Facile Synthesis and Crystal Structure of $[(PhSO_2N)_2W^{VI}Cl_2(CH_3CN)_2]$ – the Oxidative Imination of $W(CO)_6$ by N,N-Dichlorophenylsulphonamide

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Crystal Structure, Tungsten(VI), Nitrene

The reaction of N,N-dichlorophenylsulphonamide with tungsten hexacarbonyl in refluxing CCl_4 leads in good yield to the yellow polymeric complex $[(PhSO_2N)_2WCl_2]_x$, which may be converted to the octahedral nitrene complex $[(PhSO_2N)_2WCl_2(CH_3CN)_2]$ by recrystallisation from acetonitrile. Crystals of the acetonitrile complex are triclinic, space group $P\bar{1}$, $a = 820.7(2)$, $b = 1128.8(3)$, $c = 1286.9(3)$ pm, $\alpha = 89.25(3)$, $\beta = 89.54(3)$, $\gamma = 72.67(2)°$, $Z = 2$, $R = 0.027$ for 2527 unique observed reflections.

Nitrene complexes are formulated as intermediates in the transition-metal catalysed cleavage of the N_2 molecule [1, 2]. Several synthetic routes have been developed in recent years for the preparation of mononitrene complexes [3]. Transition metal complexes with bisnitrene ligands are rare [4–6]. Recently we reported the syntheses and crystal structures of six-membered metalla-dithiatriazenes containing two metal-nitrogen multiple bonds [7, 8]. It has been reported that elemental sulphur and N,N-dichlorophenylsulphonamide form $S(NSO_2Ph)_2$ by oxidative imination [9]. We have investigated the reaction of $Mo(CO)_6$ and $W(CO)_6$ with $PhSO_2NCl_2$ in order to establish whether a similar reaction is possible with transition metal compounds.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. The solvents were carefully dried over P_4O_{10} prior to use. The apparatus and commercially available materials were dried in vacuum (10^{-2} mbar). Infrared spectra were recorded on a Perkin Elmer 180 spectrometer with Nujol mulls, ^1H NMR spectra on Bruker WP 80 SY, ^{13}C NMR spectra on Bruker AM 250 spectrometers.

Dichloro-bis-N-(phenylsulphonyl)imido-tungsten(VI), $[(PhSO_2N)_2WCl_2]_x$

To a suspension of $W(CO)_6$ (5.3 g, 15 mmol) in CCl_4 (150 ml) was added dropwise a solution of $PhSO_2NCl_2$ (9.1 g, 40 mmol) in CCl_4 (70 ml) at 50–60 °C within 5 h. During the addition carbon monoxide was evolved and a dark yellow solid was formed. To complete the reaction the mixture was refluxed for 16 h. During the heating a small amount of chlorine was evolved. The resulting yellow solid was removed by filtration, washed with 3 portions (50 ml) of CCl_4 and dried *in vacuo*. Yield 6.1 g (72%); m.p. 235 °C (decomp.).

$[C_{12}H_{10}Cl_2N_2O_4S_2W]_x$
Calcd C25.49 H1.77 Cl12.57 N4.96 S11.30 W32.54,
Found C25.1 H1.7 Cl13.2 N4.7 S11.7 W31.6.

IR: 1586 m, 1451 vs, 1298 vs, 1191 s, 1178 s, 1145 sh, 1120 vs, 1083 sh, 1065 vs, 1036 sh, 1015 vs, 1001 vs, 752 m, 734 vs, 680 s, 645 m, 622 vs, 610 m, 584 vs, 552 m, 520 m, 337 vs cm^{-1}. ^1H NMR in CH_3CN solution: multiplet at δ 7.35–8.02 ppm. The ^{13}C NMR spectrum in CD_3CN/CH_3CN showed four signals for non-equivalent ^{13}C nuclei: δ 128.43, 130.34, 134.55, and 139.34 ppm.

$[(PhSO_2N)_2WCl_2(CH_3CN)_2]$

2 g of $[(PhSO_2N)_2WCl_2]_x$ were dissolved in CH_3CN (40 ml). When the CH_3CN was slowly removed from the yellow solution, an orange crystalline solid was formed in quantitative yield.

$C_{16}H_{16}Cl_2N_4O_4S_2W$
Calcd C 29.68 H 2.47 N 8.66,
Found C 29.4 H 2.6 N 8.3.

IR: 3062 w, 2323 s/2298 m (νC≡N), 1582 m, 1450 vs, 1378 s, 1365 m, 1335 sh, 1325 vs ($\nu_{as}SO_2$), 1307 m, 1291 m, 1170 sh, 1162 vs (ν_sSO_2), 1091 s, 1055 vs (νW=N), 1000 m, 950 w, 944 m, 757 m,

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729 vs, 687 s, 612 vs, 572 s, 542 m, 340 sh/325 s (νW−Cl) cm^{-1}.

$[Ph_3PNPPh_3]_2(Cl_5Mo{\equiv}N)$

$Mo(CO)_6$ (3.96 g, 15 mmol) and $PhSO_2NCl_2$ (9.05 g, 40 mmol) were reacted under the same conditions as described above. The crude product showed IR absorptions similar to the tungsten derivative. 2.0 g of the crude product were suspended in CH_2Cl_2 (50 ml) and $[Ph_3PNPPh_3]Cl$ (3.0 g) was added at room temperature. A clear solution was formed; this was layered with *n*-hexane and after 3 weeks at 4 °C red crystals were formed, which were recovered by filtration. Yield 1.69 g; m.p. 194 °C.

$C_{72}H_{60}Cl_5MoN_3P_4$

Calcd	Cl 13.00	N 3.08	P 9.09	S 0.00,
Found	Cl 13.9	N 3.2	P 8.8	S 0.02.

IR ν(Mo≡N) 1062 cm^{-1}. The literature [10] value for $[Ph_4As]_2[Cl_5Mo{\equiv}N]$ is 1059 cm^{-1}.

Results and Discussion

The bisnitrene complex $[(PhSO_2N)_2WCl_2]_x$ is formed by oxidative addition of N,N-dichlorophenylsulphonamide to $W(CO)_6$ and elimination of carbon monoxide according to the following equation:

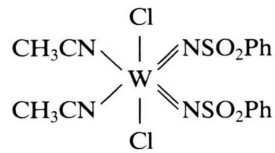
$$W(CO)_6 + 2\ PhSO_2NCl_2 \xrightarrow{CCl_4} \left[\begin{array}{c} Cl \\ \diagdown \\ W \\ \diagup \\ Cl \end{array}\!\!\begin{array}{l} \diagup\!\!\!= NSO_2Ph \\ \\ \diagdown\!\!\!= NSO_2Ph \end{array}\right] + 6\ CO + Cl_2$$

An intermediate such as $[Cl_2W{=}NSO_2Ph]_x$ could not be isolated. The addition of a second nitrene ligand, rather than the addition of further chlorine, is favoured. This selectivity was only observed in the case of $W(CO)_6$. In contrast $Mo(CO)_6$ reacts with $PhSO_2NCl_2$ with formation of $[Cl_4Mo{=}NSO_2Ph]_x$ and other products. During the working-up procedure bis(triphenylphosphine)iminium chloride $[Ph_3P{=}N{=}PPh_3]Cl$ was added, which converted the nitrene to the nitrido-complex

$$Cl_4Mo{=}NSO_2Ph + 2\ Cl^- \xrightarrow{2\ [Ph_3PNPPh_3]^+} [Ph_3PNPPh_3]_2[Cl_5Mo{\equiv}N] + ClSO_2Ph$$

This is the reverse reaction of the addition of $PhSO_2Cl$ to the nucleophilic nitrogen of $[MoN(S_2CNR_2)_3]$ [11].

In the structure of



the tungsten may be considered to be coordinated octahedrally by two chlorine atoms, two nitrene groups and two acetonitrile molecules. The nitrene ligands occupy *cis*-positions and the two acetonitrile molecules lie *trans* to them. The Cl(1)−W−Cl(2) angle is 157.3° instead of the idealised linear arrangement. The W−N bond [mean 177.6(5) pm] is surprisingly long for a linear nitrene geometry; such distances are usually only observed for bent imido geometry [3, 12].

X-ray structure determination, crystal data

$C_{16}H_{16}Cl_2N_4O_4S_2W$, M_r = 647.2, triclinic, a = 820.7(2), b = 1128.8(3), c = 1286.9(3) pm, α =

Table I. Atomic co-ordinates (×10^4) for $[(PhSO_2N)_2WCl_2(CH_3CN)_2]$ with estimated standard deviations in parentheses.

	x	*y*	*z*
W	89(1)	2479(1)	2475(1)
S(1)	2976(2)	3245(1)	3943(1)
S(2)	1135(2)	2264(1)	− 61(1)
N(1)	1666(6)	2985(4)	3135(3)
N(2)	792(6)	2335(4)	1170(4)
N(3)	−1313(6)	2529(5)	4014(4)
N(4)	−2110(6)	1807(5)	2004(4)
Cl(1)	−1968(2)	4388(2)	2270(1)
Cl(2)	1210(2)	377(1)	2948(1)
O(11)	4663(5)	2536(4)	3633(3)
O(12)	2592(7)	4553(4)	4052(3)
O(21)	1969(6)	3166(5)	− 350(4)
O(22)	1978(5)	995(4)	− 292(3)
C(3)	−2006(7)	2605(5)	4758(4)
C(4)	−3273(8)	1577(6)	1722(4)
C(5)	−2926(9)	2719(6)	5751(4)
C(6)	−4779(8)	1272(7)	1371(6)
C(11)	2510(7)	2592(5)	5114(4)
C(12)	3007(8)	1327(5)	5232(5)
C(13)	2616(10)	803(7)	6146(5)
C(14)	1787(10)	1550(7)	6929(5)
C(15)	1312(10)	2804(7)	6818(5)
C(16)	1650(9)	3356(6)	5896(5)
C(21)	− 937(7)	2707(5)	− 587(4)
C(22)	−1755(10)	3927(6)	− 747(5)
C(23)	−3428(12)	4253(8)	−1137(8)
C(24)	−4178(11)	3358(9)	−1343(7)
C(25)	−3331(9)	2158(7)	−1196(5)
C(26)	−1700(8)	1814(6)	− 806(5)

89.25(3), β = 89.54(3), γ = 72.67(2)° (refined from 2θ values of 30 strong reflections in the range 20–30°), monochromated MoKα radiation (λ = 71.069 pm), space group $P\bar{1}$, Z = 2, D_x = 1.90 g cm^{-3}, μ = 5.6 mm^{-1}.

Data collection and processing

Stoe-Siemens four-circle diffractometer, $2\theta_{max}$ 45°, index ranges h −8 to +5, k −12 to +12, l −13 to +13, 5917 profile-fitted [13] intensities, 2959 unique (R_{int} 0.022), 2527 with $F > 4\sigma(F)$ used for all calculations. Empirical absorption correction (ψ-scans, transmissions 0.26–0.51), crystal decay *ca.* 10% (correction based on check reflection intensities).

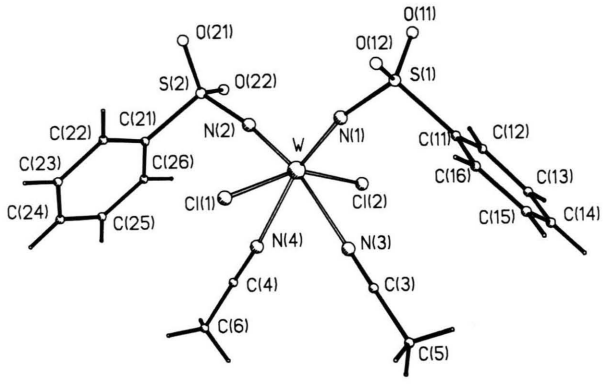


Figure. The molecule of $[(PhSO_2N)_2WCl_2(CH_3CN)_2]$.

Table II. Bond lengths (pm) and angles (°) for $[(PhSO_2N)_2WCl_2(CH_3CN)_2]$ with estimated standard deviations in parentheses.

W–N(1)	178.7(5)	W–N(2)	176.5(5)
W–N(3)	227.5(5)	W–N(4)	224.6(6)
W–Cl(1)	232.1(2)	W–Cl(2)	234.9(2)
S(1)–N(1)	159.3(5)	S(1)–O(11)	143.4(4)
S(1)–O(12)	142.4(5)	S(1)–C(11)	175.8(6)
S(2)–N(2)	160.6(5)	S(2)–O(21)	142.9(6)
S(2)–O(22)	142.7(4)	S(2)–C(21)	176.2(6)
N(3)–C(3)	110.1(8)	N(4)–C(4)	112.5(9)
C(3)–C(5)	146.7(9)	C(4)–C(6)	145.5(10)
C(11)–C(12)	137.0(8)	C(11)–C(16)	137.9(8)
C(12)–C(13)	138.7(10)	C(13)–C(14)	136.4(9)
C(14)–C(15)	135.8(10)	C(15)–C(16)	139.7(9)
C(21)–C(22)	135.4(8)	C(21)–C(26)	136.9(10)
C(22)–C(23)	140.7(12)	C(23)–C(24)	136.1(15)
C(24)–C(25)	133.7(11)	C(25)–C(26)	137.5(10)
N(1)–W–N(2)	104.0(2)	N(1)–W–N(3)	88.9(2)
N(2)–W–N(3)	167.1(2)	N(1)–W–N(4)	167.3(2)
N(2)–W–N(4)	88.6(2)	N(3)–W–N(4)	78.5(2)
N(1)–W–Cl(1)	98.7(1)	N(2)–W–Cl(1)	96.3(1)
N(3)–W–Cl(1)	81.2(1)	N(4)–W–Cl(1)	81.3(1)
N(1)–W–Cl(2)	95.7(1)	N(2)–W–Cl(2)	97.2(2)
N(3)–W–Cl(2)	81.5(1)	N(4)–W–Cl(2)	80.9(1)
Cl(1)–W–Cl(2)	157.3(1)	N(1)–S(1)–O(11)	107.8(2)
N(1)–S(1)–O(12)	108.1(3)	O(11)–S(1)–O(12)	119.2(3)
N(1)–S(1)–C(11)	104.0(3)	O(11)–S(1)–C(11)	107.3(2)
O(12)–S(1)–C(11)	109.4(3)	N(2)–S(2)–O(21)	108.8(3)
N(2)–S(2)–O(22)	106.9(2)	O(21)–S(2)–O(22)	118.0(3)
N(2)–S(2)–C(21)	103.2(2)	O(21)–S(2)–C(21)	109.2(3)
O(22)–S(2)–C(21)	109.8(3)	W–N(1)–S(1)	166.5(3)
W–N(2)–S(2)	171.5(3)	W–N(3)–C(3)	177.1(5)
W–N(4)–C(4)	173.4(5)	N(3)–C(3)–C(5)	179.4(8)
N(4)–C(4)–C(6)	179.3(6)	S(1)–C(11)–C(12)	119.1(4)
S(1)–C(11)–C(16)	119.8(5)	C(12)–C(11)–C(16)	121.1(5)
C(11)–C(12)–C(13)	119.5(5)	C(12)–C(13)–C(14)	119.8(6)
C(13)–C(14)–C(15)	120.7(7)	C(14)–C(15)–C(16)	120.7(6)
C(11)–C(16)–C(15)	118.1(6)	S(2)–C(21)–C(22)	119.2(5)
S(2)–C(21)–C(26)	119.4(4)	C(22)–C(21)–C(26)	121.4(6)
C(21)–C(22)–C(23)	117.9(8)	C(22)–C(23)–C(24)	120.2(7)
C(23)–C(24)–C(25)	120.7(8)	C(24)–C(25)–C(26)	120.2(8)
C(21)–C(26)–C(25)	119.6(6)		

Structure analysis and refinement

Conventional heavy atom methods, refinement on F to R 0.027, R_w 0.026 [all non-H atoms anisotropic, H atoms included in refinement using a riding model; weighting scheme $w^{-1} = \sigma^2(F) + 0.0003\ F^2$; extinction correction of the form $F_{corr} = F_{calc}/(1 + xF^2_{calc}/\sin 2\theta)^{0.25}$ where x refined to $9(1) \times 10^{-7}$].

Atomic coordinates and derived parameters are given in the Tables*.

* Further crystallographic details (structure factors, H atom coordinates, temperature factors) can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Fed. Rep. of Germany. Please quote the Deposition Number CSD 51290 and the exact literature reference.

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