Anionic Tungsten Carbonyl Complexes Containing Dithiocarboxylate, Dithiocarbamate, and Xanthate Ligands

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The reaction of $Et_4N[W(CO)_5Cl]$ with sodium dithiobenzoate, ethylxanthate, or various dithiocarbamates gave the corresponding salts $Et_4N[W(CO)_4(SSCX)]$ (X = Ph, NEt₂, N(H)*t*-Bu, NPh₂, OEt) which contain the dithio ligand in a chelating bonding mode. Two of them (X = N(H)*t*-Bu, NPh₂) were characterized by X-ray crystallography. The tungsten atom resides in the center of a slightly distorted octahedron surrounded by a symmetrically bidentate planar dithio ligand and four CO groups. Reaction with PPh₃ or PMe₃ at elevated temperature gave the tricarbonyl complexes $Et_4N[W(CO)_3(PR_3)(SSCX)]$ and in one case a ring-opened addition product, $Et_4N[W(CO)_4(PMe_3)(SC(S)OEt)]$. For two of them X-ray structure determinations were carried out. A comparison of the four structures shows that while the W–C bond length decreases progressively with increasing electron density at the tungsten atom, the W–S and W–P bond lengths remain essentially constant.

Key words: Tungsten, Dithiocarboxylate Complexes, Dithiocarbamate Complexes, Xanthate Complexes, Carbonyl Complexes

Introduction

We have shown recently that certain tungsten carbonyl anions such as $[W(CO)_5(CN)]^-$ or the thiolate complexes [W(CO)₅(SR)]⁻ are sufficiently lipophilic to be absorbed by the lipid bilayer membrane of living cells [1-5]. This leads to a change in the dielectric properties of the membrane which can be monitored by a number of methods, most notably the "electrorotation" experiment [6]. Some of the tungsten carbonyl anions exhibit stronger effects and a markedly lower cytotoxicity compared to more conventional anions such as dipicrylamide or tetraphenylborate, which can be very important when in comes to practical applications [7]. In order to gain some insight into the relationship between structure and activity we decided to include tungsten tetracarbonyl complexes of dithiocarboxylates, dithiocarbamates, and xanthates in our studies. The bidentate coordination of these anions was expected to confer improved stability to these systems.

Dithiocarbamates and xanthates have been used extensively as ligands [8]. Their metal complexes are found in applications as diverse as agrochemicals, vulcanization promotors, or analytical reagents [9]. Dithiocarbamate complexes of the group 6 metals fall into roughly three categories: High oxidation state (d⁰, d¹, d²) complexes with additional π donor (mostly oxo or sulfido) ligands [10–15], medium oxidation state (d⁴) complexes with additional π acceptor (carbonyl, alkyne) ligands [16–24], and anionic d⁶ carbonyl complexes [25–31]. Similar compounds containing xanthates [25, 27, 28, 32] or dithiocarboxylates [33–35] as ligands have also been reported in the literature. In the d⁶ complexes the dithio anions may act as either mono- or chelating bidentate ligands wheras the chelating mode prevails for the electronic configurations d⁰ – d⁴.

Results and Discussion

Synthesis

Tetraethylammonium-chloropentacarbonyltungstate [36] reacts readily with the sodium salts of the various dithioanions to give the tetracarbonyltungstates 1-3 (eq (1)).

Monitoring the progress of the reaction by infrared spectroscopy showed that the corresponding

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Table 1. Characteristic infrared absorptions (cm^{-1}) of the tetracarbonyltungstates 1-3, recorded from acetonitrile solutions.

	A ₁	A ₁	B ₁	B ₂
1	1994	1877	1859	1822
2a	1995	1865	1843	1801
2b	1995	1866	1842	1801
2c	1996	1868	1845	1804
3	2002	1874	1854	1812

pentacarbonyl anions were involved as intermediates, but no particular effort was made to isolate them. The products were obtained as microcrystalline, air-stable compounds. The dithiobenzoate complex 1 has a deep purple color while the dithiocarbamate and xanthate derivatives are bright yellow. 2a had previously been synthesized in 55% vield directly from [W(CO)₆], Et₄NCl and sodiumdiethyldithiocarbamate [30]. Due to their ionic structure, 1-3 are soluble only in polar organic solvents such as THF, acetone, dichloromethane or acetonitrile. Their infrared spectra in the CO stretching region (Table 1) display the expected four bands which are shifted to low wavenumbers as a result of the negative charge. The ¹³C NMR signals of the carbonyl groups (Table 2) are shifted to low field and exhibit the expected couplings with ¹⁸³W [34].

CO/PR₃ exchange

The reactions of **2a** and **3** with triphenylphosphine and trimethylphosphine were checked in order to test the lability of the ligands at tungsten and to increase the lipophilicity of the anion. In contrast to an earlier notion [37] we found that **2a** and **3** do react with triphenylphosphine to give the tricarbonyl complexes **4a** and **5** (eq. (2)). **4a** had previously been obtained from [W(CO)₃(py)₃], PPh₃ and sodiumethylxanthate in unspecified yield [37]. With the better donor trimethylphosphine, the dithiocarbamate **2a** gave the analogous substitution product **4b**; the xanthate **3**, however, yielded the ring opened complex **6** (eq. (3)).

Table 2. Characteristic 13 C NMR resonances of the tetracarbonyltungstates 1-3, recorded from [D₆]-acetone solutions.

		,		01	
	CO (cis)	$^{1}J(W-C)$ (Hz)	CO (trans)	$^{1}J(W-C)$ (Hz)	СХ
1	203.1	128	213.5	168	248.1
2a	204.6	128	214.0	172	214.5
2b	204.8	128	214.1 ^a		217.8
2c	204.3	127	213.7	173	219.3
3	203.3	128	212.7	175	229.9
a B	road				

Table 3. Characteristic ${}^{13}C$ and ${}^{31}P$ NMR resonances of the tricarbonyltungstates **4a**, **4b**, **5**, recorded from $[D_6]$ -acetone solutions.

	¹³ C NMR			³¹ P NMR	
	$CO = {}^{2}J(P-C)$	$CO = {}^{2}J(P-C)$	CX	$PR_3 = {}^1J(W-P)$	
	(cis) (Hz)	(trans) (Hz)		(Hz)	
4a	217.3 48	219.8 6	213.4	24.8 190	
4b	218.4 49	221.2 6	215.1 ^a	-27.9 193	
5	214.7 43	218.6 6	227.3 ^b	29.0 205	

^a ³*J*(P-C) 4 Hz; ^b ³*J*(P-C) 6 Hz.



The phosphine derivatives are again yellow, airstable compounds which are, like their precursor complexes, also soluble in polar solvents. That **6** is a tetracarbonyl complex is immediately obvious from its infrared spectrum which exhibits bands at 1998, 1882, 1866 and 1824 cm⁻¹, very similar to the spectra of **1**-**3** or the complexes $Et_4N[W(CO)_4(PR_3)CI]$ [38] to which it might be reasonably compared. The tricarbonyl complexes **4a**, **4b**, and **5** have still lower CO frequencies. The ¹³C resonances of the CO ligands are shifted even further downfield and exhibit the requisite ³¹P-¹³C couplings (Table 3). Interestingly, and perhaps disappointingly, the chemical shift of the dithiocar-



Fig 1. Structure of the anion of Et₄N[W(CO)₄ (SSCN(H)tBu)] (2b), hydrogen atoms [except for H(1)] omitted for clarity. Space group $P2_1/n$. Selected bond lengths [pm], angles [°], and torsion angles [°] (estimated standard deviations in parentheses): W(1)-S(1) 257.68(8), W(1)–S(2) 258.90(8), S(1)–C(5) 170.8(3), S(2)–C(5) 172.3(3), N(1)-C(5)132.8(4), W(1) - C(1)195.3(3), W(1)-C(2) 194.0(3), W(1)-C(3) 202.6(4), W(1)-C(4) 202.6(3); S(1)-W(1)-S(2) = 68.06(2),S(1)-C(5)-S(2)114.77(17), S(1)–W(1)–C(2) 167.86(9), S(2)–W(1)–C(1) 167.88(10), C(1)-W(1)-C(2) 91.45(13), C(3)-W(1)-C(4) 176.94(13); S(1)-C(5)-N(1)-C(6) -4.5(5).

bamate and xanthate carbon changes very little upon CO/PR_3 exchange and, at least when compounds **5** and **6** are compared, does not allow any distinction between mono- and bidentate coordination.

Structures

The structures of the anions of **2b** (Fig. 1), **2c** (Fig. 2), **4a** (Fig. 3), and **5** (Fig. 4) exhibit a fairly regular octahedral coordination of the tungsten atom.

Deviations arise from the small bite angle of the bidentate sulfur ligand which restricts the S-W-S angle to 68°. The trans pair of ligands is slightly bent away from the coordinated dithio ligand such that the C-W-C (trans) angles in 2b and 2c, and the P-W-C (trans) angles in 4a and 5, are reduced to values between 171 and 177°. The W-S bond lengths are close to those in 2a [30], and the W-P bond lengths in 4a and 5 are almost identical to those in the neutral complex [W(CO)₅(PPh₃)] [39]. The dithio ligands are coordinated symmetrically, i. e. the two W-S and C-S bond lengths in each complex are almost identical. The four-membered rings are nearly planar, the largest deviation occurs in 2b where the planes defined by S(1)-W(1)-S(2) and S(1)-C(5)-S(2) span an angle of $12.3(2)^{\circ}$. Inspection of the unit cell reveals that in this case the distortion is caused by close packing of the N(H)*t*-Bu group against the Et₄N⁺ cation. The phosphine substitution products 4a and 5 have even smaller interplanar angles $[9.0(3)^{\circ} \text{ and } 4.0(2)^{\circ}, \text{ respec-}$



Fig 2. Structure of the anion of Et₄N[W(CO)₄(SSCNPh₂)] (2c), hydrogen atoms omitted for clarity. Space group $P\overline{1}$. Selected bond lengths [pm], angles [°], and torsion angles [°] (estimated standard deviations in parentheses): W(1)-S(1) 257.59(7), W(1)-S(2) 259.59(7), S(1)-C(5) 170.3(3), S(2)–C(5) 170.7(3), N(1)–C(5) 134.7(3). W(1)–C(1) 200.6(3), W(1)-C(2) 194.5(3), W(1)-C(3)195.6(3), W(1)-C(4) 202.4(3); S(1)-W(1)-S(2) 67.78(2), S(1)-C(5)-S(2) 115.49(15), S(1)-W(1)-C(3) 168.04(9), S(2)-W(1)-C(2) 167.72(9), C(1)-W(1)-C(4) 171.11(11), C(2)-W(1)-C(3) 90.45(12); S(1)-C(5)-N(1)-C(30) 11.3(4), S(2)-C(5)-N(1)-C(20) 15.6(4). The second independent anion in the cell has nearly identical geometric data.



Fig 3. Structure of the anion of Et₄N[W(CO)₃(PPh₃) (SSCNEt₂)] (4a), hydrogen atoms omitted for clarity. Space group $P\overline{1}$. Selected bond lengths [pm], angles [°], and torsion angles [°] (estimated standard deviations in parentheses): W(1)-S(1) 258.95(11), W(1)-S(2) 258.17(10), W(1)-P(1) 254.12(10), S(1)-C(4) 171.6(4), S(2)-C(4) 171.5(4), N(1)-C(4) 133.4(5), W(1)-C(1) 196.5(5), W(1)-C(2)192.9(5), W(1)-C(3) 194.1(5); S(1)-W(1)-S(2) 67.87(3), 98.88(4), S(2)-W(1)-P(1)S(1)-W(1)-P(1)90.11(3). S(1)-C(4)-S(2) 114.6(2), S(1)-W(1)-C(3) 168.68(16), S(2)-W(1)-C(2) 167.33(18), P(1)-W(1)-C(1) 173.33(16), C(2)-W(1)-C(3) 90.5(2); S(1)-C(4)-N(1)-C(5) 2.9(6), S(2)-C(4)-N(1)-C(7) 4.8(6).

tively]. In these cases the dithio ligands are bent away from the PPh_3 ligand indicating that the distortion is caused by steric repulsion. In **2b**, **4a** and **5** the dithio





Fig 4. Structure of the anion of Et₄N[W(CO)₃(PPh₃) (SSCOEt)] (5), hydrogen atoms omitted for clarity. Space group $P2_1/n$. Selected bond lengths [pm], angles [°], and torsion angles [°] (estimated standard deviations in parentheses): W(1)–S(1) 261.10(7), W(1)–S(2) 259.72(7), W(1)–P(1) 168.7(3), S(2)-C(4)168.6(3). W(1) - C(2)193.1(3), W(1)-C(3) 195.6(3); S(1)-W(1)-S(2) 67.60(2), S(1)-W(1)-P(1)87.94(2), S(2)-W(1)-P(1)96.01(2). S(1)-C(4)-S(2) 118.39(17), S(1)-W(1)-C(2) 168.16(9), S(2)-W(1)-C(1) 171.90(9), P(1)-W(1)-C(3) 171.30(9), C(1)-W(1)-C(2) 86.53(12); S(2)-C(4)-O(4)-C(5) - 1.2(4).

ligands are almost perfectly planar. In **2c** the dihedral angles around the C(5)–N(1) bond deviate significantly from the expected 0 or 180° , certainly as a result of the bulkiness of the two phenyl groups.

Conclusions

The synthesis of anionic tungsten carbonyl complexes designed for their possible application as reagents to modify the dielectric properties of lipid membranes was the principal goal of this work. In our hands, the reaction of Et₄N[W(CO)₅Cl] with salts of the anionic ligands gave cleaner products than any other method [25-35,37]. The characterization of these compounds by IR and ¹³C NMR spectroscopy (Tables 1, 2) gave the expected results. The data listed in Table 1 show that the dithiocarbamate ligands are even better electron donors than dithiobenzoate or ethylxanthate. This points to a contribution of a resonance structure with a C=N double bond (eq. (4)) which is in line with the observed NMR resonance of this C atom at higher field (Table 2) and also with the planar geometry around the N atom.

Some regular geometric trends emerge when the structures of 2c and 4a are compared with those of their parent compounds $[W(CO)_6]$ [40] and $[W(CO)_5(PPh_3)]$ [39]. With successive replacement of

CO groups by the better donors PPh₃ or dithiocarbamate, the W-C bonds become shorter due to the increased back donation into the π^* levels of the remaining CO ligands. This contraction is roughly three times as big for the W-C bonds trans to the new ligand than those cis (e. g. -4.2 vs. -1.5 pm for the pair [W(CO)₆] and $[W(CO)_5(PPh_3)]$, and -9.8 vs. -3.3 pm for the pair $[W(CO)_6]$ and **2c**). This rule of thumb even holds for the pair 2c/4a, where the W–C bond *trans* to P (and *cis* to S) contracts by -5.0 pm while the other two shrink only by -1.5 pm. The interrelation of M–C and M-P bond lengths and electron density has been noted quite some time ago and is usually discussed within a σ/π bonding model [41,42]. The similarity of the W–P bond lengths of $[W(CO)_5(PPh_3)]$, 4a, and 5 then indicates that σ bonding effects, which should give rise to a lengthening of the W-P bond upon replacing two CO ligands by a dithiocarbamate or xanthate, and π bonding effects, which should lead to a contraction, almost cancel. This is perfectly in line with the notion that PR₃ ligands are to some degree capable of undergoing π interactions with low-valent transition metal complexes [43].

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. – IR: Bruker IFS 25. – ¹H NMR: Bruker AMX 400, Jeol JNM-LA 300, δ values relative to TMS. The signals of the Et₄N⁺ cation [δ = 1.35 (tt, J = 7.3 Hz, J' = 1.8 Hz, 12 H, NCH₂CH₃), 3.40 (q, J = 7.3 Hz, 8 H, NCH₂CH₃)] are similar for all compounds and have therefore been omitted from the lists of spectral data. – ¹³C NMR: Bruker AMX 400, Jeol JNM-LA 300, δ values relative to TMS, assignments routinely checked by DEPT spectra. In some cases the signals of quarternary carbon atoms were too weak to be detected. The signals of the Et₄N⁺ cation [δ = 7.6 (s, NCH₂CH₃), 53.0 (t, J = 3 Hz, NCH₂CH₃)] are similar for all compounds and have therefore been omitted from the lists of spectral data. – ³¹P NMR: Bruker AMX 400, Jeol JNM-LA 300, δ val-

	2b	2c	4a	5
Empirical formula	$C_{17}H_{30}N_2O_4S_2W$	$C_{25}H_{30}N_2O_4S_2W$	C34H45N2O3PS2W	C ₃₂ H ₄₀ NO ₄ PS ₂ W
Formula mass	574.42	670.51	808.70	781.63
Crystal colour/habit	yellow plate	orange block	yellow prism	yellow plate
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	11.0161(11)	10.8057(7)	9.5615(8)	9.0861(6)
b [Å]	11.9892(12)	15.1922(10)	10.3885(8)	16.8115(11)
c [Å]	17.6605(17)	16.7423(11)	17.6669(14)	21.2534(14)
α [°]	90	88.127(1)	100.503(1)	90
β [°]	106.399(2)	84.885(1)	94.924(1)	93.123(1)
γ[°]	90	80.161(1)	90.823(1)	90
V [Å ³]	2237.6(4)	2696.8(3)	1718.3(2)	3241.7(4)
θ[°]	1.96 - 28.26	1.81 - 28.28	1.99-28.29	2.39 - 28.29
h	-14 to 14	-14 to 14	-12 to 12	-12 to 12
k	-15 to 15	-20 to 19	-13 to 13	-22 to 22
1	-23 to 23	-22 to 21	-23 to 23	-27 to 28
Ζ	4	4	2	4
μ (Mo-K $_{\alpha}$) [mm ⁻¹]	5.371	4.470	3.565	3.778
Crystal size [mm]	$0.15 \times 0.15 \times 0.05$	$0.20 \times 0.20 \times 0.15$	$0.20\times0.15\times0.15$	$0.20 \times 0.20 \times 0.10$
$D_{\text{calcd.}} [\text{gcm}^{-3}]$	1.705	1.651	1.563	1.601
T [K]	173(2)	173(2)	173(2)	173(2)
Reflections coll.	43621	61863	39365	54554
Indep. reflections	5316	12521	7992	7600
Parameter	246	621	364	375
$R_1(I > 2\sigma(I))$	0.0272	0.0248	0.0364	0.0267
R_1 (all data)	0.0327	0.0275	0.0383	0.0280
$wR_2(I > 2\sigma(I))$	0.0578	0.0536	0.0925	0.0576
wR_2 (all data)	0.0595	0.0547	0.0936	0.0583
Diff. peak/hole [eÅ ⁻³]	1.161 / -0.627	1.038 / -0.426	2.258/-2.317	1.037/-0.354
CCDC	298204	298202	298203	298201

Table 4. Details of the structure determinations of compounds **2b**, **2c**, **4a**, and **5**

ues relative to 85% H ₃ PO ₄ . – Elemental analyses: Analyt-
ical Laboratory of the Institut für Anorganische Chemie
The following starting materials were obtained as described
in the literature: Et ₄ N[W(CO) ₅ Cl] [36], Et ₄ N[SSCPh] [44],
xanthates and dithiocarbamates [45]. All other reagents were
used as purchased.

$Et_4N[W(CO)_4(SSCPh)]$ (1)

A solution of $Et_4N[W(CO)_5Cl]$ (490 mg, 1.00 mmol) and $Et_4N[SSCPh]$ (290 mg, 1.02 mmol) in THF (15 ml) was heated under reflux for 30 min. More THF (20 ml) was added, and the mixture filtered over silica/celite. The filtrate was evaporated to dryness and the residue washed with diethyl ether. Yield 270 mg (47%), dark purple microcrystalline powder.

M. p. 52 °C (dec). $^{-1}$ H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 7.31 - 7.38$ (m, 2 H, C₆H₅), 7.47 - 7.52 (m, 1 H, C₆H₅), 8.02 - 8.09 (m, 2 H, C₆H₅). $^{-13}$ C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 123.1$ (s, C₆H₅), 128.3 (s, C₆H₅), 132.0 (s, C₆H₅), 147.7 (s, C₆H₅), 203.1 (s, J(W, C) = 128 Hz, *cis*-CO), 213.5 (s, J(W, C) = 168 Hz, *trans*-CO), 248.1 (s, SSC). - C₁₉H₂₅NO₄S₂W (579.39): calcd. C 39.39, H 4.35, N 2.42, S 11.07; found C 38.89, H 4.38, N 2.32, S 11.50.

$Et_4N[W(CO)_4(SSCX)]$ (2a – c, 3)

A solution of $Et_4N[W(CO)_5Cl]$ (980 mg, 2.00 mmol) and sodium dithiocarbamate or xanthate (2.05 mmol) in acetonitrile (20 ml) was heated under reflux for 2 h. Gas evolution was observed, and the yellow solution turned dark brown. The solvent was removed under vacuum, and the residue dissolved in THF/acetone 10:1 and filtered over a layer of silica gel (1 cm) and celite (5 cm). The yellow-brown filtrate was evaporated to dryness and the residue washed with diethyl ether.

2a: Yield 0.89 g (78%), yellow powder. – M. p. 68 °C (dec). – ¹H NMR (400 MHz, acetone-d₆, 20 °C): δ = 1.19 (t, *J* = 7.0 Hz, 6 H, NCH₂CH₃), 3.67 (q, *J* = 7.0 Hz, 4 H, NCH₂CH₃). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): δ = 12.6 (s, NCH₂CH₃), 44.2 (s, NCH₂CH₃), 204.6 (s, *J*(W,C) = 128 Hz, *cis*-CO), 214.0 (s, *J*(W,C) = 172 Hz, *trans*-CO), 214.5 (s, SSCN). – C₁₇H₃₀N₂O₄S₂W (574.42): calcd. C 35.55, H 5.26, N 4.88, S 11.16; found C 35.35, H 5.29, N 4.95, S 11.05.

2b: Yield 0.77 g (67%), brown powder. – M. p. 55 °C (dec). – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 1.50$ (s, 9 H, NC(CH₃)₃), NH signal not detected. – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 28.8$ (s, NC(CH₃)₃), 55.3 (s, NC(CH₃)₃), 204.8 (s, J(W,C) = 128 Hz, *cis-CO*),

214.2 (s, trans-CO), 217.8 (s, SSCN). - $C_{17}H_{30}N_2O_4S_2W$ (574.42): calcd. C 35.55, H 5.26, N 4.88, S 11.16; found C 35.24, H 4.86, N 4.31, S 11.52.

2c: Yield 0.66 g (49%), yellow-brown powder. – M. p. 52 °C (dec). – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta =$ 7.23 – 7.44 (m, 10 H, C₆H₅). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta =$ 127.8 (s, C₆H₅), 129.1 (s, C₆H₅), 129.8 (s, C₆H₅), 144.9 (s, C₆H₅), 204.3 (s, *J*(W,C) = 127 Hz, *cis*-CO), 213.7 (s, *J*(W,C) = 173 Hz, *trans*-CO), 219.3 (s, SSCN). – C₂₅H₃₀N₂O₄S₂W (670.51): calcd. C 44.78, H 4.51, N 4.18, S 9.56; found C 43.95, H 4.78, N 3.98, S 9.52.

3: Yield 1.01 g (93%), yellow powder. – M. p. 74 °C (dec). – ¹H NMR (400 MHz, acetone-d₆, 20 °C): δ = 1.34 (t, J = 7.0 Hz, 3 H, OCH₂CH₃), 4.43 (q, J = 7.0 Hz, 2 H, OCH₂CH₃). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): δ = 14.0 (s, OCH₂CH₃), 66.7 (s, OCH₂CH₃), 203.3 (s, J(W,C) = 128 Hz, *cis*-CO), 212.7 (s, J(W,C) = 175 Hz, *trans*-CO), 229.9 (s, SSCO). – C₁₅H₂₅NO₅S₂W (547.35): calcd. C 32.92, H 4.60, N 2.56, S 11.72; found C 32.64, H 4.47, N 2.44, S 11.72.

$Et_4N[W(CO)_3(PR_3)(SSCX)]$ (4a, 4b, 5) and $Et_4N[W(CO)_4(PMe_3)(SC(S)OEt)]$ (6)

A solution of **2a** or **3** (0.25 mmol) and PPh₃ (0.10 g, 0.38 mmol) or PMe₃ (80 μ l, 0.77 mmol) in acetonitrile (10 ml) was heated under reflux until the starting material was completely consumed (IR). The mixture was evaporated to dryness and the excess phosphine removed by extraction with diethyl ether and hexane.

4a: Yield 0.18 g (90%), yellow solid. – M. p. 34 °C (dec). – IR (CH₃CN): $\tilde{v} = 1889$, 1772, 1757 (CO) cm⁻¹. – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 0.94$ (t, J = 7.0 Hz, 6 H, NCH₂CH₃), 3.34 (q, ³J(H,H) = 7.0 Hz, 4 H, NCH₂CH₃), 7.22 – 7.30 (m, 8 H, PC₆H₅), 7.35 – 7.40 (m, 2 H, PC₆H₅), 7.61 – 7.68 (m, 5 H; PC₆H₅). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 12.6$ (s, NCH₂CH₃), 44.0 (s, NCH₂CH₃), 127.8 (d, J = 8 Hz, m-PC₆H₅), 128.8 (d, J = 1 Hz, p-PC₆H₅), 135.4 (d, J = 11 Hz, o-PC₆H₅), 137.9 (d, J = 28 Hz, i-PC₆H₅), 213.4 – 213.5 (br, SSCN), 217.3 (d, J = 48 Hz, CO), 219.8 (d, J = 6 Hz, CO). – ³¹P{¹H} NMR (162 MHz, acetone-d₆, 20 °C): $\delta = 24.8$ (s, J(W,P) = 190 Hz). – C₃₄H₄₅N₂O₃PS₂W (808.70) – calcd. C 50.50, H 5.61, N 3.46, S 7.93; found C 50.31, H 5.52, N 3.22, S 8.13.

4b: Yield 0.12 g (76%), yellow microcrystalline powder. M. p. 24 °C (dec). – IR (THF): $\tilde{\nu} = 1883$, 1766, 1746 (CO) cm⁻¹. – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 1.17$ (t, J = 7.0 Hz, 6 H, NCH₂CH₃), 1.36 (d, J =6.2 Hz, 9 H, PCH₃), 3.55 – 3.73 (m, 4 H, NCH₂CH₃). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 12.8$ (s, NCH₂CH₃), 16.6 (d, J = 19 Hz, PCH₃), 44.2 (s, NCH₂CH₃), 215.1 (d, J = 4 Hz, SSCN), 218.4 (d, J(W,C) = 165 Hz, J(P,C) = 49 Hz, CO), 221.2 (d, J(W,C) = 179 Hz, J(P,C) = 6 Hz, CO). $-{}^{31}P{}^{1}H{}$ NMR (162 MHz, acetone-d₆, 20 °C): $\delta = -27.9$ (s, J(W,P) = 193 Hz). $- C_{19}H_{39}N_2O_3PS_2W$ (622.49): calcd. C 36.66, H 6.32, N 4.50, S 10.30; found C 36.41, H 5.91, N 4.22, S 10.05.

5: Yield 0.19 g (97%), orange-yellow solid. M. p. 66 °C (dec). – IR (CH₃CN): $\tilde{\nu} = 1898$, 1784, 1767 (CO) cm⁻¹. – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 1.11$ (t, J = 7.0 Hz, 3 H, OCH₂CH₃), 3.96 (q, J = 7.0 Hz, 2 H, OCH₂CH₃), 7.26–7.31 (m, 8 H, PC₆H₅), 7.36–7.40 (m, 2 H, PC₆H₅), 7.62–7.68 (m, 5 H; PC₆H₅). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 14.0$ (s, OCH₂CH₃), 65.5 (s, OCH₂CH₃), 128.0–135.2 (m, PC₆H₅), 137.7 (d, J = 30 Hz, *i*-PC₆H₅), 214.7 (d, J = 43 Hz, CO), 218.6 (d, J = 182 Hz, J = 6 Hz, CO), 227.3 (d, J = 6 Hz, SSCO). – ³¹P{¹H} NMR (162 MHz, acetone-d₆, 20 °C): $\delta = 29.0$ (s, J(W,P) = 205 Hz). – C₃₂H₄₀NO₄PS₂W (781.63): calcd. C 49.17, H 5.16, N 1.79, S 8.21; found C 48.96, H 5.13, N 1.63, S 7.79.

6: Yield 0.15 g (96%), yellow microcrystalline powder. M. p. 62 °C. – IR (THF): $\tilde{v} = 1998$, 1882, 1866, 1824 (CO) cm⁻¹. – ¹H NMR (400 MHz, acetone-d₆, 20 °C): $\delta = 1.34$ (t, J = 7.0 Hz, 3 H, OCH₂CH₃), 1.48 (d, J = 7.4 Hz, 9 H, PCH₃), 4.46 (q, J = 7.0 Hz, 2 H, OCH₂CH₃). – ¹³C{¹H} NMR (100 MHz, acetone-d₆, 20 °C): $\delta = 14.4$ (s, OCH₂CH₃), 19.3 (d, J = 25 Hz, PCH₃), 68.6 (s, OCH₂CH₃), 206.3 d, J(W,C) = 127 Hz, J(P,C) = 9 Hz CO), 212.3 (d, J(W,C) = 153 Hz, J(P,C) = 31 Hz, CO), 212.3 (d, J(W,C) = 160 Hz, J(P,C) = 5 Hz, CO), 227.2 (d, J(P,C) = 4 Hz, SSCO). – ³¹P{¹H} NMR (162 MHz, acetone-d₆, 20 °C): $\delta = -32.8$ (s, J(W,P) = 220 Hz). – C₁₈H₃₄NO₅PS₂W (623.43): calcd. C 34.68, H 5.50, N 2.25, S 10.29; found C 34.08, H 5.31, N 2.01, S 10.16.

X-ray structure determinations

Single crystals of **2b**, **2c**, **4a**, or **5** were sealed to a glass fiber with frozen hydrocarbon oil. A Bruker Smart Apex CCD instrument with D8 goniometer was used for data collection (graphite monochromator, Mo-K_{α} radiation, $\lambda = 0.71073$ Å). The structures were solved using Patterson methods and refined with full-matrix least squares against F² (SHELXS-97) [46]. Hydrogen atoms were included in their calculated positions and refined in a riding model. The details of the measurements are summarized in Table 4. Further data may be obtained from the Cambridge Crystallographic Data Centre. **2b**: CCDC 298204, **2c**: CCDC 298202, **4a**: CCDC 298203, **5**: CCDC 298201. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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