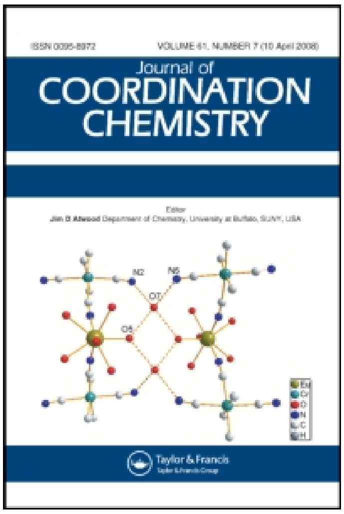

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DIPHENYLPHOSPHINOFERROCENE AS A LIGAND BONDED TO SEVEN-COORDINATE ORGANOMETALLIC COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react in CH_2Cl_2 at room temperature with two equivalents of PPh_2Fe (PPh_2Fe = diphenylphosphinoferrocene) to give the new seven-coordinate complexes $[MI_2(CO)_3(PPh_2Fe)_2]$ *via* displacement of the labile acetonitrile ligands. Reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of PPh_2Fe in CH_2Cl_2 at room temperature initially gives $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$ which cannot be isolated and rapidly dimerises to give $[M(\mu\text{-}I)I(CO)_3(PPh_2Fe)]_2$. The preparation of the new "mixed" complexes $[MI_2(CO)_3L(PPh_2Fe)]$ from reaction of $[MI_2(CO)_3(NCMe)_2]$ with L (L = PPh_3, $AsPh_3$ and $SbPh_3$) in CH_2Cl_2 followed by an *in situ* reaction with PPh_2Fe is also described.

Keywords: molybdenum, tungsten, diphenylphosphinoferrocene, complexes, seven-coordinate

INTRODUCTION

Seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) have become increasingly important due to the catalytic activity of the seven-coordinate complexes $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$). Bencze and coworkers[1] have shown the complexes $[MX_2(CO)_3L_2]$ to be active catalysts for the ring-opening polymerisation of norbornene and norbornadiene, and the rate-determining step for this process is the cleavage of the metal-phosphorus or arsenic bond.

Although the six-coordinate zero-valent complexes $[M(CO)_5(PPh_2Fe)]$ and $[M(CO)_4(PPh_2Fe)_2]$ (M = Mo or W) have been prepared and their redox properties investigated,[2] hitherto there have been no examples of seven-coordinate complexes reported of molybdenum(II) or tungsten(II) containing PPh_2Fe (**1**) as an attached ligand. In recent years we have been investigating the chemistry of the highly versatile complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W),[3] and in this paper we wish to describe the reactions of $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$) with the sterically bulky ligand PPh_2Fe (**1**).

EXPERIMENTAL

All reactions were carried out under nitrogen using standard Schlenk techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared according to literature methods[3] and PPh_2Fe, PPh_3, $AsPh_3$ and $SbPh_3$ *etc.*, were purchased from

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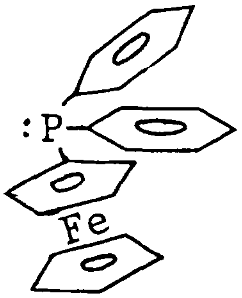

commercial sources. We are very grateful for the kind donation of [Mo(CO)$_6$] from Amax Speciality Metals Ltd. Dichloromethane was distilled before use.

^{1}H n.m.r. spectra were recorded on a Jeol FX 60 MHz n.m.r. spectrometer. I.r. spectra were recorded on a Perkin-Elmer 197 i.r. spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were measured on a Carlo Erba Elemental Analyser MOD 1106 (using helium as the carrier gas). The molecular weights of [M(μ – I)I(CO)$_3$(PPh$_2$Fe)]$_2$ were determined by Rast's method[4] using camphor as the solvent. Magnetic susceptibilities were measured using a Johnson-Mathey magnetic susceptibility balance.

MoI$_2$(CO)$_3$(PPh$_2$Fe)$_2$

To [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.4g, 0.775 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added PPh$_2$Fe (0.574g, 1.55 mmol). After stirring for 60 minutes, filtration and removal of the solvent *in vacuo* gave the olive green crystalline complex [MoI$_2$(CO)$_3$(PPh$_2$Fe)$_2$] (yield = 0.57g, 67%), which was recrystallised from CH$_2$Cl$_2$.

In a similar reaction of [WI$_2$(CO)$_3$(NCMe)$_2$] with two equivalents of PPh$_2$Fe in CH$_2$Cl$_2$ gave the new compound [WI$_2$(CO)$_3$(PPh$_2$Fe)$_2$].

[Mo(μ – I)I(CO)$_3$(PPh$_2$Fe)]$_2$

To [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.3g, 0.582 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3), with continuous stirring under a stream of dry nitrogen was added PPh$_2$Fe (0.215g, 0.582 mmol). After stirring for 2 hours, filtration and removal of solvent *in vacuo* gave the black crystalline complex [Mo(μ – I)I(CO)$_3$(PPh$_2$Fe)]$_2$ (yield = 0.34g, 72%), which was recrystallised from CH$_2$Cl$_2$. Molecular weight determined for $C_{50}H_{38}I_4O_6P_2Fe_2Mo_2$; Found: 1560; Calcd.: 1608.

In a similar reaction of [WI$_2$(CO)$_3$(NCMe)$_2$] with one equivalent of PPh$_2$Fe in CH$_2$Cl$_2$ for 2 hrs gave the new iodide-bridged dimer [W(μ – I)I(CO)$_3$(PPh$_2$Fe)]$_2$. Molecular weight determined for $C_{50}H_{38}I_4O_6P_2Fe_2W_2$; Found: 1864 Calcd.: 1784.

MoI$_2$(CO)$_3$(PPh$_3$)(PPh$_2$Fe)

To [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.3g, 0.582 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added PPh$_3$ (0.153g, 0.582 mmol). After stirring for one minute, PPh$_2$Fe (0.215g, 0.582 mmol) was added and the mixture was stirred for a further 90 minutes. After filtration, removal of the solvent *in vacuo* gave the dark brown crystalline complex [MoI$_2$(CO)$_3$(PPh$_3$)(PPh$_2$Fe)] (yield = 0.416g, 67%), which was recrystallised from CH$_2$Cl$_2$.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L in CH_2Cl_2 followed by PPh_2Fe gave the new compounds $[MI_2(CO)_3L(PPh_2Fe)]$ (see Table I for reaction times).

RESULTS AND DISCUSSION

Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of PPh_2Fe afforded the new seven-coordinate complexes $[MI_2(CO)_3(PPh_2Fe)_2]$ *via* successive substitution of acetonitrile ligands. Reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of PPh_2Fe initially gave "$[MI_2(CO)_3(NCMe)(PPh_2Fe)]$" which could not be isolated since they rapidly dimerised to afford the iodide-bridged dimers $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$. Reaction of $[MI_2(CO)_3(NCMe)_2]$ in CH_2Cl_2 *with* L (L = PPh_3, $AsPh_3$ or $SbPh_3$), followed by reaction *in situ* with PPh_2Fe afforded good yields of the new "mixed" complexes $[MI_2(CO)_3L(PPh_2Fe)]$. All the new complexes (1–10) have been fully characterised by elemental analysis (C, H and N) (Table I), i.r. and ^1H n.m.r. spectroscopy (Table II). The complexes are moderately soluble in CH_2Cl_2 and $CHCl_3$, but insoluble in hydrocarbon solvents. The compounds are all moderately air-sensitive, although they can be stored for prolonged periods under vacuum.

The formation of the bis PPh_2Fe complexes $[MI_2(CO)_3(PPh_2Fe)_2]$ from reaction of $[MI_2(CO)_3(NCMe)_2]$ and PPh_2Fe is perhaps surprising since PPh_2Fe is a very bulky ligand. It is likely to have a very large "cone angle",^{5} and hence it might be expected that the "16-electron" $[MI_2(CO)_2(PPh_2Fe)_2]$ dicarbonyl complexes would

TABLE I
Physical and analytical data for the complexes $[MI_2(CO)_3(PPh_2Fe)_2]$, $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$ and $[MI_2(CO)_3L(PPh_2Fe)]^a$.

Complex	Colour	Yield %	Found (Calcd.)% C	Found (Calcd.)% H
(1) $[MoI_2(CO)_3(PPh_2Fe)_2]$	Olive Green	67	47.9 (48.1)	3.6 (3.3)
(2) $[WI_2(CO)_3(PPh_2Fe)_2]$	Brown	65	45.2 (45.4)	3.5 (3.5)
(3) $[Mo(\mu-I)I(CO)_3(PPh_2Fe)]_2$	Black	72	37.4 (37.4)	2.4 (2.4)
(4) $[W(\mu-I)I(CO)_3(PPh_2Fe)]_2$	Brown	72	33.8 (33.7)	2.2 (2.1)
(5) $[MoI_2(CO)_3(PPh_3)(PPh_2Fe)]$	Dark Brown	67	46.7 (48.4)	3.4 (3.2)
(6) $[WI_2(CO)_3(PPh_3)(PPh_2Fe)]$	Golden Brown	55	44.8 (44.8)	3.2 (3.0)
(7) $[MoI_2(CO)_3(AsPh_3)(PPh_2Fe)]$	Dark Brown	58	47.1 (46.5)	3.2 (3.1)
(8) $[WI_2(CO)_3(AsPh_3)(PPh_2Fe)]$	Orange	53	43.4 (43.1)	3.1 (2.8)
(9) $[MoI_2(CO)_3(SbPh_3)(PPh_2Fe)]$	Dark Brown	55	44.6 (44.6)	3.2 (2.9)
(10) $[WI_2(CO)_3(SbPh_3)(PPh_2Fe)]$	Dark Orange	64	42.1 (41.5)	2.8 (2.7)

[a] Reaction times for $L + [MoI_2(CO)_3(NCMe)_2] \rightarrow [MoI_2(CO)_3(NCMe)L] + PPh_2Fe \rightarrow [MoI_2(CO)_3L(PPh_2Fe)]$ are (5): PPh_3, 1 minute, PPh_2Fe, 90 minutes; (7); $AsPh_3$, 3 minutes, PPh_2Fe, 90 minutes: (9): $SbPh_3$, 5 minutes, PPh_2Fe, 90 minutes. Similar times were recorded for the analogous tungsten complexes (6), (8) and (10).

TABLE II
I.r. and ^1H n.m.r. data for the complexes $[MI_2(CO)_3(PPh_2Fe)_2]$, $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$ and $[MI_2(CO)_3L(PPh_2Fe)]$.

Complex	$\nu(CO)^a$ cm^{-1}	^1H n.m.r. data (δ) ppm^b	
		Ferrocenyl resonances	Ph
(1)	2012(m), 1960(s), 1900(m)	4.31 (brm, 10H), 4.72 (brm, 8H)	7.6 (brm, 20H)
(2)	2012(m), 1960(m), 1920(m)	4.28 (brm, 10H), 4.76 (brm, 8H)	7.67 (brm, 20H)
(3)	2032(m), 2008(s), 1950(m)	4.2 (brm, 10H) 4.77 (brm, 8H)	7.68 (brm, 20H)
(4)	2015(s), 2000(s), 1930(s)	4.46 (brm, 10H) 4.75 (brm, 8H)	7.66 (brm, 20H)
(5)	2010(m), 1980(m), 1915(m)	4.24 (brm, 5H), 4.65 (brm, 4H)	7.55 (brm, 25H)
(6)	2010(m), 1940(m), 1910(m)	4.2 (brm, 5H), 4.8 (brm, 4H)	7.4 (brm, 25H)
(7)	2016(m), 1965(m), 1920(m)	4.21 (brm, 5H), 4.66 (brm, 4H)	7.37 (m, 25H)
(8)	2014(s), 1982(s), 1917(s)	4.19 (m, 5H) 4.76 (m, 4H)	7.39 (brm, 25H)
(9)	2015(s), 1958(s), 1898(m)	4.14 (m, 5H), 4.64 (m, 4H)	7.52 (brm, 25H)
(10)	2016(s), 1958(s), 1920(m)	4.14 (m, 5H), 4.68 (m, 4H)	7.40 (brm, 25H)

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

be formed. Several bisphosphine complexes of the type $[MX_2(CO)_2L_2]$ have been isolated[6] and shown to be carbon monoxide carriers. However, it has been observed that the diiodide complexes $[MI_2(CO)_3L_2]$ appear to lose carbon monoxide less readily than their dichloro and dibromo derivatives.[6] The structure of the complexes $[MI_2(CO)_3(PPh_2Fe)_2]$ and also of the "mixed" componds $[MI_2(CO)_3L(PPh_2Fe)]$ (see later) are very likely to have capped octahedral geometry, since the vast majority of complexes of the type $[MX_2(CO)_3L_2]$ have been shown by X-ray crystallography to have this geometry.[7] Also, the complexes $[MI_2(CO)_3(PPh_2Fe)_2]$ and $[MI_2(CO)_3L(PPh_2Fe)]$ have similar i.r. spectral properties {ν(CO)} to analogous seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ which have been shown to have capped octahedral geometry.

Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of PPh_2Fe must initially afford the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$. These are analogous to the compounds $[MI_2(CO)_3(NCMe)L](L = PPh_3, AsPh_3$ or $SbPh_3)$ which have been isolated and fully characterised.[8] However, even with very short reaction times, the complexes $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$ had started to dimerise and hence it was not possible to isolate the monoacetonitrile complexes in a pure state. Several unsuccessful attempts were made to prepare $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$ by carrying out the reactions at low temperature in order to slow down the dimerisation process. Although the electronic effects of a phenyl group and a ferrocenyl group (*i.e.*, PPh_3 versus PPh_2Fe) will be similar, the rapid dimerisation of $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$ compound to $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$ can be explained because of the very large size of the ligand PPh_2Fe (**1**). PPh_2Fe will force out the acetonitrile ligand more readily than the smaller PPh_3 ligand. It is likely that this reaction goes *via* a dissociative mechanism since Tripathi and co-workers[9] have reacted $[Mo(CO)_5L]$ ($L = PPh_3$, $AsPh_3$ or $SbPh_3$) with X_2 ($X = Cl$, Br or I) in hexane to give the "16-electron" compounds $[MoX_2(CO)_3L]$. The complexes $[MI_2(CO)_3(PPh_2Fe)]$ can dimerise *via* attack of the iodide lone pairs of the metal centre. The dimeric nature of these $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$ complexes is confirmed by molecular weight (see Experimental) and magnetic susceptibility measurements which show the compounds to be diamagnetic. Hence they are highly unlikely to be the "16-electron" complexes $[MI_2(CO)_3(PPh_2)Fe)]$, analogous to the $[MoX_2(CO)_3L]$ complexes isolated by Tripathi and coworkers.[9] The complexes $[MoX_2(CO)_3L]$ were rapidly precipitated from hexane and hence not allowed to dimerise in solution.[9] The geometry of the dimeric complexes $[M(\mu-I)I(CO)_3(PPh_2Fe)]_2$ is highly likely to be based on two capped octahedra with the two bridging iodide ligands occupying octahedral sites, and with a carbonyl ligand capping a $[MI_3(CO)_2(PPh_2Fe)]$ face. Cotton and co-workers[10] have reported the X-ray crystal structure of $[W(\mu-Br)Br(CO)_4]_2$, which has the two tungsten atoms in capped octahedral environments with a carbonyl ligand capping a $[WBr_3(CO)_3]$ octahedron.

Several attempts were made to form "mixed" complexes of the type $[MI_2(CO)_3L(PPh_2Fe)]$ $\{L = PPh_3, AsPh_3, py \text{ and } P(OPh)_3\}$ *via* $[MI_2(CO)_3(NCMe)(PPh_2Fe)]$ but since these complexes start to dimerise almost as soon as they were formed no mixed pure complexes could be obtained by this route. However, reaction of $[MI_2(CO)_3(NCMe)_2]$ with L in CH_2Cl_2 gives $[MI_2(CO)_3(NCMe)L]$ ($L = PPh_3$, $AsPh_3$ or $SbPh_3$)[8] which when reacted *in situ* with PPh_2Fe affords good yields of the new "mixed" compounds $[MI_2(CO)_3L(PPh_2Fe)]$.

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REFERENCES

1. L. Bencze and A. Kraut-Vass, *J. Mol. Catal.*, **28,** 369 (1985); L. Bencze, A. Kraut-Vass and L. Prókai, *J. Chem. Soc., Chem. Commun.*, 911 (1985).
2. J.C. Kotz and C.L. Nivert, *J. Organomet. Chem.*, **52,** 387 (1973); J.C. Kotz, C.L. Nivert, J.M. Lieber and R.C. Reed, *J. Organomet. Chem.*, **91,** 87 (1975).
3. P.K. Baker, S.G. Fraser and E.M. Keys, *J. Organomet. Chem.*, **309,** 319 (1986).
4. F.G. Mann and B.C. Saunders, "Practical Organic Chemistry", (Longman's, Green and Co. Ltd., 1954), pp. 342–344.
5. C.A. Tolman, *Chem. Rev.*, **77,** 313 (1977).
6. R. Colton and I.B. Tomkins, *Aust. J. Chem.*, **19,** 1143 (1966); R. Colton and I.B. Tomkins, *Aust. J. Chem.*, **19,** 1519 (1966); M.W. Anker, R. Colton and I.B. Tomkins, *Aust. J. Chem.*, **20,** 9 (1967); R. Colton and C.J. Rix, *Aust. J. Chem.*, **22,** 305 (1969); J.R. Moss and B.L. Shaw, *J. Chem. Soc.*, A, 595 (1970). R. Colton, *Coord. Chem. Rev.*, **6,** 269 (1971).
7. A. Mawby and G.E. Pringle, *J. Inorg. Nucl. Chem.*, **34,** 517 (1972); M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 1329 (1972); G. Schmid, R. Boese and E. Welz, *Ber.*, **108,** 260 (1975); M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 1984 (1975); R. Boese and U. Müller, *Acta Ctyst.*, **B32,** 582 (1976); M.G.B. Drew and A.P. Wolters, *Acta Cryst.*, **B23,** 205 (1977); M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 557 (1977).
8. P.K. Baker and S.G. Fraser, *Polyhedron*, **5,** 1381 (1986).
9. S.C. Tripathi, S.C. Shrivastava and D.P. Pandey, *Transition Met. Chem.*, **2,** 52 (1977).
10. F.A. Cotton, L.R. Falvello and J.H. Meadows, *Inorg. Chem.*, **24,** 514 (1985).