 \times 0.40 \times 0.65$ mm^3), triclinic $Ci/1$, $P - 1$ (2); cell: a 10.333(5), b 12.19(1), c 16.31(1) Å, α 77.67(6), β 73.49(4), γ 68.78(6)°; V 1822.0 Å^3, $Z = 2$; empirical absorption correction: 6 reflections $4.0 < 2\Theta < 36.0°$. Transmission factor (min/ max) 0.60/1.00, μ 3.75 mm^{-1}. $F(000)$ 904, d(calc) = 1.67 g cm^{-3}; Syntex R3. Mo Kα radiation, graphite monochromator, 6475 unique observed reflections; 4110 independent reflections ($I > 2.5\sigma(I)$). Structure solution by means of Patterson and Fourier methods. $R = 0.064$, $R_w = 0.051$; residual electron density (max/min) $1.25/-1.32$ e Å^{-3}, shift/esd (max) 0.6 (disordered toluene; without 0.07), $GOOF = 1.95$.

Acknowledgements

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