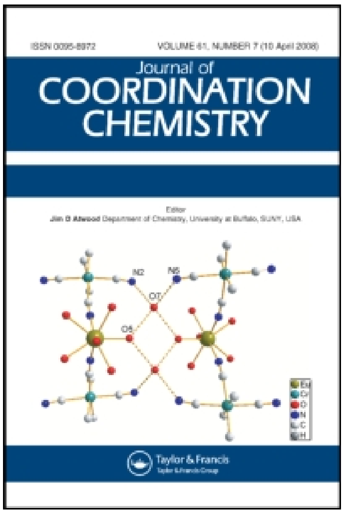

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# THE FIRST EXAMPLES OF TRIPHENYLPHOSPHINEOXIDE AND TRIPHENYLPHOSPHINESULPHIDE SEVEN-COORDINATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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**To cite this Article** Baker, Paul K. and Kendrick, Dafydd ap(1988) 'THE FIRST EXAMPLES OF TRIPHENYLPHOSPHINEOXIDE AND TRIPHENYLPHOSPHINESULPHIDE SEVEN-COORDINATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)', Journal of Coordination Chemistry, 17: 4, 355 — 358
**To link to this Article: DOI:** 10.1080/00958978808073928
**URL:** http://dx.doi.org/10.1080/00958978808073928

*J. Coord. Chem.* 1988, Vol. 17. pp. 355–358
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# COMMUNICATION: THE FIRST EXAMPLES OF TRIPHENYLPHOSPHINEOXIDE AND TRIPHENYLPHOSPHINESULPHIDE SEVEN-COORDINATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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*(Received December 12, 1987)*

**Keywords:** Molybdenum(II), tungsten(II), seven-coordinate, triphenylphosphine sulphide, triphenylphosphineoxide

## INTRODUCTION

Seven-coordinate complexes of molybdenum(II) and tungsten(II) have become increasingly important in recent years; in particular the compounds $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = $PPh_3$ or $AsPh_3$) have been shown to be catalysts for the ring-opening polymerisation of norbornene and norbornadiene.[1,2] It is believed that it is the ease of phosphine or arsine dissociation in these compounds which is the rate determining step in the mechanism. Although many examples of bisphosphine seven-coordinate compounds of the type $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl, Br or I; L = $PR_3$) have been reported,[3–6] hitherto no examples of seven-coordinate complexes containing the phosphorus(v) ligands triphenylphosphineoxide or triphenylphosphinesulphide have been described. We wish to report in this communication the preparation of some new seven-coordinate complexes of molybdenum(II) and tungsten(II) containing triphenylphosphineoxide and triphenylphosphinesulphide as attached ligands.

## EXPERIMENTAL

All reactions were carried out under nitrogen using standard Schlenk techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) were prepared by the published method.[7] All chemicals were purchased from commercial sources. Elemental analyses for C, H and N were obtained using a Carlo Erba Elemental Analyser MOD 1106 (with helium as carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer.

### (1) $[MoI_2(CO)_3(OPPh_3)_2].CH_2Cl_2$

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.969 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$), with continuous stirring under a stream of dry nitrogen was added $OPPh_3$ (0.54 g,

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1.940 mmol). The mixture was stirred for 18 hours. After filtration, removal of the solvent *in vacuo* gave the brown crystalline complex $[MoI_2(CO)_3(OPPh_3)_2].CH_2Cl_2$, (yield = 0.78 g, 75%), which was recrystallised from $CH_2Cl_2$. The room temperature $^1H$ n.m.r. spectrum ($CDCl_3$) showed resonances at $\delta = 5.3$ (s,2H,$CH_2$) and 7.54 (m, 30H, Ph).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of L (L = $OPPh_3$ and $SPPh_3$), gave the new compounds $[MI_2(CO)_3L_2]$.

### (5) $[MoI_2(CO)_3(PPh_3)(OPPh_3)]$

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.969 mmol) dissolved in $CH_2Cl_2$ (15 $cm^3$), with continuous stirring under a stream of dry nitrogen was added $PPh_3$ (0.254 g, 0.968 mmol). After stirring for one minute $OPPh_3$ (0.27 g, 0.970 mmol) was added and the mixture was stirred for a further 18 hours. After filtration, removal of the solvent *in vacuo* gave the brown crystalline complex $[MoI_2(CO)_3(PPh_3)(OPPh_3)]$ (yield = 0.84 g, 89%), which was recrystallised from $CH_2Cl_2$.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of $PPh_3$ followed by an *in situ* reaction with one equivalent of L (L = $OPPh_3$ and $SPPh_3$) gave the new compounds $[MI_2(CO)_3(PPh_3)L]$.

## RESULTS AND DISCUSSION

The starting materials for this research are the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) which are prepared by reacting the zerovalent trisacetonitrile compounds $[M(CO)_3(NCMe)_3]$ *in situ* with one equivalent of $I_2$ which affords quantitative yields of the seven-coordinate compounds. The complexes $[MI_2(CO)_3(NCMe)_2]$(M = Mo or W) react with two equivalents of L (L = $OPPh_3$ or $SPPh_3$) in $CH_2Cl_2$ at room temperature to give high yields of the acetonitrile substituted products $[MI_2(CO)_3L_2]$ (*1–4*). Reaction of $[MI_2(CO)_3(NCMe)_2]$(M = Mo or W) with one equivalent of $PPh_3$ gives the monoacetonitrile compounds $[MI_2(CO)_3(NCMe)(PPh_3)]$ which have been isolated and fully characterised.[8] These monoacetonitrile compounds $[MI_2(CO)_3(NCMe)(PPh_3)]$ when reacted *in situ* with one equivalent of L (L = $OPPh_3$ or $SPPh_3$) in $CH_2Cl_2$ at room temperature give the novel mixed compounds $[MI_2(CO)_3(PPh_3)L]$ (*5–8*). The new complexes (*1–8*) described in this communication have been characterised by elemental analysis (C, H and N, Table I) and infrared spectroscopy (Table II). Complex (*1*) was confirmed as a $CH_2Cl_2$ solvate from repeated elemental analyses and $^1H$ n.m.r. spectroscopy (see experimental). The *bis* $OPPh_3$ and $SPPh_3$ complexes (*1–4*) are very air-sensitive in solution and must be stored in the solid state under nitrogen. The mixed compounds (*5–8*) are much less air-sensitive although they should be stored under a nitrogen atmosphere. All the complexes (*1–8*) are soluble in polar solvents such as $CHCl_3$ and $CH_2Cl_2$, but only slightly soluble in diethylether.

The reactions of $[MI_2(CO)_3(NCMe)_2]$(M = Mo or W) and $[MI_2(CO)_3(NCMe)(PPh_3)]$ with L (L = $OPPh_3$ or $SPPh_3$) are likely to proceed by dissociative mechanisms since the complexes $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)(PPh_3)]$ obey the effective atomic number rule and are highly crowded. Evidence to support these proposed dissociative mechanisms comes from some work by Tripathi and coworkers[9] who prepared and isolated the six-coordinate 16 electron molybdenum(II) complexes $[MoX_2(CO)_3L]$ (X = Cl, Br or I; L = $PPh_3$, $AsPh_3$ or

$SbPh_3$). These are synthesised by reacting [$Mo(CO)_5L$] with one equivalent of $X_2$ in hexane. The complexes [$MoX_2(CO)_3L$] are analogous to the proposed intermediates [$MI_2(CO)_3(NCMe)$] and [$MI_2(CO)_3(PPh_3)$] resulting from loss of acetonitrile from the seven-coordinate complexes.

TABLE I
Physical and analytical data for the seven-coordinate complexes [$MI_2(CO)_3L_2$] and [$MI_2(CO)_3(PPh_3)L$].

| Complex | Colour | Yield(%) | Found (Calcd)% | |
|---|---|---|---|---|
| | | | C | H |
| (*1*) [$MoI_2(CO)_3(OPPh_3)_2$].$CH_2Cl_2$ | Brown | 75 | 44.6(44.7) | 3.1(3.0) |
| (*2*) [$WI_2(CO)_3(OPPh_3)_2$] | Golden brown | 75 | 43.3(43.4) | 2.8(2.8) |
| (*3*) [$MoI_2(CO)_3(SPPh_3)_2$] | Brown | 84 | 46.2(45.8) | 3.3(3.0) |
| (*4*) [$WI_2(CO)_3(SPPh_3)_2$] | Green | 90 | 42.7(42.2) | 3.0(2.7) |
| (*5*) [$MoI_2(CO)_3(PPh_3)(OPPh_3)$] | Brown | 89 | 47.7(48.1) | 3.0(3.1) |
| (*6*) [$WI_2(CO)_3(PPh_3)(OPPh_3)$] | Golden brown | 87 | 43.8(44.1) | 3.1(2.9) |
| (*7*) [$MoI_2(CO)_3(PPh_3)(SPPh_3)$] | Brown | 81 | 47.7(47.3) | 3.3(3.1) |
| (*8*) [$WI_2(CO)_3(PPh_3)(SPPh_3)$] | Yellow | 89 | 43.5(43.4) | 3.0(2.8) |

TABLE II
Infrared data[a] for the seven-coordinate complexes [$MI_2(CO)_3L_2$] and [$MI_2(CO)_3(PPh_3)L$].

| Complex | $\nu(CO)cm^{-1}$ |
|---|---|
| (*1*) | 2050(s), 1995(s) and 1935(s) |
| (*2*) | 2055(s), 1990(s) and 1905(s) |
| (*3*) | 2070(m), 2010(s) and 1955(s) |
| (*4*) | 2070(m), 2015(s) and 1930(s) |
| (*5*) | 1995(s), 1925(s) and 1890(s) |
| (*6*) | 1995(s), 1930(s) and 1905(s) |
| (*7*) | 2030(m), 1962(s) and 1925(s) |
| (*8*) | 2020(m), 1962(s) and 1915(s) |

[a] Spectra recorded as $CHCl_3$ thin films between NaCl plates; m, medium; s, strong.

The structures of these seven-coordinate complexes are likely to be of the capped octahedral kind since the geometry of most of the seven-coordinate complexes of molybdenum(II) or tungsten(II) have such a geometry.[10-16] Attempts are currently being made to grow single crystals for x-ray crystallography of these seven-coordinate complexes containing triphenylphosphineoxide and triphenylphosphinesulphide as attached ligand.

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