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New syntheses of $[Et_4N][(C_5H_{10}NCS_2)M(CO)_4]$ (M=Cr, Mo and W): Insertion reaction of carbon disulfide into the metal–nitrogen bond

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Abstract

The complex $(pip)_2M(CO)_4$ (pip=$C_5H_{10}NH$; M=Cr, Mo or W) reacted with ^nBuLi and CS_2 in the presence of Et_4NBr to give $[Et_4N][(C_5H_{10}NCS_2)M(CO)_4]$(M=Cr (**1**), Mo (**2**), W (**3**)) in high yield. The reaction is initiated by the abstraction of the NH proton of the piperidine ligand by ^nBuLi, followed by insertion of CS_2 into the M–N bond to give the dithiocarbamate metal complexes. The complex $[Et_4N][(C_4H_8NCS_2)W(CO)_4]$ (**4**) was similarly prepared. Complexes **1**–**4** were characterized by elemental analysis and IR, mass and NMR spectroscopy. In addition, the molecular structures of **3** and **4** were determined by single-crystal X-ray diffraction analysis, which confirmed the dihapticity of the dithiocarbamte ligands in **3** and **4**. Compound **3** is monoclinic, space group $P2_1$, with $a = 9.964(2)$ Å, $b = 12.724(1)$ Å, $c = 10.268(3)$ Å, $\beta = 117.12(2)°$ and $Z = 2$. Compound **4** is orthorhombic, space group $Pna2_1$, with $a = 31.424(5)$ Å, $b = 8.281(1)$ Å, $c = 17.137(2)$ Å and $Z = 8$. The structure was refined to the final conventional R of 0.029 and R_w of 0.020. The HMBC (^1H-detected heteronuclear multiple bond correlation) technique was used to assign the ^{13}C chemical shift of the CS_2 group of the dithiocarbamate ligand.

Keywords: Chromium; Molybdenum; Tungsten; Dithiocarbamate; Carbon disulfide; Insertion

1. Introduction

The preparation of dithiocarbamate (dtc) brings in syntheses of metal carbonyl derivatives of this ligand and also studies on the unusual structure and reactions of these complexes [1–17]. The synthesis of dithiocarbamate metal complexes of the type $[Et_4N][(Et_2NCS_2)M(CO)_4]$ (M=Mo [12b], W [12c]) from the direct reaction of $M(CO)_6$ with NaS_2CNEt_2 in the presence of Et_4NCl in MeCN has been reported. The yields were moderate, i.e. 76% and 55% for M=Mo and W, respectively. Since the organic dithiocarbamate molecule was prepared from the reaction of amine and CS_2, we suggest that the direct insertion of CS_2 into the M–N bond would be an alternative synthetic method for dithiocarbamate complexes. Previous examples that used this synthetic strategy are (1) insertion of CS_2 into the metal dialkylamides to form the tetrakis- or pentakis-N,N-dialkyldithiocarbamato metal complexes $M(S_2CNR_2)_4$ (Eq. (1)) [18], (2) insertion of CS_2 into the Ni–amine bond to give the nickel(II) dithiocarbamate complex (Eq. (2)) [19] and (3) the reaction of $Fp(amine)^+$ ($Fp=C_5H_5(CO)_2Fe$) with a mixture of CS_2 and ^tBuOK to yield the monodentate dtc complex (Eq. (3)) [20].

$$M(NR_2)_n + nCS_2 \rightarrow M(S_2CNR_2)_n \qquad (1)$$

$n = 4$, R=Me, Et or Pr and M=Ti, V or Zr

$n = 5$, R=Me, Et and M=Ta

$$Ni(NHR_2)_4^{+2} + 2CS_2 \rightarrow Ni(S_2CNR_2)_2 + 2R_2NH_2^+$$

R = alkyl or hydrogen (2)

$$[Cp(CO)_2FeNHR_2]^+ PF_6^- \xrightarrow{CS_2 + \text{base}} Cp(CO)_2Fe - \eta^1 - SC(S)NR_2$$

R=Me, Et, or $SiMe_3$ (3)

$$[Re(CO)_2(PPh_3)_2(mat)] + CS_2 \rightarrow [Re(CO)_2(PPh_3)_2\{S_2CNMe(C_3H_2NS)\}] \qquad (4)$$

mat = anion of 2-(methylamino)thiazole

The bonding mode of bidentate and/or unidentate dithiocarbamate groups of the complexes prepared via

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Eqs. (1)–(3) was only established by IR and NMR spectroscopy.

Rossi et al. [21] reported the crystal structure (Eq. (4)) of the Re dithiocarbamate complex prepared in low yield (15%) from the insertion reaction of CS_2 into the Re–N bond. Most of the CS_2 insertions into M–N bonds were carried out under severe reaction conditions and with low yields and interestingly the insertion method has never been applied to the synthesis of the dithiocarbamate complexes of Group VI metals.

We are interested in finding a high-yield preparation for the synthesis of dithiocarbamate metal complexes. We report here the insertion of CS_2 into the metal–nitrogen bond with Cr, Mo, W to form the η^2-dithiocarbamate carbonyl complexes in > 90% yields under mild conditions. The molecular structure of $[Et_4N][(C_5H_{10}NCS_2)W(CO)_4]$ (**3**) and $[Et_4N][(C_4H_8NCS_2)W(CO)_4]$ (**4**) was confirmed by X-ray diffraction analysis.

2. Experimental

2.1. General procedure

All manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using the Schlenk technique or in a nitrogen-filled glove-box. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. n-Hexane, diethyl ether and THF were purified by distillation from sodium–benzophenone ketyl, acetonitrile and dichloromethane from calcium hydride and methanol from magnesium. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer, using cells equipped with calcium fluoride windows. NMR spectra were recorded on a Bruker AC-200 or an AM-300 WB FT-NMR spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 elemental analyzer. Mass spectra were recorded on a JEOL SX-102A spectrometer. Metal hexacarbonyls, piperidine, Et_4NBr and CS_2 were purchased from Strem, Janssen, Merck and TCI, respectively, and were used as received. The compounds $(C_5H_{10}NH)_2M(CO)_4$ (M=Cr, Mo and W) and $(C_4H_8NH)_2M(CO)_4$ were prepared according to the literature methods [22].

2.2. Synthesis of $[Et_4N][(C_5H_{10}NCS_2)Cr(CO)_4]$ (1)

An aliquot of 1.6 M ^nBuLi–n-hexane (0.4 ml, 0.64 mmol) was added to a flask containing $(pip)_2Cr(CO)_4$ (0.17 g, 0.51 mmol) in MeCN (20 ml). The solution turned orange immediately. CS_2 (0.13 g, 1.6 mmol) was then added to the solution. The reaction mixture was stirred for 1 min and filtered through Celite. The filtrate was reduced in volume, followed by the addition of Et_4NBr (0.12 g, 0.52 mmol) in 10 mL of methanol. On cooling to below 0°C, yellow-orange solid **1** formed, which was filtered, washed with n-hexane (2 × 10 ml) and subsequently dried under vacuum. Further purification was accomplished by recrystallization from dichloromethane–hexane (yield 0.21 g, 91%). IR (KBr, ν_{CO}): 1981(m), 1854(vs), 1836(vs), 1796(s), 1782(vs) cm^{-1}, ν_{CN} = 1470(m) cm^{-1}. ^1H NMR (298 K, CD_3CN, 200 MHz): δ 1.20 (tt, 12H, NCH_2CH_3, $^3J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.3$ Hz); 1.54 (m, 6H, $NCH_2CH_2CH_2$); 3.15 (quartet, 8H, NCH_2CH_3, $J_{H-H} = 7.3$ Hz); 3.83 (m, 4H, NCH_2–). ^{13}C NMR (298 K, CD_3CN, 50 MHz): δ 7.60 (NCH_2CH_3); 24.57 ($NCH_2CH_2CH_2$); 26.03 ($NCH_2CH_2CH_2$); 47.30 (NCH_2–); 52.92 (NCH_2CH_3); 209.71 (CS_2); 219.57 (CO); 231.20 (CO). MS (FAB, NBA, m/z): 556 ($M + Et_4N^+$; for ^{54}Cr and ^{34}S). Anal. Calcd. for $C_{18}H_{30}CrN_2O_4S_2$: C, 47.56; H, 6.66; N, 6.16. Found: C, 47.40; H, 6.56; N, 6.00%.

2.3. Synthesis of $[Et_4N][(C_5H_{10}NCS_2)Mo(CO)_4]$ (2)

This orange–yellow compound (0.27 g) was obtained in 93% yield (from 0.22 g of $(C_5H_{10}NH)_2Mo(CO)_4$) by a procedure similar to that for **1**. IR (KBr, ν_{CO}): 1993(m), 1861(m), 1838(vs), 1804(vs), 1787(s) cm^{-1}, ν_{CN} = 1471(m) cm^{-1}. ^1H NMR (298 K, CD_3CN, 200 MHz): δ 1.21 (tt, 12H, NCH_2CH_3, $^3J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.3$ Hz); 1.58 (m, 6H; $NCH_2CH_2CH_2$); 3.15 (quartet, 8H, NCH_2CH_3, $J_{H-H} = 7.3$ Hz); 3.90 (m, 4H, NCH_2–). ^{13}C NMR (298 K, CD_3CN, 50 MHz): δ 7.60 (NCH_2CH_3); 24.73 ($NCH_2CH_2CH_2$); 26.18 ($NCH_2CH_2CH_2$); 48.21 (NCH_2–); 53.05 (NCH_2CH_3); 208.57 (CO); 211.60 (CS_2); 223.43 (CO). MS (FAB, NBA, m/z): 602 ($M + Et_4N^+$; for ^{100}Mo and ^{34}S). Anal. Calcd. for $C_{18}H_{30}MoN_2O_4S_2$: C, 43.36; H, 6.08; N, 5.62. Found: C, 43.25; H, 5.98; N, 5.55%.

2.4. Synthesis of $[Et_4N][(C_5H_{10}NCS_2)W(CO)_4]$ (3)

This orange–yellow compound (0.22 g) was obtained in 92% yield (from 0.19 g of $(C_5H_{10}NH)_2W(CO)_4$) by a procedure similar to that for **1**. IR (KBr, ν_{CO}): 1987(m), 1854(m), 1830(vs), 1800(vs), 1783(s) cm^{-1}, ν_{CN} = 1476(m) cm^{-1}. ^1H NMR (298 K, CD_3CN, 200 MHz): δ 1.21 (tt, 12H, NCH_2CH_3, $^3J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.3$ Hz); 1.59 (m, 6H, NCH_2CH_2–CH_2); 3.15 (quartet, 8H, NCH_2CH_3, $J_{H-H} = 7.3$ Hz); 3.82 (m, 4H, NCH_2–). ^{13}C NMR (298 K, CD_3CN, 50 MHz): δ 7.55 (NCH_2CH_3); 24.68 ($NCH_2CH_2CH_2$); 25.99 (NCH_2-CH_2CH_2); 47.53 (NCH_2–); 52.89 (NCH_2–CH_3); 204.01 (CO); 212.98 (CS_2); 213.83 (CO). MS (FAB, NBA, m/z): 688 ($M + Et_4N^+$; for ^{186}W and ^{34}S). Anal. Calcd. for $C_{18}H_{30}WN_2O_4S_2$: C, 36.86; H, 5.17; N, 4.78. Found; C, 36.94; H, 5.43; N, 4.92%.

Table 1
Crystal and intensity collection data for $[Et_4N][(C_5H_{10}NCS_2)W(CO)^4]$ (**3**) and $[Et_4N][(C_4H_8NCS_2)W(CO)_4]$ (**4**)

Parameter	**3**	**4**
Molecular formula	$C_{18}H_{20}N_2O_4S_2W$	$C_{17}H_{28}N_2O_4S_2W$
Space group	$P2_1$	$Pna2_1$
a (Å)	10.268(3)	31.424(5)
b (Å)	12.724(1)	8.281(1)
c (Å)	9.964(2)	17.137(2)
β (°)	117.12(2)	
V (Å^3)	1158.6(4)	4459.4(10)
Z	2	8
Crystal dimensions (mm)	0.35 × 0.5 × 0.5	0.5 × 0.5 × 0.55
Radiation	Mo Kα, $\lambda = 0.7107$ Å	
μ (cm^{-1})	52.873	54.926
2θ range (°)	2–50	2–50
Scan type	$\theta/2\theta$	
Total number of reflections	2136	4055
Unique reflections $I > 2\sigma(I)$	1974	3142
R	0.023	0.029
R_w	0.022	0.020
G_0F	1.92	1.51

Table 3
Selected bond distances (Å) and bond angles (°) for **3**

W–S1	2.6061(21)	C3–O3	1.171(11)
W–S2	2.5649(22)	C4–O4	1.144(10)
W–C1	1.993(8)	C5–N1	1.335(9)
W–C2	1.984(9)	C6–C7	1.498(12)
W–C3	1.919(9)	C6–N1	1.480(10)
W–C4	2.046(8)	C7–C8	1.521(15)
S1–C5	1.708(7)	C3–C9	1.519(14)
S2–C5	1.705(7)	C9–C10	1.490(14)
C1–O1	1.147(10)	C10–N1	1.457(11)
C2–O2	1.150(10)		
S1–W–S2	67.83(6)	W–S2–C5	89.00(24)
S1–W–C1	93.31(23)	W–C1–O1	174.5(7)
S1–W–C2	100.59(24)	W–C2–O2	178.4(7)
S1–W–C3	169.12(25)	W–C3–O3	177.8(9)
S1–W–C4	87.90(23)	W–C4–O4	176.9(8)
S2–W–C1	95.82(24)	S1–C5–S2	115.5(4)
S2–W–C2	168.15(23)	S1–C5–N1	122.0(5)
S2–W–C3	101.9(3)	S2–C5–N1	122.5(5)
S2–W–C4	89.54(24)	C7–C6–N1	108.1(7)
C1–W–C2	87.2(3)	C6–C7–C8	111.9(8)
C1–W–C3	91.3(3)	C7–C8–C9	110.1(8)
C1–W–C4	174.6(3)	C8–C9–C10	109.1(8)
C2–W–C3	89.5(4)	C9–C10–N1	111.6(10)
C2–W–C4	87.4(3)	C5–N1–C6	125.0(6)
C3–W–C4	88.4(3)	CS–N1–C10	123.6(7)
W–S1–C5	87.58(24)	C6–N1–C10	111.4(7)

2.5. Synthesis of $[Et_4N][(C_4H_8NCS_2)W(CO)_4]$ (4)

This orange–yellow compound (0.25 g) was obtained in 92% yield (from 0.21 g of $(C_4H_8NH)_2W(CO)_4$) by a procedure similar to that for **1**. IR (KBr, ν_{CO}): 1996(m), 1859(m), 1810(vs), 1772(s) cm^{-1}, ν_{CN} = 1479(m) cm^{-1}. ^{1}H NMR (298 K, CD_3CN, 200 MHz): δ 1.21 (tt, 12H, NCH_2CH_3, $^3J_{N-H} = 1.87$ Hz, $J_{H-H} = 7.3$ Hz); 1.94 (m, 4H, NCH_2CH_2); 3.17 (quartet, 8H, NCH_2CH_3, $J_{H-H} = 7.3$ Hz); 3.58 (m, 4H, NCH_2–). ^{13}C NMR (298 K, CD_3CN, 50 MHz): δ 7.60 (NCH_2CH_3); 25.40 (NCH_2CH_2); 50.25 (NCH_2–); 53.09 (NCH_2CH_3); 204.41 (CO); 210.18 (CS_2); 213.84 (CO). MS (FAB, NBA, m/z): 674 ($M^+ + Et_4N^+$; for ^{186}W and ^{34}S). Anal. Calcd. for $C_{17}H_{28}WN_2O_4S_2$: C, 35.67; H, 4.94; N, 4.89. Found: C, 35.74; H, 5.03; N, 4.97%.

Table 2
Atomic parameters x, y, z and B_{eq} for **3**

Atom	x	y	z	B_{eq}
W	0.30553(3)	−0.25851(5)	0.68383(3)	3.570(18)
S1	0.33076(23)	−0.15129(16)	0.47403(24)	4.05(11)
S2	0.13478(23)	−0.32672(17)	0.41881(24)	4.20(11)
C1	0.4725(9)	−0.3529(7)	0.7175(9)	4.5(5)
C2	0.4427(9)	−0.1805(6)	0.8662(9)	4.8(5)
C3	0.2518(9)	−0.3455(8)	0.8080(9)	5.3(5)
C4	0.1472(8)	−0.1544(6)	0.6675(9)	4.5(5)
C5	0.1955(7)	−0.2285(5)	0.3452(8)	3.6(4)
C6	0.1846(9)	−0.1254(7)	0.1269(9)	4.7(5)
C7	−0.0566(10)	−0.0541(7)	0.0434(11)	6.1(6)
C8	−0.0751(11)	−0.1132(8)	−0.0735(11)	7.3(6)
C9	−0.1151(9)	−0.2033(8)	0.0007(10)	6.4(6)
C10	0.0165(9)	−0.2703(12)	0.0843(8)	5.5(6)
N1	0.1376(7)	−0.2100(5)	0.1972(7)	4.2(3)
O1	0.5699(7)	−0.4085(5)	0.7483(7)	6.1(4)
O2	0.5245(7)	−0.1371(S)	0.9727(7)	7.2(4)
O3	0.2189(7)	−0.4013(6)	0.8809(8)	7.9(5)
O4	0.0599(7)	−0.0973(5)	0.6649(9)	7.7(5)

ESDs refer to the last digit printed.

2.6. ^{1}H–^{13}C Long-range shift correlation NMR spectroscopy

The multiple-bond ^{1}H–^{13}C shift correlation spectra (1K × 1K) of **1**, **2** and **3** were obtained from a 256 × 2048 data matrix, with 128 scans (preceded by two dummy scans) per 11 value and a delay time between scans of 1.2 s. The total measuring time was 18 h. Radiofrequency power was used to provide a 3.3 kHz ^{13}C radiofrequency field, and 70 ms ^{13}C pulse widths (corresponding to 82° rather than 90° flip angles) were used. The ^{13}C spectra width was 235 ppm in three experiments. In the t_2 dimension, a square sine-bell filter and 4 Hz exponential line broadening were used prior to Fourier transformation. No digital filtering was used in the t_1 dimension.

2.7. X-ray Crystallography

A yellow crystal of **3** was mounted on the top of a glass fiber with epoxy cement. A rotational photograph indicated the crystal diffracted well. The unit cell constants were determined from 25 reflections with 2θ in the range 18.62–26.20. These were consistent with a monoclinic system and the space group was subsequently determined to be $P2_1$ from systematic absences.

Routine $\theta/2\theta$ data collection was used to scan the possible 2136 reflections in the range 2–49.8°. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. The structure factors were obtained after Lorentz and polarization corrections. Empirical absorption corrections based on azimuthal scans of reflections of eulerian angle (chi) near 90° were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.

The tungsten atom was located in a Patterson synthesis and the remaining atoms were found with alternating difference Fourier maps and least-squares refinements. Anisotropic thermal parameters were used for all the atoms except the hydrogen atoms. The final residuals of the refinement were $R = 0.023$ and $R_w = 0.022$. The procedures for the crystal structure analysis of **4** were similar to that of **3** with $R = 0.029$ and $R_w = 0.020$. Basic information pertaining to crystal parameters and structural refinement is summarized in Table 1. Tables 2 and 3 list positional parameters and selected bond distances and angles, respectively, for **3** and Tables 4 and 5 for **4**.

Table 4
Atomic parameters x, y, z, and B_{eq} for **4**

Atom	x	y	z	B_{eq}
W1A	0.728957(14)	0.37799(5)	0.50000	3.679(20)
S1A	0.77282(10)	0.2157(3)	0.60312(17)	4.36(14)
S2A	0.80919(8)	0.3653(3)	0.46571(16)	4.16(14)
C1A	0.7360(3)	0.5881(12)	0.5557(7)	5.1(7)
C2A	0.6721(3)	0.3652(12)	0.5450(6)	4.8(6)
C3A	0.7053(3)	0.5073(12)	0.4172(7)	4.6(6)
C4A	0.7181(3)	0.1676(13)	0.4412(6)	4.9(6)
C5A	0.8178(3)	0.2592(11)	0.5492(6)	3.3(5)
N6A	0.85548(25)	0.2142(9)	0.5719(5)	3.9(4)
C7A	0.8642(3)	0.1110(14)	0.6407(7)	5.3(6)
C8A	0.9098(4)	0.0532(14)	0.6283(8)	7.5(8)
C9A	0.9280(3)	0.1871(14)	0.5804(8)	6.5(7)
C10A	0.8948(3)	0.2542(12)	0.5271(6)	4.5(6)
O1A	0.7387(3)	0.7116(9)	0.5878(5)	7.8(5)
O2A	0.63758(22)	0.3597(10)	0.5743(5)	7.2(5)
O3A	0.6910(3)	0.5884(9)	0.3681(5)	7.6(5)
O4A	0.71057(24)	0.0499(9)	0.4094(5)	6.4(5)
W1B	0.478280(13)	0.31876(5)	0.30020(4)	3.562(20)
S1B	0.55755(9)	0.3297(4)	0.34234(16)	4.13(14)
S2B	0.52597(9)	0.1477(4)	0.20935(18)	4.94(15)
C1B	0.4653(3)	0.1302(12)	0.3734(6)	4.7(6)
C2B	0.4543(3)	0.4693(11)	0.3760(6)	4.3(6)
C3B	0.4221(4)	0.2826(13)	0.2547(7)	6.3(7)
C4B	0.4854(3)	0.5130(14)	0.2360(7)	5.6(7)
C5B	0.5690(3)	0.2177(11)	0.2618(6)	3.7(5)
N6B	0.60877(23)	0.1894(10)	0.2379(5)	3.9(4)
C7B	0.6446(3)	0.2546(13)	0.2812(7)	6.0(7)
C8B	0.6828(3)	0.1896(19)	0.2329(7)	9.0(10)
C9B	0.6652(5)	0.1013(20)	0.1704(10)	12.8(13)
C10B	0.6195(4)	0.0946(15)	0.1697(7)	6.6(7)
O1B	0.45432(25)	0.0308(8)	0.4148(5)	6.7(5)
O2B	0.43796(23)	0.5611(9)	0.4193(4)	5.8(4)
O3B	0.38994(21)	0.2590(10)	0.2244(5)	7.6(5)
O4B	0.4866(3)	0.6282(9)	0.1970(5)	7.7(5)

ESDs, refer to the last digit printed.

Table 5
Selected bond distances (Å) and bond angles (°) for **4**

W1A–S1A	2.613(3)	W1B–S1B	2.595(3)
W1A–S2A	2.591(3)	W1B–S2B	2.584(3)
W1A–C1A	1.997(10)	W1B–C1B	2.044(11)
W1A–C2A	1.948(10)	W1B–C2B	1.952(11)
W1A–C3A	1.927(11)	W1B–C3B	1.954(12)
W1A–C4A	2.042(11)	W1B–C4B	1.962(12)
S1A–C5A	1.726(10)	S1B–C5B	1.702(10)
S2A–C5A	1.701(10)	S2B–C5B	1.724(10)
C1A–O1A	1.165(13)	C1B–O1B	1.140(13)
C2A–O2A	1.197(12)	C2B–O2B	1.180(13)
C3A–O3A	1.166(13)	C3B–O3B	1.153(14)
C4A–O4A	1.140(13)	C4B–O4B	1.165(14)
C5A–N6A	1.301(12)	C5B–N6B	1.335(12)
N6A–C7A	1.482(13)	N6B–C7B	1.452(13)
N6A–C10A	1.492(12)	N6B–C10B	1.447(13)
C7A–C8A	1.527(15)	C7B–C8B	1.556(16)
C8A–C9A	1.493(17)	C8B–C9B	1.409(21)
C9A–C10A	1.495(16)	C9B–C10B	1.438(20)
S1A–W1A–S2A	67.62(9)	S1B–W1B–S2B	68.28(9)
S1A–W1A–C1A	93.8(3)	S1B–W1B–C1B	92.7(3)
S1A–W1A–C2A	100.8(3)	S1B–W1B–C2B	99.4(3)
S1A–W1A–C3A	170.9(3)	S1B–W1B–C3B	169.8(3)
S1A–W1A–C4A	89.1(3)	S1B–W1B–C4B	91.0(3)
S2A–W1A–C1A	92.1(3)	S2B–W1B–C1B	93.8(3)
S2A–W1A–C2A	168.4(3)	S2B–W1B–C2B	167.2(3)
S2A–W1A–C3A	103.4(3)	S2B–W1B–C3B	101.5(3)
S2A–W1A–C4A	90.9(3)	S2B–W1B–C4B	92.6(3)
C1A–W1A–C2A	87.7(4)	C1B–W1B–C2B	90.1(4)
C1A–W1A–C3A	84.9(4)	C1B–W1B–C3B	87.0(4)
C1A–W1A–C4A	176.4(4)	C1B–W1B–C4B	173.4(4)
C2A–W1A–C3A	88.1(4)	C2B–W1B–C3B	90.8(4)
C2A–W1A–C4A	89.7(4)	C2B–W1B–C4B	83.9(5)
C3A–W1A–C4A	92.6(4)	C3B–W1B–C4B	90.3(5)
W1A–S1A–C5A	87.9(3)	W1B–S1B–C5B	87.6(3)
W1A–S2A–C5A	89.1(3)	W1B–S2B–C5B	87.5(3)
W1A–C1A–O1A	177.9(8)	W1B–C1B–O1B	173.5(8)
W1A–C2A–O2A	178.2(9)	W1B–C2B–O2B	176.6(9)
W1A–C3A–O3A	178.6(9)	W1B–C3B–O3B	176.4(9)
W1A–C4A–O4A	177.6(8)	W1B–C4B–O4B	175.2(8)
S1A–C5A–S2A	115.3(5)	S1B–C5B–S2B	116.1(6)
S1A–C5A–N6A	121.7(7)	S1B–C5B–N6B	122.9(7)
S2A–C5A–N6A	123.0(7)	S2B–C5B–N6B	121.0(7)
C5A–N6A–C7A	124.9(8)	CSB–N6B–C7B	120.2(8)
C5A–N6A–C10A	122.4(8)	C5B–N6B–C10B	124.1(9)
C7A–N6A–C10A	112.6(7)	C7B–N6B–C10B	115.7(8)
N6A–C7A–C8A	104.1(9)	N6B–C7B–C8B	101.4(9)
C7A–C8A–C9A	101.7(9)	C7B–C8B–C9B	106.3(10)
C8A–C9A–C10A	110.2(9)	C8B–C9B–C10B	114.7(13)
N6A–C10A–C9A	100.4(8)	N6B–C10B–C9B	101.9(10)

3. Results and discussion

3.1. Synthesis and spectroscopic study of the dithiocarbamate complexes

Complexes of the type $[Et_4N][(C_5H_{10}NCS_2)M(CO)_4]$ (M=Cr (**1**); M=Mo (**2**); M=W (**3**)) were prepared by the reactions of $(C_5H_{10}NH)_2M(CO)_4$ (M=Cr, Mo, W) with BuLi and CS_2, followed by addition of Et_4NBr. These three complexes were prepared under mild conditions and the yields were 91%, 93% and 92% for Cr, Mo and W complexes, respectively. This method gives better yields than the direct reaction of $M(CO)_6$ with NaS_2CNEt_2 in refluxing CH_3CN. The reaction of $(C_5H_{10}NH)_2M(CO)_4$ (M=Cr, Mo, W) with CS_2 without participation of a BuLi gave no desired product at room temperature and only a small amount of CS_2-insertion product, possibly $(C_5H_{11}NHCS_2)M(CO)_4$, was obtained in refluxing MeCN. This product is unstable and cannot be purified by recrystallization. The complex $(C_4H_8NCS_2)W(CO)_4$- (**4**) can be similarly prepared in 92% yield from the reaction of ^{n}BuLi, CS_2 with $(C_4H_8NH)_2W(CO)_4$. To obtain complexes **1–3** in high yield, it is necessary to use CH_3CN as the solvent. Even though ^{n}BuLi might deprotonate the solvent, we believe that the abstraction of the NH proton either directly by ^{n}BuLi or by some base formed from the deprotonation of the solvent is the crucial step for the high-yield formation of the product.

The IR spectrum of **1** shows four terminal carbonyl groups (C_{2v}, $2A_1 + B_1 + B_2$), 1981(m), 1854(vs), 1836(vs), 1796(s). The absorption bands at 1470 cm^{-1} for **1**, 1471 cm^{-1} for **2** and 1476 cm^{-1} for **3** are indicative of the presence of the CN groups [12b,c] with some double-bond character. The stretching frequencies[23] for the C–N and the C=N groups fall in the regions 1250–1350 and 1640–1690 cm^{-1}, respectively. The ^1H NMR spectra show two sets of multiplet resonances, at δ 1.54 and 3.83 for **1**, δ 1.58 and 3.90 for **2** and δ 1.59 and 3.82 for **3** with a ratio of 4 : 6, assignable to the piperidine ring of the dithiocarbamate ligand. The ^{13}C NMR spectra of these complexes indicate three resonances in the δ 200–235 region for the terminal COs and the carbon atom of the CS_2 group. The HMBC (^1H-detected heteronuclear multiple bond correlation) experiment was used to assign the chemical shift of the carbon atom of the CS_2 group. Fig. 1 shows the $^1H–^{13}C$ long-range correlated spectrum for complex **2**. The cross peak at ^1H δ 3.90 and ^{13}C δ 211.6 indicate the correlation of the α-CH_2 of the piperidine and the carbon atom of the CS_2 group. In the ^{13}C NMR spectra, the CS_2 groups for **1** and **3** gave resonances at δ 209.7 and 213.0, respectively. The assignment is also based on the HMBC experiments. FAB mass spectra of the anionic dithiocarbamate complexes gave $[Et_4N]_2[(C_5H_{10}NCS_2)M(CO)_4]^+$ as the base peak, i.e. the complex ion pair picks up Et_4N^+ to form a cation for detection.

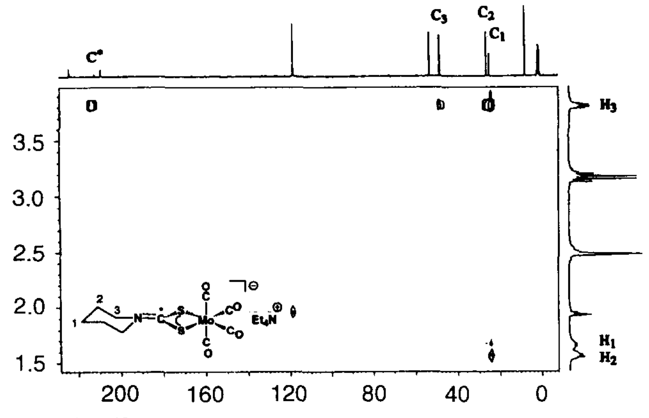


Fig. 1. $^1H–^{13}C$ multiple bond shift correlation (HMBC) spectrum of complex $[Et_4N][(C_5H_{10}NCS_2)Mo(CO)_4]$ (**2**).

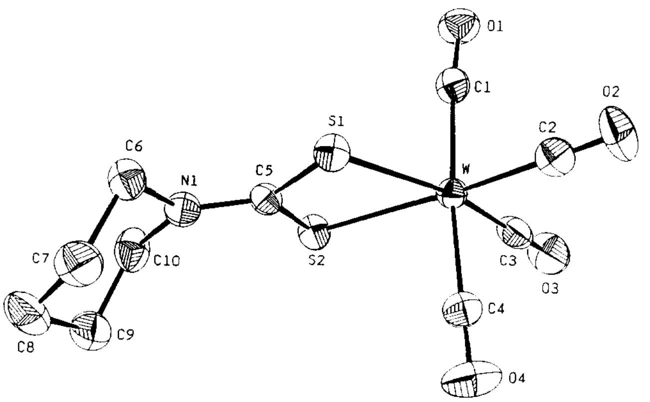


Fig. 2. ORTEP diagram of the anionic complex $[Et_4N][(C_5H_{10}NCS_2)W(CO)_4]$ (**3**).

3.2. Molecular structure of 3 and 4

The crystals of $[Et_4N][(C_5H_{10}NCS_2)W(CO)_4]$ (**3**) conform to the space group $P2_1$ with two molecules per unit cell. Fig. 2 shows an ORTEP diagram of the anion of **3**. It can be seen that both sulfur atoms of the incoming CS_2 molecule are coordinated to the W metal center, and the carbon atom is bonded to the nitrogen atom of the piperidine ring. The CS_2 molecule has been inserted into one of the W–N bonds of the starting material $(C_5H_{10}NH)_2W(CO)_4$ with the formation of two W–S bonds and one N–C bond. The crystal consists of the anion $[(C_5H_{10}NCS_2)W(CO)_4]^-$ with Et_4N^+ as the counter cation. The structure of the anion of **3** possess a C_2 non-crystallographic axis through the W, C(5) and N(1) atoms and thus acquires pseudo-C_{2v} symmetry. Table 3 lists the selected bond distances and angles for **3**. The crystals of **4** conform to the space group $Pna2_1$ with two independent molecules (A and B) in the unit cell. There is no essential strutural difference between

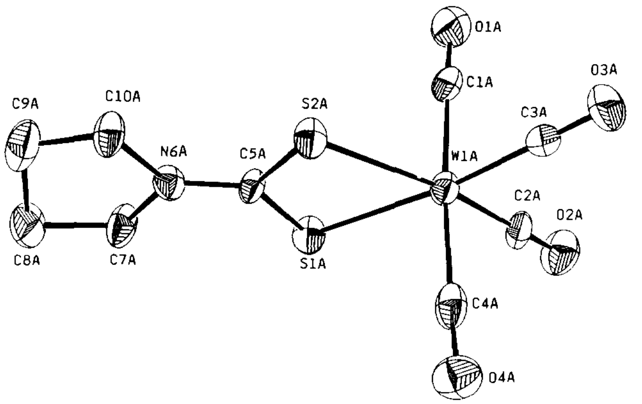
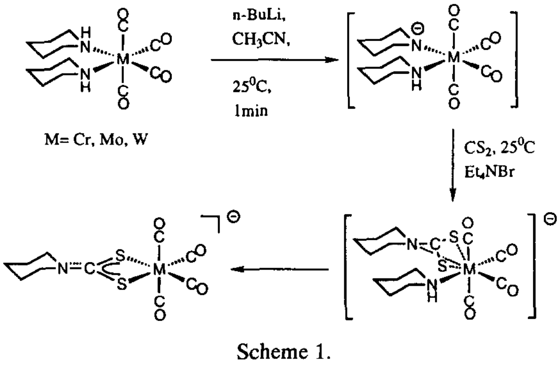


Fig. 3. ORTEP diagram of the anionic complex $[\mathrm{Et_4N}][(\mathrm{C_4H_8NCS_2})\mathrm{W(CO)_4}]$ (4).

them. Fig. 3 shows an ORTEP diagram of the anion of 4. The selected bond distances and angles for 4 are listed in Table 5. For 3, the geometry around the metal atom is a distored octahedron with a small SWS angle of 67.83(6)° and a small dihedral angle of 4.9(8)° between the planes WS(1)S(2) and WC(2)C(3), which were also observed for 4 (67.62(9), 68.28(9)° and 1.73(9), 3.67(8)°). The short C–N bond length (1.335(9) Å for 3 and 1.301(12), 1.335(12) Å for 4) indicates considerable partial double-bond character as is typical for the chelating 1,1-dithiolate ligands [2]. The coplanarity around the nitrogen atom (C5–C6–C10–N1 for 3 and C5–C7–C10–N6 for 4) is also consistent with the partial double bond character. All the C–S distances are about equal and are within the range 1.705(7)–1.726(10) Å.

The possible pathway for the formation of 1, 2 and 3 is shown in Scheme 1. The first step is abstraction of the NH proton of the piperidine ligand, resulting in an amide anion. This is followed by the insertion of a CS_2 into the M–N bond with loss of the other piperidine ligand. The nucleophilic attack of negatively charged nitrogen to the carbon atom of CS_2 weakens the M–N bond, possibly assisted by the better coordinating ability of the S atom thus causing the formation of the two M–S bonds.



Scheme 1.

The CS_2 insertion reaction into the M–N bond promoted by the abstraction of a proton on the nitrogen atom of the piperidine ligand by ^{n}BuLi in CH_3CN to form the η^2-dithiocarbamate ligand described above is, to our knowledge, the first example to be reported. It is noteworthy that this type of reaction provides an easy entry to the complex containing an η^2-dithiocarbamate ligand. Previous methods for the preparation of such a complex by the reaction of a metal complex with an organic dithiocarbamate ligand and Et_4NBr in refluxing solvents [12b,c] gave lower yields. The base-promoted CS_2 insertion found in the reaction of $[\mathrm{Cp(CO)_2Fe\text{-}NHR_2}]^+\mathrm{PF_6}^-$ with ^{t}BuOK–CS_2 formed the η^1-coordinated complex $\mathrm{Cp(CO)_2Fe\text{-}\eta^1\text{-}SC(S)NR_2}$ [20]. In our system with a Group VI transition metal, this method also gave a lower yield of the η^2-coordinated dithiocarbamate complex.

Supplementary material

Complete tables of atomic parameters, anisotropic thermal parameters and bond distances and angles are available from the author (7 pages).

Acknowledgment

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