Polyhedron Vol. 2, No. 8, pp. 797–801, 1983
Printed in Great Britain.

0277–5387/83 $3.00 + .00
Pergamon Press Ltd.

SOME TRIMETHYL PHOSPHINE AND TRIMETHYL PHOSPHITE COMPLEXES OF TUNGSTEN(IV)

ERNESTO CARMONA,* LUIS SÂNCHEZ and MANUEL L. POVEDA
Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla,
Sevilla, Spain

and

RICHARD A. JONES,* and JOHN G. HEFNER
Chemistry Department, University of Texas at Austin, Austin, TX 78712, U.S.A.

(*Received* 18 *January* 1983; *accepted* 24 *January* 1983)

Abstract—Direct reduction of WCl_6 with PMe_3 in toluene at 120°C in a sealed tube affords the complexes $[WCl_4(PMe_3)_x]$ ($x = 2, 3$). $[WCl_4(PMe_3)_3]$ abstracts oxygen from equimolar amounts of water in wet acetone or tetrahydrofuran to give $[WOCl_2(PMe_3)_3]$ in very high yields. This procedure has been successfully applied to the high yield synthesis of other known oxotungsten(IV) complexes, $[WOCl_2(PR_3)_3]$ ($PR_3 = PMe_2Ph$ and $PMePh_2$). Metathesis reactions of $[WOCl_2(PMe_3)_3]$ with NaX give $[WOX_2(PMe_3)_3]$ (X = NCO, NCS) and $[WOX_2(PMe_3)]$ ($X = Me_2NCS_2$). The synthesis of the trimethylphosphite analogue, $[WOCl_2(P(OMe)_3)_3]$, is also described and the structures of the new complexes assigned on the basis of IR and ^1H and ^{31}P NMR spectroscopy.

In recent years we have been interested in the preparation and properties of trimethylphosphine complexes of Group VI metals, particularly molybdenum. This work has resulted in the synthesis of dinitrogen, ethylene, acyl and related complexes,[1,2] with the metal in oxidation states 0 or +2. Adequate starting reagents for these preparations are the chlorophosphine complexes $[MoCl_3(PMe_3)_3]$ and $[MoCl_2(PMe_3)_4]$. A natural extension of this work was the preparation of the tungsten analogues. However, at the time our work started little was known on the chemistry of trimethylphosphine derivatives of tungsten chlorides. In our search for a suitable starting material we have found that the tungsten(IV) complexes $[WCl_4(PMe_3)_x]$ ($x = 2, 3$) can be prepared in high yields by the PMe_3 reduction of WCl_6 in toluene, at 120°C in a sealed Carius tube. While our work was in progress Sharp and Schrock[3a] reported the preparation of these and other related complexes, including the metal–metal bonded dimer $[W_2Cl_4(PMe_3)_4]$. In this paper we wish to report our synthesis for the W(IV) complexes, $[WCl_4(PMe_3)_x]$ ($x = 2, 3$), and their facile conversion into the oxo species $[WOCl_2(PMe_3)_3]$ by oxygen abstraction from water in wet acetone or tetrahydrofuran (THF). The preparations and properties of the oxo-trimethylphosphite analogue, $[WOCl_2(P(OMe)_3)_3]$, and other related complexes are also reported. We finally show the generality of the oxygen abstraction process for the conversion of $[WCl_4(PR_3)_2]$ complexes into the corresponding oxo-derivatives $[WOCl_2(PR_3)_3]$, by applying it to the synthesis of the known compounds $[WOCl_2(PR_3)_3]$ ($PR_3 = PMe_2Ph$, $PMePh_2$), previously prepared in rather low yields.[4] The reactions leading to these complexes are summarized in the Scheme.

RESULTS AND DISCUSSION

(1) *Tetrachlorobis- and tris-(trimethylphosphine) tungsten(IV)*

Although previous attempts to prepare $[WCl_4(PR_3)_2]$ complexes, directly from WCl_6 without reducing agents other than the phosphine in either cold or boiling THF yielded only oily materials,[4] it was later shown[5] that these complexes can be obtained in good yields by carrying out the reaction in boiling benzene (eqn 1)

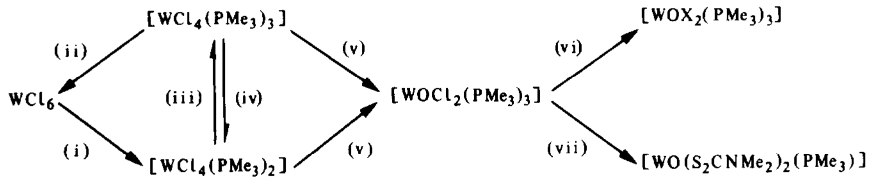
$$WCL_6 + 3PR_3 \xrightarrow[\text{reflux}]{C_6H_6} [WCl_4(PR_3)_2] + R_3PCl_2 \quad (1)$$

$$(PR_3 = PMe_2Ph,\ PMePh_2).$$

We have successfully applied this procedure to the synthesis of the trimethylphosphine analogue,

---

*Authors to whom correspondence may be addressed.



Scheme. (i) PMe_3 (less than 3 equiv), toluene, 120°C, 12–18 hr; (ii) as in (i), excess PMe_3; (iii) PMe_3, THF or toluene; (iv) reflux in toluene; (v) H_2O, PMe_3, THF or acetone, 40–50°C, 3 hr; (vi) KNCO or KNCS, THF, 3–4 hr; (vii) anhydrous NaS_2CNMe_2, THF, 3 hr.

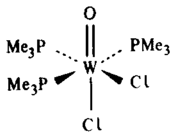
$[WCl_4(PMe_3)_2]$. The reaction is best carried out in a sealed tube to avoid loss of volatile PMe_3. Thus, when WCl_6 and PMe_3 (*ca.* 1:2.5 molar ratio) are reacted in toluene at 120°C in a Carius tube, $[WCl_4(PMe_3)_2]$ is formed in high yields. Using more than 3 equiv of PMe_3 a mixture of red $[WCl_4(PMe_3)_2]$ and red–purple $[WCl_4(PMe_3)_3]$ is obtained. These complexes can be easily converted into one another, addition of PMe_3 to solutions of the former causing precipitation of the latter, while moderate heating of solutions of $[WCl_4(PMe_3)_3]$ produces loss of PMe_3 and formation of $[WCl_4(PMe_3)_2]$. Both complexes are moderately stable to air in the solid state but decompose quickly in solution. $[WCl_4(PMe_3)_2]$ is monomeric in solution (cryoscopically in benzene) and paramagnetic with $\mu_{eff} = 1.87$ M.B. (Evans's method[6]), in the range expected for this type of complex [7]. Despite its paramagnetism it shows a relatively sharp NMR signal at δ – 25.2 ppm. $[WCl_4(PMe_3)_3]$ gives also a sharp NMR signal (δ – 8.2 ppm) but its low solubility has precluded solution molecular weight and magnetic moment determinations. As mentioned above these two complexes have been independently prepared[3a] from WCl_4 and PMe_3. The crystal structure of $[WCl_4(PMe_e)_3]$ has been determined.[3b]

(2) *Oxotungsten(IV) complexes*

Complexes of composition $[WOCl_2(PR_3)_3]$ are known[4] for several monotertiary phosphines ($PR_3 = PMe_2Ph$, $PMePh_2$, PEt_2Ph) and were prepared in rather poor yields (*ca.* 30%) by reaction of WCl_6 with the phosphine in ethanol for $PR_3 = PMe_2Ph$, and in the presence of zinc in the case of the less reducing phosphines $PMePh_2$ and PEt_2Ph. We have now prepared the trimethylphosphine analogue $[WOCl_2(PMe_3)_3]$ in 80% yield by an oxygen–atom abstraction reaction between $[WCl_4(PMe_3)_x]$ ($x = 2$, 3) and stoicheiometric amounts of water, in the presence of an excess of PMe_3 to accept the generated hydrogen chloride, (eqn 2)

$$[WCl_4(PMe_3)_2] + H_2O + 3PMe_3 \rightarrow [WOCl_2(PMe_3)_3] + 2HCl{\cdot}PMe_3. \qquad (2)$$

Stirring a solution of $[WCl_4(PMe_3)_2]$, or a suspension of $[WCl_4(PMe_3)_3]$, in wet acetone or THF, at 40–50°C in the presence of PMe_3, produces a change in colour to dark-blue and precipitation of a white microcrystalline solid, identified as $[HPMe_3]^+Cl^-$ by comparison of its IR and NMR spectra with those of an authentic sample. When the reaction is complete and after work up, moderately air-stable dark blue crystals of $[WOCl_2(PMe_3)_3]$ can be collected. This compound has been prepared independently by Wilkinson *et al.*[8] The IR spectrum of the complex shows absorptions characteristic of the PMe_3 ligands but no band due to $\nu(W=O)$ can be observed. This is very likely due to overlapping with the strong, broad absorption centred at 940 cm^{-1}, characteristic of coordinated trimethylphosphine.[9] As in other related complexes[4] $[WOCl_2(PMe_3)_3]$ is monomeric in benzene solution and diamagnetic. The ^1H NMR spectrum in CH_2Cl_2 shows a triplet at δ 1.57 and a doublet at 1.60 ppm (intensity ratio 2:1). This spectrum may be interpreted in terms of a *meridional* arrangement of the phosphine ligands and this along with the fact that the IR spectra of the complexes $[WOX_2(PMe_3)_3]$ X = NCO, NCS) show two bands due to $\nu(C–N)$ of the X ligands (see later) suggest stereochemistry as in I.



(I)

The procedure described above for the preparation of $[WOCl_2(PMe_3)_3]$ is of general use and can be applied to the high yield synthesis of other known oxotungsten(IV) complexes. Thus, $[WOCl_2(PMe_2Ph)_3]$, initially prepared in 25% yield by reaction of WCl_6 with PMe_2Ph in ethanol,[4] is obtained in *ca.* 75% yield by interaction of $[WCl_4(PMe_2Ph)_2]$ with equimolecular amounts of water, in the presence of PMe_2Ph (see Experimental Section). Similarly, $[WOCl_2(PMePh_2)_3]$ can be prepared by this same procedure in *ca.* 70%

yield, (eqn 3)

$$[WCl_4(PR_3)_2] + H_2O + 3PR_3 \rightarrow [WOCl_2(PR_3)_3] + 2HCl{\cdot}PR_3 \qquad (3)$$

($PR_3 = PMe_2Ph$, 75%; $PR_3 = PMePh_2$, 70%).

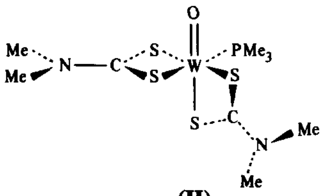
The trimethylphosphite derivative, $[WOCl_2\{P(OMe)_3\}_3]$, can be isolated in *ca.* 80% yield, as purple crystals, by the sodium amalgam reduction of $WOCl_4$ in the presence of $P(OMe)_3$. The IR spectrum has $\nu(W=O)$ at 955 cm^{-1}, and the ^1H NMR shows a multiplet at δ 3.82, that provides no information with regard to the stereochemistry of the complex. The $^{31}P\{^1H\}$ NMR spectrum consists of a triplet at δ 134.88 [^2J(P–P) = 23.5 Hz; ^1J(W–P) = 316.9 Hz) and a doublet at 128.08 (^1J(W–P) = 257.0 Hz]. This is consistent with either a *facial* or a *meridional* distribution of the phosphite ligands.

Metathesis reactions of the chlorotrimethylphosphine complex $[WOCl_2(PMe_3)_3]$ with the appropriate potassium pseudohalide, yield $[WO(NCO)_2(PMe_3)_3]$ and $[WO(NCS)_2(PMe_3)_3]$ as dark blue crystalline materials. The Nujol-mull IR spectra show two strong bands at 2230 and 2190 cm^{-1} (cyanate complex) and 2060 and 2040 cm^{-1} (thyocyanate complex) attributed to ν(C–N) of the NCO and NCS ligands respectively. This and the appearance of the ^1H methyl resonances for these complexes as a triplet and a doublet (intensity ratio 2:1) strongly support structure of the type **I**.

The ease of the metathetical replacement of the chlorine atoms in $[WOCl_2(PMe_3)_3]$, provided an opportunity to synthesize the related oxodithiocarbamatetungsten(IV) complexes $[WO(S_2CNR_2)_2(PMe_3)]$ by similar procedures. Compounds of this type are to our knowledge unknown, although for both Mo and W a series of complexes of composition $[MO(S_2CNR_2)_2(R^1C_2R^2)]$ has been reported.[10,11] While for M = Mo these complexes are usually prepared by reaction of the known $[MoO(S_2CNR_2)_2]$ with the appropriate ligands,[10] for tungsten the corresponding $[WO(S_2CNR_2)_2]$ are still unknown, and the acetylene complexes $[WO(S_2CNR_2)_2(R^1C_2R^2)]$ have been obtained by the intermetal oxygen–atom transfer reaction[11] depicted in eqn (4),

$$[W(S_2CNR_2)_2(CO)(R^1C{\equiv}CR^2)] + [Mo_2O_3\{S_2P(OEt)_2\}_4] \rightarrow [WO(S_2CNR_2)_2(R^1C{\equiv}CR^2)] + 2[MoO(S_2P(OEt)_2)_2] + CO. \qquad (4)$$

The complex oxodichlorotris(trimethylphosphine)tungsten(IV), $[WOCl_2(PMe_3)_3]$, reacts with anhydrous NaS_2CNMe_2, in THF, at room temperature to afford dark red crystals of $[WO(S_2CNMe_2)_2(PMe_3)]$ in *ca.* 70% yield. In addition to absorptions due to the PMe_3 ligand, the IR spectrum of this moderately air-stable solid is characterized by a strong band at 930 cm^{-1} due to the W=O stretch and two absorptions at 1540 and 1515 cm^{-1} which are assigned to the C=N stretch of the coordinated dithiocarbamate ligands. While the $^{31}P\{^1H\}$ NMR spectrum is a singlet at temperatures between 25° and −80°C (δ −19.8 ppm, ^1J(W–P) = 210.9 Hz) the ^1H NMR spectrum shows temperature dependence. At 35°C (CD_2Cl_2) the spectrum consist of three methyl signals at δ 3.81, 3.66 and 3.34 ppm (intensity ratio 1:1:2) for the dithiocarbamate groups and a doublet at 1.44 ppm (^2J(P–H) = 9.2 Hz) for the PMe_3 protons. Upon lowering the temperature, the singlet at 3.34 broadens, and at 20°C gives rise to an unresolved doublet. On further cooling this signal becomes a sharp doublet of resonances, no additional changes being observed down to −80°C. At this temperature four distinct ^1H methyl resonances at 3.81, 3.66, 3.37 and 3.30 ppm are observed for the $Me_2NCS_2^-$ ligands. This spectrum is consistent with structure type **II**.



(II)

Although a more detailed NMR study is required before any definite conclusion can be reached, it is tempting to assume that the averaging of the two low temperature methyl signals at 3.37 and 3.30 ppm, to give a singlet at 3.34 ppm in the 35°C spectrum, is due to fast exchange of the two methyl groups of the monodentate dithiocarbamate ligand in the short-lived 5-coordinate intermediate, $[WO(S_2CNMe_2)(SC(=S)NMe_2)(PMe_3)]$, formed by rupture of the W–S bond trans to oxygen. This assumption is supported by the high *trans*-influence of the oxo ligand which is well documented in this type of complex.[11,12]

EXPERIMENTAL

Microanalyses were by Pascher Microanalytical Laboratory, Bonn. Molecular weights were measured cryoscopically, in benzene, under nitrogen. The spectroscopic instruments used were a Perkin–Elmer model 577 for IR spectra, and a Perkin–Elmer R-12A (^1H), a Varian EM 390 (^1H) and Varian FT-80 (^1H, $^{31}P\{^1H\}$) for NMR measurements. Magnetic susceptibilities were obtained in solution by the Evans method.

All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use.

The light petroleum used had b.p. 40–60°C. PMe_3 was prepared according to the literature method.[13] The complexes $[WCl_4(PR_3)_2]$ ($PR_3 = PMe_2Ph$, $PMePh_2$) were prepared by a slight modification of the method of Galyer and Wilkinson.[5] Details of the preparations are given below. NaS_2CNMe_2 was dried by heating at 90°C under vacuum for 6–7 days.

Tetrachlorobis(trimethylphosphine)tungsten(IV)

A thick-walled 250 cm^3 Carius tube, provided with a stirring-bar, was charged with WCl_6 (19.8 g, *ca.* 50 mmol). Toluene (100 cm^3) and PMe_3 (14.0 cm^3, *ca.* 140 mmol) were successively added via syringe, the resulting mixture frozen at liquid nitrogen temperature and the tube sealed under *vacuo*. The mixture was allowed to reach room temperature and then heated at 120°C for 12–18 hr, with occasional shaking to facilitate the reaction. The resulting dark red solution was transferred while hot (boiling water external bath) and the remaining solid extracted with several portions of hot toluene until no more $[WCl_4(PMe_3)_2]$ was left (*ca.* 4 × 75 cm^3). The solution was reduced in volume (to *ca.* 100 cm^3) and cooled at −30°C overnight. 14 g of well formed red crystals impurified by relatively small amounts of a yellow powder (Cl_2PMe_3)[14] were obtained. Another crop (4 g) of less pure product was recovered from the mother liquor. The total yield of crude, but pure enough for most synthetic purposes, $[WCl_4(PMe_3)_2]$ was *ca.* 75%. The compound can be purified by recrystallisation from hot toluene. [Found C, 15.4 (15.1); H, 3.9 (3.8); Cl, 29.4 (29.7)% *M*, 462 (444).]

IR (KBr) bands at: 2980, 2940, 1410, 1290, 1275, 1250, 1095, 1010, 935, 835, 785, 720, 650 cm^{-1}. NMR data $^1H(C_6H_6)$: −25.2 bs. $\mu_{eff} = 1.86\ \mu_B$.

Tetrachlorotris(trimethylphosphine)tungsten(IV)

To a magnetically stirred solution of $[WCl_4(PMe_3)_2]$ (0.95 g, *ca.* 2 mmol) in THF an excess of PMe_3 (0.3 cm^3, *ca.* 3 mmol) was slowly added. Dark red–purple microcrystals of the title compound immediately formed. The mixture was kept overnight at −30°C to complete crystallisation, the resulting solid filtered off, washed with petroleum or Et_2O and vacuum dried. The yield was *ca.* 90%. Recrystallisation can be achieved from hot toluene in a closed flask to avoid loss of PMe_3. [Found C, 19.5 (19.5); H, 5.0 (4.9); Cl, 25.6 (25.6)%.]

IR (KBr) bands at: 2980, 2950, 1420, 1295, 1230, 1100, 950, 850, 800, 780, 730, 665 cm^{-1}. NMR data $^1H(C_6H_6)$: −8.2 bs.

Oxodichlorotris(trimethylphosphine)tungsten(IV)

To a stirred solution of $[WCl_4(PMe_3)_2]$ (0.95 g, *ca.* 2 mmol) in THF or acetone (40 cm^3), PMe_3 (0.7 cm^3, *ca.* 7 mmol) was added. Immediate formation of red purple microcrystals of $[WCl_4(PMe_3)_3]$ was observed. To the resulting suspension were added a few drops of deoxygenated water and the mixture stirred at 45°C. the reaction was followed by the disappearance of insoluble $[WCl_4(PMe_3)_3]$ and more water added if required. A large excess of water should be avoided since considerable decomposition takes place. The stirring was continued at this temperature until all the initial $[WCl_4(PMe_3)_3]$ had been taken into solution (*ca.* 2 hr) and then for another hour. The mixture was evaporated to dryness and the residue extracted with Et_2O (40 cm^3). Filtration and cooling at −30°C afforded the title compound as dark-blue crystals in *ca.* 80% yield. [Found C, 21.5 (21.5); H, 5.5 (5.4)%. *M*, 490 (499).]

IR (Nujol mull) bands at: 1375, 1300, 1280, 1260, 950, 850, 800, 720, 660 cm^{-1}.

NMR. ^1H (C_6H_6): 1.57t (18), $J(P\text{-}H)_{ap} = 4$ Hz; 1.60d (9), $J(P\text{-}H) = 10$ Hz.

Oxodichlorotris(dimethylphenylphosphine)tungsten (IV)

The complex $[WOCl_2(PMe_2Ph)_3]$ was prepared in *ca.* 75% yield as dark blue crystals (from hot ethanol) following a procedure identical to that described above for $[WOCl_2(PMe_3)_3]$. The parent complex, $[WCl_4(PMe_2Ph)_2]$ was prepared as follows:

To a suspension of WCl_6 (4.8 g, *ca.* 12 mmol) in benzene (100 cm^3) were added 4 cm^3 of PMe_2Ph (*ca.* 30 mmol). A grey oil formed in the bottom of the flask making stirring difficult. The mixture was refluxed for 12–18 hr when a red solution and a brown solid were obtained. The solid was decanted, the solution filtered while still hot and then evaporated until precipitation took place. Complete precipitation was achieved by addition of Et_2O (*ca.* 20 cm^3) and cooling at −30°C overnight. Yield 60%.

The complex $[WCl_4(PMePh_2)_2]$ was similarly prepared and reacted with water under the conditions mentioned above, to give mauve crystals (from Et_2O–THF) of $[WOCl_2(PMePh_2)_3]$ in 80% yield. Both oxocomplexes were identified by comparison of their IR and ^1H NMR spectra with those of authentic samples.[4]

Oxochlorotris(trimethylphosphite)tungsten(IV)

Freshly prepared $WOCl_4$ (3.62 g, *ca.* 5.63 mmol) was loaded into a 500 cm^3-pressure bottle with four equivalents of Na–Hg amalgam (1.5 cm^3 of a *ca.* 1% in Na). The contents were pumped on for *ca.* 1 hr. The pressure vessel was cooled to −78°C and degassed THF (150 cm^3) and $P(OMe)_3$ (5.3 cm^3, *ca.* 45 mmol) were added. The bottle was pressurized to 40 psi with hydrogen. The reaction vessel was allowed to warm slowly to room temperature and stirred for 12 hr. The volatile materials were removed under vacuum leaving a purple oil. This was extracted into Et_2O (50 cm^3), filtered, evaporated to *ca.* 25 cm^3 and cooled at −20°C. Purple crystals of $[WOCl_2(P(OMe)_3)_3]$ were collected and dried under vacuum. Yield: 80%. [Found C, 17.0 (16.8); H, 4.2 (4.2); Cl, 10.9 (11.0); P, 14.4 (14.4)%.]

IR (Nujol mull) bands at: 2855, 1371, 1309, 1267, 1188, 1021, 955, 669 cm^{-1}.

NMR: ^1H (C_6D_6): 3.82 mult. $^{31}P\{^1H\}$ (C_6D_6): 134.88t, $^2J(P\text{–}P) = 23.5$ Hz, $^1J(W\text{–}P) = 316.9$ Hz; 128.08d, $^1J(W\text{–}P) = 257.0$ Hz.

Oxobis (cyanate) tris (trimethylphosphine) tungsten (IV)

$[WOCl_2(PMe_3)_3]$ (0.5 g, *ca.* 1 mmol) and dried (100°C, 24 hr) KCNO (0.2 g, excess) were stirred at room temperature in THF (40 cm^3) over a period of 3–4 hr. The solvent was then stripped *in vacuo* and the residue extracted with 50 cm^3 of Et_2O. The resulting suspension was centrifuged and small dark blue needles of $[WO(NCO)_2(PMe_3)_3]$ were collected in *ca.* 80% yield by cooling at 0°C overnight. [Found C, 25.7 (25.8); H, 5.3 (5.3)%].

IR (Nujol mull) bands at: 2230, 2190, 1375, 1350, 1335, 1300, 1285, 950, 725, 665, 620 cm^{-1}.

RMN: ^1H (CH_2Cl_2): 1.60t (18), $J(P\text{–}H)_{ap} = 4$ Hz; 1.70d (9), $J(P\text{–}H) = 8$ Hz.

Metathesis with KSCN was accomplished in a similar way to give small blue crystals of $[WO(NCS)_2(PMe_3)_3]$ (from Et_2O–THF) in *ca.* 80% yield. [Found C, 24.4 (24.3); H, 5.0 (5.0)%.]

IR (Nujol mull) bands at: 2060, 2040, 1380, 1305, 1290, 1260, 965, 945, 835, 720, 665 cm^{-1}.

RMN: ^1H (CH_2Cl_2): 1.80t (18), $J(P\text{–}H)_{ap} = 4$ Hz; 1.88d (9), $J(P\text{–}H) = 8$ Hz.

Oxobis(N,N - dimethyldithiocarbamate)trimethyl - phosphinetungsten(IV)

30 cm^3 of THF were syringed into a mixture of $[WOCl_2(PMe_3)_3]$ (0.5 g, *ca.* 1 mmol) and anhydrous NaS_2CNMe_2 (0.5 g, excess). The dark blue crystals of the tungsten compound dissolved immediately giving a dark red solution. The mixture was stirred for *ca.* 3 hr at room temperature and the solvent removed *in vacuo*. Extraction with 30 cm^3 of a 1 : 1 mixture of Et_2O : CH_2Cl_2 and centrifugation afforded a dark red solution from which dark red crystals of $[WO(S_2CNMe_2)_2(PMe_3)]$ were collected in *ca.* 70% yield after partial removal of the solvent and cooling at −30°C. [Found C, 22.2 (20.9); H, 4.4 (4.1); N, 5.7 (5.4)%.]

IR (Nujol mull) bands at: 1545, 1520, 1400, 1390, 1280, 1275, 1240, 1150, 1140, 1050, 1040, 950, 935, 930, 895, 850, 830, 730, 720, 660 cm^{-1}.

^{1}NMR: ^1H (CD_2Cl_2, −80°C): 3.81s (3); 3.66s (3); 3.37s (3); 3.30s (3); 1.44d (9), $J(P\text{–}H) = 9.2$ Hz. $^{31}P\{^1H\}$ (CD_2Cl_2, −80°C): −19.8; $J(W\text{–}P) = 210.9$ Hz.

Acknowledgements—We thank the Spanish C.A.I.C.Y.T. (E.C.) and the Robert A. Welch Foundation and the University Research Institute of the University of Texas at Austin (R.A.J.) for support.

REFERENCES

1. E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood and R. D. Rogers, *Polyhedron* 1983, **2**, 185; E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Am. Chem. Soc.* in the press.
2. E. Carmona, L. Sánchez, M. L. Poveda, J. M. Marín, J. L. Atwood and R. D. Rogers, *J. Chem. Soc., Chem. Comm.* 1983, 161.
3. [a]P. R. Sharp and R. R. Schrock, *J. Am. Chem. Soc.* 1980, **102**, 1430; [b]J. L. Atwood and R. D. Rogers, personal communication.
4. A. V. Butcher, J. Chatt, G. J. Leigh and P. L. Richards, *J. Chem. Soc., Dalton Trans.* 1972, 1064.
5. A. L. Galyer, Ph.D. Thesis. Imperial College, London (1976); A. L. Galyer and G. Wilkinson, unpublished results.
6. D. F. Evans, *J. Chem. Soc.* 1959, 2003.
7. C. A. McAuliffe and W. Levason, In *Phosphine, Arsine and Stibine Complexes of the Transition Elements.* Elsevier, Amsterdam (1979); Z. Dori, *Prog. Inorg. Chem.* 1981, **28**, 239.
8. Kwok W. Chiu, David Lyons and G. Wilkinson, *Polyhedron* 1983, **2**, 803.
9. See for instance H. F. Klein and H. H. Karsch, *Chem. Ber.* 1976, **109**, 2524.
10. W. E. Newton, J. W. McDonald, J. L. Corbin, L. Ricard and R. Weiss, *Inorg. Chem.* 1980, **19**, 1997.
11. J. L. Templeton, B. C. Ward, G. J.-J. Chen, J. W. McDonald and W. E. Newton, *Inorg. Chem.* 1980, **20**, 1248.
12. D. Coucouvanis, *Prog. Inorg. Chem.* 1979, **26**, 301.
13. W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal Org. Chem.* 1974, **4**, 149.
14. R. Appel and H. Schöler, *Chem. Ber.* 1977, **110**, 2382.