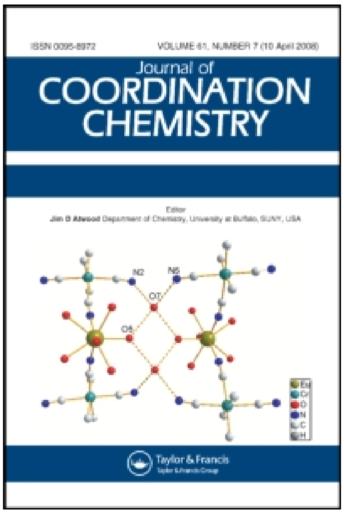

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SOME NEW ETHYLXANTHATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

Paul K. Baker[a]; Kevin R. Flower[a]
[a] Department of Chemistry, University College of North Wales, Bangor, Gwynedd, UK

To cite this Article Baker, Paul K. and Flower, Kevin R.(1987) 'SOME NEW ETHYLXANTHATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)', Journal of Coordination Chemistry, 15: 4, 333 — 336
To link to this Article: DOI: 10.1080/00958978708079789
URL: http://dx.doi.org/10.1080/00958978708079789

J. Coord. Chem. 1987, Vol. 15, p. 333-336
Photocopying permitted by license only

COMMUNICATION

SOME NEW ETHYLXANTHATE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

PAUL K. BAKER† and KEVIN R. FLOWER

Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, UK

(Received April 7, 1986)

Keywords: Molybdenum, Tungsten, ethylxanthate, complexes, synthesis

INTRODUCTION

Transition-metal complexes containing molybdenum-sulphur bonds are of continuing interest since they play an important role in the nitrogenase enzyme system. Many examples of dithiocarbamate organometallic complexes of molybdenum(II) and tungsten(II) are known: in particular the compounds $[M(CO)_n(S_2CNR_2)_2]$ (M = Mo and W; n = 2 and 3; R = Me, Et and ^iPr) have a wide range of chemistry.[1-5] Until now very few monoxanthate organometallic complexes of molybdenum(II) and tungsten(II) have been prepared, and here we wish to report the synthesis and spectral properties of the new monoethylxanthate complexes $[MI(CO)_3L(S_2COEt)]$ (M = Mo and W; L = PPh_3, $AsPh_3$ and $SbPh_3$) which are prepared by reaction of $[MI_2(CO)_3(NCMe)_2]$[6] with L in CH_2Cl_2, followed by further reaction *in situ* with NaS_2COEt.

EXPERIMENTAL

$[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) were prepared according to literature methods[6] and $[M(CO)_6]$, PPh_3, $AsPh_3$, $SbPh_3$ and KS_2COEt were purchased from commercial sources. Dichloromethane was distilled before use. ^1H n.m.r. spectra were recorded on a Jeol FX60 n.m.r. spectrometer (all spectra were recorded against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using helium carrier gas).

$MoI(CO)_3(PPh_3)(S_2COEt)$

To $MoI_2(CO)_3(NCMe)_2$ (0.5 g, 0.97 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.25 g, 0.97 mmol). After stirring for one minute, KS_2COEt(0.135 g, 0.96 mmol) was added and the mixture was stirred for a further 3 hours. After filtration, removal of the solvent *in vacuo* gave brown crystals of $[MoI(CO)_3(PPh_3)(S_2COEt)]$ (yield = 0.4 g, 60%), which was recrystallised from CH_2Cl_2.

TABLE I
Analytical data for the $[MI(CO)_3L(S_2COEt)]^a$ complexes

	M	L	Colour	Yield %	Found (Calcd.) %
(1)	Mo	PPh_3	Brown	60	C 42.05 (41.74) H 3.08 (2.90)
(2)	Mo	$AsPh_3$	Brown	65	C 39.54 (39.23) H 3.01 (2.72)
(3)	Mo	$SbPh_3$	Brown	66	C 36.17 (36.87) H 2.9 (2.56)
(4)	W	PPh_3	Orange	68	C 36.82 (37.02) H 2.56 (2.90)
(5)	W	$AsPh_3$	Orange	62	C 34.67 (35.04) H 2.39 (2.43)
(6)	W	$SbPh_3$	Orange	63	C 33.28 (33.14) H 2.37 (2.30)

[a] reaction times for L + $[MI_2(CO)_3(NCMe)_2] \rightarrow [MI_2(CO)_3(NCMe)L]$ and $KS_2COEt \rightarrow [MI(CO)_3L(S_2COEt)]$: (1) PPh_3, 1 minute, KS_2COEt, 3 hours; (2) $AsPh_3$, 3 minutes, KS_2COEt, 3 hours; (3) $SbPh_3$, 5 minutes, KS_2COEt, 3 hours. Similar times were recorded for the tungsten complexes (4), (5) and (6).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L followed by KS_2COEt gave the new compounds $[MI(CO)_3L(S_2COEt)]$ (see Table I for reaction times).

RESULTS AND DISCUSSION

Elemental analysis (Table I) and infrared and ^1H n.m.r. spectroscopy (Table II) support the formulation of the new complexes as being $[MI(CO)_3L(S_2COEt)]$ (M = Mo and W; L = PPh_3, $AsPh_3$ and $SbPh_3$). Since the complexes $[MI_2(CO)_3(NCMe)L]$ (M = Mo and W; L = PPh_3, $AsPh_3$ and $SbPh_3$) have been prepared[7] and fully characterised it was decided to prepare the ethylxanthate complexes from the $[MI_2(CO)_3(NCMe)L]$ complexes which are in turn prepared by reaction of $[MI_2(CO)_3(NCMe)_2]$[6] with L in CH_2Cl_2, followed by reaction *in situ* with NaS_2COEt to give good yields of the new compounds, $[MI(CO)_3L(S_2COEt)]$. The compounds are moderately stable in the solid state when stored under argon and are soluble in CH_2Cl_2 and $CHCl_3$.

In view of the previously reported X-ray crystal structures of related seven-coordinate complexes[8–16], all having capped octahedral geometry, it is highly likely that the ethylxanthate complexes will have a similar geometry since their carbonyl infrared pattern closely resembles other analogous seven-coordinate complexes with this coordination geometry.

We are currently investigating the catalytic activity of these $[MI(CO)_3L(S_2COEt)]$ compounds since the seven-coordinate complexes $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = PPh_3 and $AsPh_3$) have recently been discovered to be catalysts in the ring opening polymerisation of norbornene.[17,18]

REFERENCES

1. R. Colton, G.R. Scollary and I.B. Tomkins, *Aust. J. Chem.*, **21**, 15 (1968).
2. J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc.*, **102**, 6568 (1980).
3. E. Carmona, K. Doppert, J.M. Marin, M.L. Poveda, L. Sanchez and R. Sanchez-Delgado, *Inorg. Chem.*, **23**, 530 (1984).

TABLE II
IR[a] and ^{1}H n.m.r.[b] data for the $[MI(CO)_3L(S_2COEt)]$ complexes.

	M	L	ν(CO) cm^{-1}	ν(CS) cm^{-1}	^{1}H n.m.r. data (δ)[b]		
					Ph	CH_2	CH_3
(1)	Mo	PPh_3	2040(s), 1950(s) and 1875(s)	860(w)	7.38(s, 15H)	4.25(q, 2H, 7.32Hz)	1.34(t, 3H, 7.32Hz)
(2)	Mo	$AsPh_3$	2040(s), 1970(s) and 1945(s)	850(w)	7.40(s, 15H)	3.91(q, 2H, 7.32Hz)	1.14(t, 3H, 7.32Hz)
(3)	Mo	$SbPh_3$	2040(s), 1970(s) and 1940(s)	860(w)	7.44(s, 15H)	4.06(q, 2H, 7.32Hz)	1.17(t, 3H, 7.32Hz)
(4)	W	PPh_3	2035(s), 1950(s) and 1935(m)	870(w)	7.49(s, 15H)	4.30(q, 2H, 6.84Hz)	1.29(t, 3H, 6.84Hz)
(5)	W	$AsPh_3$	2030(s), 1950(s) and 1920(s)	860(w)	7.42(s, 15H)	3.95(q, 2H, 7.32Hz)	1.17(t, 3H, 7.32Hz)
(6)	W	$SbPh_3$	2030(s), 1950(s) and 1930(m)	865(w)	7.47(s, 15H)	4.15(q, 2H, 7.32Hz)	1.25(t, 3H, 7.32Hz)

[a]Spectra recorded in $CHCl_3$; w, weak; m, medium; s, strong. [b]Spectra recorded in $CDCl_3$ (+25°C) and referenced to Me_4Si.

4. J.A. Broomhead and C.G. Young, *Aust. J. Chem.*, **35**, 277 (1982).
5. J.R. Morrow, T.L. Tonker, J.L. Templeton and W.R. Kenan Jr., *J. Am. Chem. Soc.*, **107**, 6956 (1985).
6. P.K. Baker, E.M. Keys and S.G. Fraser, *J. Organometal. Chem.*, in press.
7. P.K. Baker and S.G. Fraser, *Polyhedron*, in press.
8. A. Mawby and G.E. Pringle, *J. Inorg. Nucl. Chem.*, **34**, 517 (1972).
9. M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 1329 (1972).
10. M.G.B. Drew, A.W. Johans and A.P. Wolters, *J. Chem. Soc., Chem. Commun.*, 819 (1971).
11. M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 626 (1972).
12. M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 1984 (1975).
13. M.G.B. Drew and A.P. Wolters, *Acta Cryst.*, **B33**, 205 (1977).
14. G. Schmid, R. Boese and E. Welz, *Chem. Ber.*, **108**, 260 (1975).
15. R. Boese and U. Müller, *Acta Cryst.*, **B32**, 582 (1976).
16. M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 557 (1977).
17. L. Bencze and A. Kraut-Vass, *J. Mol. Catal.*, **28**, 369 (1985).
18. L. Bencze, A. Kraut-Vass and L. Prókai, *J. Chem. Soc., Chem. Commun.*, 911 (1985).