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REACTIONS OF BIMETALLIC GROUP VI COMPLEXES

II *. PHOSPHINE AND PHOSPHITE DERIVATIVES; LIGAND TRANSFER AND OXIDATIVE DECARBONYLATION; THE CRYSTAL STRUCTURE OF $[(C_5H_5)(OC)_2\overline{W(\mu\text{-}SMe)(\mu\text{-}I)W}(CO)_3I]$ **

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Summary

Triphenylphosphine and trimethylphosphite react with $[(C_5H_5)(OC)_2\overline{M(\mu\text{-}SMe)M'}(CO)_5]$ (M, M′ = Mo, W) (II) to give $[(C_5H_5)(OC)_2LM(\mu\text{-}SMe)M'(CO)_5]$ which on heating revert to II. On prolonged heating $[(C_5H_5)(OC)_2\overline{Mo(\mu\text{-}SMe)W}(CO)_4\{P(OMe)_3\}]$ is formed. $[(C_5H_5)(OC)_3W(\mu\text{-}SMe)W(CO)_5]$ reacts with I_2 to give $[(C_5H_5)(OC)_2\overline{W(\mu\text{-}SMe)(\mu\text{-}I)W}(CO)_3I]$ for which the crystal structure has been determined.

Introduction

We recently described [1] the preparation and reversible decarbonylation of some thiolato bridged bimetallic complexes (M, M′ = Cr, Mo, W) with formation of a

$$\underset{(I)}{[(C_5H_5)(OC)_3M(\mu\text{-}SR)M'(CO)_5]} \xrightleftharpoons[h\nu(+CO)]{\Delta(-CO)} \underset{(II)}{[(C_5H_5)(OC)_2\overline{M(\mu\text{-}SR)M'}(CO)_5]}$$

metal–metal bonded species II by decarbonylation of I (eq. 1). The octacarbonyls I react with hexafluorobut-2-yne with substitution of terminal carbonyls on M (the cyclopentadienyl-metal centre). We now describe further reactions of these systems including transfer of ligands between the metal centres and oxidation of the bimetallic systems. In these reactions there is clear evidence for ready reversible cleavage of the metal–metal bond.

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* Part 1. See ref. 1.

** Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983.

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The phosphorus ligands triphenylphosphine ($M = M' = W$) or trimethylphosphite ($M = M' = W$; $M = Mo$, $M' = W$) ($R = Me$) react with II in a manner parallel to that of the carbonylation of II to I to give products III, which have retained the

$$[(C_5H_5)(OC)_2LM(\mu\text{-SMe})M'(CO)_5]$$
(III)

bridging methylthiolate groups but in which the MM′ bond has been cleaved. As with hexafluorobut-2-yne [1] the attack is at M and the reaction is similar to that observed by Vahrenkamp [2] for substitution of trimethylphosphine and phosphite into (μ-dimethylarsenido)-iron-manganese and -iron-cobalt complexes. The NMR spectra of complexes III show coupling between the cyclopentadienyl protons and the phosphorus confirming that L is substituted at M. The ^{13}C NMR spectra (Table 1) of III show a doublet ($J(^{31}P-^{13}C)$ ca. 30 Hz) consistent [3] with an essentially *trans* configuration for the P and S bonds about M.

On heating with periodic removal of volatile products the complexes III lose the phosphorus ligand, regain the metal–metal bond, and revert to II, a result in contrast to the reaction of the (μ-dimethylarsenido)iron complexes which undergo decarbonylation rather than loss of phosphorus ligand. Normally, phosphorus ligands displace carbonyls. The addition of the phosphorus ligand to the bimetallic, metal–metal bonded species II is thus reversible. It has very recently been shown [4] that carbon monoxide can displace triphenylphosphine from $[(Ph_3P)(OC)_3Ru(\mu\text{-}PPh_2)_2Co(CO)_2(PPh_3)]$. That the phosphorus ligand in the present complexes is particularly labile is shown by the reaction of IIIb ($M = M' = W$; $L = P(OMe)_3$ with hexafluorobut-2-yne to give good yields of the alkyne complex $[(C_5H_5)(CF_3C_2CF_3)(OC)W(\mu\text{-SMe})W(CO)_5]$ [1].

$$[(C_5H_5)(OC)_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}}(CO)_4\{P(OMe)_3\}]$$
(IV)

On extended heating in solution the complex $[(C_5H_5)(OC)_2\{(MeO)_3P\}Mo(\mu\text{-}SMe)W(CO)_5]$ (III) gives, in addition to decomposition products some of IV, in which L is now attached to M′ (W) rather than M (Mo), the first example in this series of reactions in which there has been attack on the pentacarbonylmetallate species. The structure of IV is established by observation of $^{183}W-^{31}P$ coupling in the NMR spectrum and by absence of observable $^{1}H-^{31}P$ coupling involving the cyclopentadienyl protons. The ^{13}C NMR spectrum of IV (Table 1) is quite different from those of II and III and shows four distinct signals in the carbonyl region for the $W(CO)_4L$ group (II shows two signals indicating a unique carbonyl and four almost equivalent carbonyls) so that we consider that the phosphite has substituted essentially *cis* to the sulphur with non-equivalence of carbonyls enforced by the presence of the metal–metal bond. The infrared spectrum of IV shows a medium peak at 1852 cm^{-1} consistent with a semi-bridged carbonyl.

Unfortunately, it was not possible to isolate analogues of IV from other complexes III and the mechanism for the formation of IV is not clear. Synthesis of III by addition of the phosphorus ligand to II gives only III with no IV so that III may be a necessary intermediate in the substitution of the phosphorus ligand into the $M'(CO)_5$ group. On the other hand, this substitution may result from slow substitution of the phosphite, released in the reaction mixture, into the $M'(CO)_5$ moiety of II. This substitution may reflect different stabilities of the W–P as compared with the Mo–P bonds.

TABLE I

^{13}C NMR SHIFTS

	SCH_3	$P(OMe)_3$	C_5H_5	$M'(CO)_4L$; L = CO, $P(OMe)_3$	$M(CO)_2L_n$ (n = 0 or 1)
$CpMo(CO)_2P(OMe)_3(\mu\text{-}SMe)W(CO)_5$ (IIIb)	29.7	53.2 d, $^2J(PC)$ 6.4 Hz	94.0	198.5 (eq) 201.4 (ax)	232.8 d, $^2J(PC)$ 38.5 Hz
$CpW(CO)_2P(OMe)_3(\mu\text{-}SMe)W(CO)_5$ (IIIc)	30.8	53.8 d, $^2J(PC)$ 6.4 Hz	92.5	199.1 (eq) 201.1 (ax)	224.9 d, $^2J(PC)$ 29.5 Hz
$CpMo(CO)_2(\mu\text{-}SMe)W(CO)_4P(OMe)_3$ (IV)	30.8	52.8 d, $^2J(PC)$ 4.6 Hz	94.0	193.5, d, $^2J(PC)$ 9.2 Hz 197.1, d, $^2J(PC)$ 10.1 Hz 203.6, d, $^2J(PC)$ 17.4 Hz 218.8, d, $^2J(PC)$ 14.7 Hz	241.6 246.1

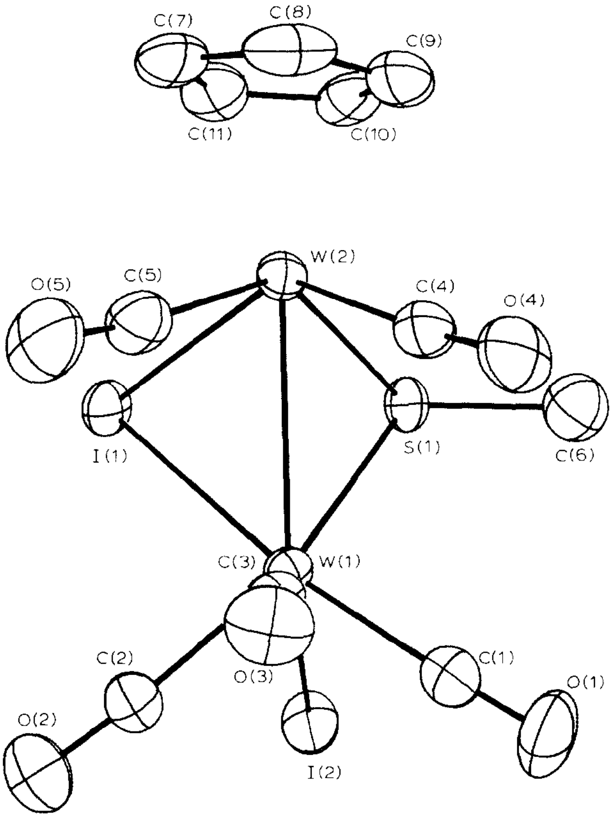

Fig. 1. A perspective view of V. For clarity hydrogen atoms are omitted, as are the less populated sites for the disordered bridging groups. 50% thermal ellipsoids are shown.

Diiodine adds oxidatively to I to give $[(C_5H_5)(OC)_2\overline{W(\mu\text{-SMe})(\mu\text{-I})W}(CO)_3I]$ (V) (Fig. 1) the structure of which has been established by X-ray diffraction. This oxidative addition is similar to that previously described by Poilblanc [5] when diiodine is added to $[Ir(\mu\text{-SBu}^t)(CO)L]_2$ where the metal–metal bond is strengthened and both iridium atoms have their oxidation state increased by one unit. In the present case it is possible to consider that the oxidation state of each tungsten of V has been increased by one unit with formation of the tungsten–tungsten bond. Oxidation of Group VI carbonyl derivatives with halogens frequently leads to 7-coordinate metal(II) derivatives [6,13].

The only identified products from the reaction of I with iodomethane are $W(CO)_6$ and $[(C_5H_5)W(CO)_3I]$ [7] implying break up of the bimetallic centre with extensive rearrangement of the groups attached to each tungsten.

The molecular structure of V (see Fig. 1 and Tables 2 and 3) contains two inequivalent tungsten atoms which are linked directly, by a single W–W bond of length 2.936(1) Å, and also indirectly through bridging SCH_3 and I groups.

The butterfly-shaped $W_2(\mu\text{-I})(\mu\text{-S})$ unit belongs to a well established structural type [8] although examples with both thiolato and halogeno bridges are rather uncommon [9]. The W–W bond length is in the range regarded as typical of single

TABLE 2

FRACTIONAL COORDINATES FOR $[(C_5H_5)(OC)_2W(\mu\text{-I})(\mu\text{-SMe})W(CO)_3I]$ (V)

Atom	x	y	z
W(1)	−0.07697(3)	0.20811(2)	0.16735(2)
W(2)	0.15622(3)	0.28537(2)	0.06026(2)
I(1) [a]	−0.15774(5)	0.29877(4)	−0.00822(3)
I(2)	−0.31817(6)	0.06373(5)	0.14231(4)
S(1) [a]	0.0616(2)	0.1101(1)	0.0617(1)
O(1)	0.0268(8)	0.0629(6)	0.3289(4)
O(2)	−0.3577(6)	0.3354(5)	0.2170(4)
O(3)	0.0670(6)	0.3466(5)	0.3262(3)
O(4)	0.3523(6)	0.2348(6)	0.2457(4)
O(5)	0.0887(8)	0.4904(5)	0.1561(4)
C(1)	−0.0152(9)	0.1145(7)	0.2700(5)
C(2)	−0.2544(8)	0.2882(6)	0.2023(5)
C(3)	0.0144(8)	0.2975(6)	0.2650(5)
C(4)	0.2765(8)	0.2521(7)	0.1801(5)
C(5)	0.1066(9)	0.4129(7)	0.1227(4)
C(6)	0.2003(10)	0.0191(9)	0.1208(6)
C(7)	0.2508(10)	0.4005(8)	−0.0378(5)
C(8)	0.3692(9)	0.3646(9)	0.0259(5)
C(9)	0.3833(9)	0.2573(9)	0.0093(6)
C(10)	0.2800(10)	0.2299(7)	−0.0642(5)
C(11)	0.1932(10)	0.3182(8)	−0.0930(5)
I(1′) [b]	0.1607(6)	0.0641(5)	0.1047(4)
S(1′) [b]	−0.1372(11)	0.2159(19)	0.0082(15)

[a] These atoms were assigned a common site occupancy factor $p = 0.92(1)$. [b] These atoms were assigned a common site occupancy factor $1 - p$.

bonds [10,11] and agrees especially well with the value of 2.937(1) Å found in $[(\mu\text{-}Ph_2AsCH_2AsPh_2)(\mu\text{-}Me_2C_2)(\mu\text{-Br})W_2(CO)_5Br]$ [12]. The thiolato and iodo bridges are very nearly symmetric. However, the bridging W–I(1) and W–S(1) bonds are slightly longer with W(1) than with W(2), possibly reflecting the greater number of carbonyls carried by W(1). Atoms I(1) and S(1) subtend similar *cis* angles of 74.4(1) and 75.1(1)° at W(1) and W(2), respectively.

The molecular skeleton, minus the bridging thiolato and iodo groups, approximates to C_s point symmetry, the non-crystallographic mirror plane being defined by the atoms W(1), W(2), C(3), O(3), and I(2). This may explain the disorder which appears to involve only the atoms I(1), S(1), and C(6). The X-ray analysis indicates that in the solid 92% of the molecules are as shown in Fig. 1, whereas the remainder have the positions of the bridging iodo and thiolato groups approximately interchanged. Evidently the steric demands of μ-I and $\mu\text{-}SCH_3$ are similar, despite the difference of ca. 0.4 Å between W–I and W–S bond lengths.

Atom W(1) is 7-coordinate. Its coordination polyhedron might be described in terms of a distorted capped octahedron, carbonyl C(3)O(3) being the capping ligand. Alternatively, and in our opinion more satisfactorily, it can be described as 4/3 piano-stool [13] with W(2), I(1), and S(1) as the three-fold upper part, and the four legs defined by I(2) and C(1), C(2), and C(3). Angles subtended by this latter group

TABLE 3

SELECTED INTERATOMIC DISTANCES AND ANGLES IN $[(C_5H_5)(OC)_2W(\mu\text{-}I)(\mu\text{-}SMe)W(CO)_3I]$ (V)

(a) Bond lengths (Å)

W(1)–W(2)	2.936(1)	W(2)–S(1)	2.456(2)
W(1)–I(1)	2.862(1)	W(2)–C(4)	1.993(8)
W(1)–S(1)	2.469(2)	W(2)–C(5)	1.992(9)
W(1)–I(2)	2.843(1)	W(2)–C(7)	2.326(9)
W(1)–C(1)	1.976(8)	W(2)–C(8)	2.264(9)
W(1)–C(2)	2.011(8)	W(2)–C(9)	2.261(9)
W(1)–C(3)	1.954(8)	W(2)–C(10)	2.373(9)
W(2)–I(1)	2.831(1)	W(2)–C(11)	2.370(8)
C–O	1.13(1)–1.16(1)	S(1)–C(6)	1.850(11)
C–C	1.37(1)–1.44(2)		

(b) Bond angles (°)

W(2)–W(1)–I(1)	58.4(1)	S(1)–W(1)–C(3)	126.2(3)
W(2)–W(1)–I(2)	136.6(1)	C(1)–W(1)–C(2)	106.1(4)
W(2)–W(1)–S(1)	53.2(1)	C(1)–W(1)–C(3)	76.2(4)
W(2)–W(1)–C(1)	119.1(3)	C(2)–W(1)–C(3)	75.8(3)
W(2)–W(1)–C(2)	125.5(3)	W(1)–W(2)–I(1)	59.5(1)
W(2)–W(1)–C(3)	86.5(3)	W(1)–W(2)–S(1)	53.6(1)
I(1)–W(1)–I(2)	93.8(1)	W(1)–W(2)–C(4)	77.0(3)
I(1)–W(1)–S(1)	74.4(1)	W(1)–W(2)–C(5)	80.3(3)
I(1)–W(1)–C(1)	165.5(3)	I(1)–W(2)–S(1)	75.1(1)
I(1)–W(1)–C(2)	84.4(2)	I(1)–W(2)–C(4)	135.8(3)
I(1)–W(1)–C(3)	116.7(3)	I(1)–W(2)–C(5)	81.3(3)
I(2)–W(1)–S(1)	89.5(1)	S(1)–W(2)–C(4)	85.9(3)
I(2)–W(1)–C(1)	79.1(3)	S(1)–W(2)–C(5)	133.9(3)
I(2)–W(1)–C(2)	77.8(3)	C(4)–W(2)–C(5)	84.1(4)
I(2)–W(1)–C(3)	136.9(3)	W(1)–I(1)–W(2)	62.1(1)
S(1)–W(1)–C(1)	92.8(3)	W(1)–S(1)–W(2)	73.2(1)
S(1)–W(1)–C(2)	154.6(3)	W(1)–S(1)–C(6)	113.1(4)
C–C–C	107(1)–109(1)	W(2)–S(1)–C(6)	114.0(4)
W–C–O	174(1)–177(1)		

of atoms at W(1) (*cis* angles 75.8(3)–79.1(3)°, *trans* angles 106.1(4) and 136.9(3)°) agree closely with corresponding values (*cis* angles 74.0(3)–78.5(2)°, *trans* angles 108.5(2) and 133.1(2)°) in the $W(CO)_3S$ portion of I for which a piano-stool formalism is obviously appropriate.

The interconversion of I to V involves replacement of one carbonyl in the $(C_5H_5)W(CO)_3S$ piano-stool of I by iodine and the formation of a W–W bond opposite to the cyclopentadienyl. This leads to a flattening of the piano-stool arrangement about W(2) in V. Thus the *cis* angles (75.1(1)–85.9(3)°) and *trans* angles (133.9(3) and 135.8(3)°) about W(2) are in general larger than corresponding values about W(1) or about the cyclopentadienyl-substituted tungsten atom in I. The coordination of W(2) is closely related to those found in $[(C_5H_5)_2W_2(CO)_4(\mu\text{-}L)]$ (W–W) where $L = C_2H_2$ [10] or $C(O)C_2(CO_2Me)_2$ [11]. Perhaps the most interesting comparison, however, is between the coordination of W(2) in V and that of the molybdenum atom in $[(C_5H_5)Mo(CO)_2(\mu\text{-}SCH_3)W(CO)_5]$ [1] where a semi-bridging carbonyl replaces the true iodo bridge of V. This suggests that the $(C_5H_5)Mo(CO)_2$ grouping in the latter complex is coordinatively unsaturated and that electronic, as well as steric, factors help to stabilise the semi-bridged carbonyl group. Coordinative unsaturation of the Mo is consistent with the general reactivity of the $CpM(CO)_2$ groups in the present complexes.

The molecular packing is of the Van der Waals type. The O(3)... C(6) intermolecular contact of 3.09(1) Å is the only which is more than 0.1 Å less than the sum of the corresponding Van der Waals radii. It is probably best explained in terms of systematic error in the position of the disordered atom C(6).

Experimental

Preparations were carried out under nitrogen using Schlenk tube techniques. Solvents were purified by standard methods. Chromatography was performed on Florisil. The complexes $[(C_5H_5)M(CO)_3(\mu\text{-}SMe)W(CO)_5]$ (I) and $[(C_5H_5)(OC)_2M(\mu\text{-}SMe)W(CO)_5]$ (II) (M = Mo, W) were prepared as previously described. Analyses were by Centre de Microanalyse du CNRS, Lyon. Mass spectra were recorded on a RIBERMAG MASS-1500 mass spectrometer; NMR spectra in $CDCl_3$ solution on a JEOL FX100 spectrometer (^1H and ^{13}C (Table 1) were referenced to Me_4Si; ^{31}P referenced to H_3PO_4/D_2O, positive shifts downfield); IR spectra (in CH_2Cl_2) were recorded on a Pye-Unicam SP200 spectrophotometer.

Preparation of complexes $[(C_5H_5)M(CO)_2(PR_3)(\mu\text{-}SMe)W(CO)_5]$ (III)

In a typical preparation a solution of triphenylphosphine or trimethylphosphite (1 mmol in 10 cm³ CH_2Cl_2) was added to a solution of complex II (1 mmol in 40 cm³ CH_2Cl_2). The reaction mixture was stirred for 15 minutes when the colour changed from black to orange-red. The solution was concentrated and chromatographed using hexane/CH_2Cl_2 as eluant to give complexes III which were recrystallised from hexane/CH_2Cl_2.

$[(C_5H_5)W(CO)_2(Ph_3P)(\mu\text{-}SMe)W(CO)_5]$ (IIIa). Orange-red solid, yield 60%. Found: C, 42.0; H, 3.2; P, 2.7; S, 3.3 $C_{31}H_{23}O_7PSW_2$ calcd.: C, 39.7; H, 2.5; P, 3.4; S, 3.3%. IR spectrum ($CDCl_3$) shows carbonyl peaks at 1878s, 1935vs, 1968s, 2045m and 2075m cm^{-1}. ^1H NMR: 7.52(m, PPh_3); 5.20(d, C_5H_5, ^3J(P–H) 1.5 Hz); 2.65 (s, SCH_3). ^{31}P NMR: 31.4.

$[(C_5H_5)Mo(CO)_2\{P(OMe)_3\}(\mu\text{-}SMe)W(CO)_5]$ (IIIb). Orange solid, yield 95%. Found: C, 27.0; H, 2.3; P, 4.2; S, 4.4. $C_{16}H_{17}MoO_{10}PSW$ calcd.: C, 27.0; H, 2.4; P, 4.3; S, 4.5%. The mass spectrum (chemical ionisation) showed ions corresponding to $[M - nCO]^+$ (n = 1–3). IR: 1870(sh), 1892s, 1935vs, 1982s and 2070m cm^{-1}. ^1H NMR: 5.33(d, C_5H_5, ^3J(P–H) 1.9 Hz); 3.71 (d, $P(OMe)_3$, ^3J(P–H) 11.6 Hz); 2.42 (s, SCH_3). ^{31}P NMR: 182.2. M.p.: 113–114°C.

$[(C_5H_5)W(CO)_2\{P(OMe)_3\}(\mu\text{-}SMe)W(CO)_5]$ (IIIc). Orange solid, yield 80%. Found: C, 24.4; H, 2.1; P, 4.0; S, 4.0. $C_{16}H_{17}O_{10}PSW_2$ calcd.: C, 24.0; H, 2.1; P, 3.9; S, 4.0%. The mass spectrum (chemical ionisation) showed ions corresponding to $[M - nCO]^+$ (n = 1–4). IR: 1885s, 1935vs, 1980m, 1990(sh) and 2075w. ^1H NMR: 5.43(d, C_5H_5, ^3J(P–H) 2.2 Hz); 3.69 (d, $P(OMe)_3$, ^3J(P–H) 12.5 Hz); 2.52 (s, SCH_3). ^{31}P NMR: 146.2 (^1J(W–P) 365 Hz). M.p.: 131°C.

Reaction of IIIc with hexafluorobut-2-yne

IIIc (0.36 g, 0.5×10^{-3} mol) reacts with hexafluorobut-2-yne to give $[(C_5H_5)(CF_3C_2CF_3)(OC)W(\mu\text{-SMe})W(CO)_5]$ purified by chromatography with elution by hexane and CH_2Cl_2 in a 65% yield and characterised by spectroscopy [1].

Preparation of $[(C_5H_5)\overline{Mo(CO)_2(\mu\text{-}SMe)W}(CO)_4\{P(OMe)_3\}]$

Complex IIIb (10.7 g, 1 mmol) was warmed in dichloromethane at 40–50°C and volatiles were removed periodically. (1) After 48 h chromatography it showed only $[(C_5H_5)\overline{Mo(CO_2(\mu\text{-SMe})W}(CO)_5$ (II) (eluted with hexane/CH_2Cl_2) (yield: 35%) and the starting material. (2) After 120 h chromatography it afforded $[(C_5H_5)Mo(CO)_2(\mu\text{-SMe})W(CO)_5]$ (II) (0.1 g yield, 17%) and complex IV (0.28 g yield, 41%), eluted with hexane/CH_2Cl_2. $[(C_5H_5)\overline{Mo(CO)_2(\mu\text{-SMe})W}(CO)_4\{P(OMe)_3\}]$ (IV); dark red solid. Found: C, 28.0; H, 2.4; P, 4.5; S, 4,4. $C_{15}H_{17}MoO_9PSW$ calcd.: C, 26.4; H, 2.5; P, 4.5; S, 4.7%. The mass spectrum (chemical ionisation) showed ions corresponding to $[M]^+$ and $[M-n\text{CO}]^+$ ($n = 1,2$). IR: 1852m, 1880(sh), 1890m, 1928s, 1948vs and 2040m cm^{-1}. ^1H NMR: 5.34(s, C_5H_5); 3.76 (d, $P(OMe)_3$, $^3J(P\text{–}H)$ 12.5 Hz); 2.78 (s, SCH_3). ^{31}P NMR: 125.7 ($^1J(W\text{–}P)$ 370 Hz). M.p. 112–113°C.

Preparation of $[(C_5H_5)(CO)_2W(\mu\text{-}SMe)(\mu\text{-}I)W(CO)_3I]$ (V)

A tetrahydrofuran (20 cm^3) solution of I_2 (0.25 g, 1 mmol) was added to a solution of $[(C_5H_5)(CO)_3W(\mu\text{-SMe})W(CO)_5]$ (0.7 g, 1 mmol) in THF (40 cm^3). The mixture was stirred for 4 h at room temperature. The solvent was evaporated and the product dissolved in dichloromethane for chromatography. Elution by hexane, hexane/dichloromethane/acetone (16/3/1) and dichloromethane afforded $W(CO)_6$ (traces), $[(C_5H_5)W(CO)_3I]$ (yield 25%) and V (yield 40%). Complex V is only slightly soluble in common organic solvents.

Air stable red crystals suitable for X-ray diffraction were obtained by vapour diffusion of hexane into a saturated solution of V in THF.

$[(C_5H_5)(CO)_2\overline{W(\mu\text{-SMe})(\mu\text{-I})W}(CO_3I]$ (V). Found: C, 15.9; H, 1.1; I, 28.7; S, 3.6; W, 38.7. $C_{11}H_8I_2O_5SW_2$ calcd.: C, 15.1; H, 0.9; I, 29.1; S, 3.7; W, 42.1%. The mass spectrum showed an ion of highest m/e at 846 $[M-\text{CO}]^+$ and ions corresponding to $[M-n\text{CO}]^+$ and $[M-n\text{CO}-\text{CH}_3]^+$ ($n=2\text{–}5$). The IR spectrum showed carbonyl peaks at 1895(sh),1935s, 1952vs, 2035m and 2070m cm^{-1}. ^1H NMR $[(CD_3)_2CO]$: 6.40 (C_5H_5); 2.56 (SCH_3). M.p. 150°C (decomp.).

Crystal Structure Analysis of V

$C_{11}H_8I_2O_5SW_2$, $M = 873.7$. Monoclinic, space group $P2_1/n$ (C^5_{2h}), a 8.829(1), b 13.168(2), c 14.781(3) Å, β 97.41(1)°, U 1704 Å^3, $Z = 4$, D_c 3.405 g cm^{-3}, $F(000) = 1503.6$, Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 175.0 cm^{-1}.

The crystal orientation, cell dimensions, Laue symmetry, and the intensities of the Bragg reflections ($\vartheta/2\vartheta$ scans) were determined with Mo radiation on an Enraf–Nonius CAD4 diffractometer equippped with a graphite monochromator [14]. The analysis was carried out with 2851 independent intensities ($\vartheta(\text{Mo-}K_\alpha) \leq 30°$. $I \geq 3\sigma(I)$). For the plate-shaped crystal, dimensions $0.33 \times 0.26 \times 0.025$ mm, the transmission factors on F^2 varied between 0.03–0.66.

The W and I atoms were located using the GX system direct methods package MITHRIL. The positions of the remaining atoms were determined from subsequent difference syntheses. The structure was then refined by the full-matrix least-squares technique. At $R = 0.056$ the appearance of the difference synthesis and the physically unreasonable S(1)–C(6) distance of 1.48 Å indicated disorder involving I(1), S(1), and C(6). After considering several models an occupancy factor p was assigned to atoms I(1) and S(1), and occupancies of $1 - p$ to the sites of I(1′) and S(1′) which were positioned from the difference synthesis close to S(1) and I(1) respectively; refinement of this model converged with $p = 0.92(1)$, $R = 0.033$, and $R_w = 0.045$ (cf. $R = 0.023$ for merging 1369 pairs of symmetry-equivalent $|F_0|$). In the final difference synthesis $|\Delta\rho| < 2.1$ eÅ^{-3} near W or I atoms, and < 0.9 eÅ^{-3} elsewhere. Scattering factors, anomalous dispersion corrections, and absorption coefficients were taken from ref. 15. All calculations were carried out on a Gould SEL 3227 computer using the GX program system [16].

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