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SYNTHESIS AND CHARACTERIZATION OF THE SEVEN-COORDINATE COMPLEXES $[MI_2(CO)_3{Ph_2P(S)CH_2P(S)Ph_2-S,S'}]$ (M = Mo or W)

PAUL K, BAKER* and SHARMAN D. HARRIS

Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, U.K.

and

MARCUS C. DURRANT and RAYMOND L. RICHARDS*

Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Colney Lane, Norwich NR4 7UH, U.K.

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Abstract—Equimolar quantities of seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and Ph₂P(S)CH₂P(S)Ph₂ reacted in CH₂Cl₂ at room temperature giving the new acetonitrile-displaced products $[MI_2(CO)_3\{Ph_2P(S)CH_2P(S)Ph_2-S,S'\}]$, (1) and (2), in good yield. The tungsten complex 2, reacted with one equivalent of Ph₂PCH₂PPh₂ giving the bis(diphenylphosphino)methane complex $[WI_2(CO)_3(Ph_2PCH_2PPh_2)]$. Copyright © 1996 Elsevier Science Ltd

Since the early report in 1962 by Mannerskantz and Wilkinson¹ of the seven-coordinate complexes $[MX_2(CO)_3(2,5-dithiahexane)]$ (M = Mo or W; X = Br, I) only a few examples of seven-coordinate complexes of molybdenum(II) and tungsten(II) containing neutral sulfur donor ligands have been reported. Two examples include the macrocyclic thioether ligand complexes $[MI_2(CO)_3(TTP)] \cdot$ CH₂Cl₂ (M = Mo or W; TTP = 1,4,8,11-tetrathiacyclotetradecane).²

In 1986,³ we described the reaction of the tris (acetonitrile) complexes fac-[M(CO)₃(NCMe)₃] (M = Mo or W, prepared *in situ*⁴) with one equivalent of I₂ to give the highly versatile seven-coordinate complexes [MI₂(CO)₃(NCMe)₂]. The reactions of the complexes [MI₂(CO)₃(NCMe)₂] with a range of neutral sulfur donor ligands have been reported.⁵ ¹⁰ In this paper, we describe an extension of this work to include the reactions of [MI₂(CO)₃(NCMe)₂] with the neutral bidentate sulfur donor ligand Ph₂P(S)CH₂P(S)Ph₂.

EXPERIMENTAL

All reactions were carried out using standard vacuum Schlenk line techniques. The starting materials, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)³ and Ph₂P(S)CH₂P(S)Ph₂¹¹ were synthesized by published methods. All chemicals were purchased from commercial sources, and CH₂Cl₂ was dried over phosphorus pentoxide and distilled before use.

Elemental analyses were obtained using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas), C and H by Mr K. Jones (Bangor), S by Mr C.J. Macdonald (Nitrogen Fixation Laboratory, Sussex). Atomic absorption readings (Mo and W) were recorded on a Video IIE aa/ae spectrophotometer. Conductivity measurements were made using a Portland Electronics conductivity bridge. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer. The ¹H NMR spectra were recorded on a Bruker AC 250 MH, NMR spectrometer at the University of Wales, and referenced to SiMe₄. The ¹³C NMR spectrum was recorded on a Bruker WH 400 NMR spectrometer at the University of Warwick, and referenced to SiMe₄.

^{*} Authors to whom correspondence should be addressed.

$[MoI_{2}(CO)_{3}\{Ph_{2}P(S)CH_{2}P(S)Ph_{2}-S,S'\}] (1)$

To $[MoI_2(CO)_3(NCMe)_2]$ (0.30 g, 0.581 mmol) dissolved in CH₂Cl₂ (20 cm³) was added Ph₂P(S)CH₂P(S)Ph₂ (0.27 g, 0.603 mmol). The mixture was stirred for 2 h and the solvent was removed *in vacuo* to produce a brown powder. This was recrystallized from NCMe to produce a brown crystalline solid $[MoI_2(CO)_3{Ph_2P(S)CH_2P(S)Ph_2 S,S'}]$ (1), which was analytically pure (yield = 0.34 g, 66%).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of $Ph_2P(S)CH_2P(S)Ph_2$ followed by recrystallization from NCMe, gave the complex $[WI_2(CO)_3\{Ph_2P(S)CH_2P(S)Ph_2-S,S'\}] \cdot CH_2Cl_2$ (2) (yield = 0.35 g, 67%).

Reaction of $[WI_2(CO)_3{Ph_2P(S)CH_2P(S)Ph_2-S,S'}] \cdot CH_2Cl_2$ (2) with $Ph_2PCH_2PPh_2$

To complex 2 (0.2 g, 0.190 mmol) dissolved in NCMe (20 cm³), at room temperature, under nitrogen was added Ph₂PCH₂PPh₂ (0.08 g, 0.208 mmol). The mixture was stirred for 2 h and the solvent was removed *in vacuo* to give a yellow product, which was recrystallized from NCMe. This product was the complex [WI₂(CO)₃(Ph₂PCH₂PPh₂)] (**3**), which has been reported previously¹² (yield = 0.12 g, 70%).

RESULTS AND DISCUSSION

The reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W),³ with an equimolar amount of $Ph_2P(S)$ $CH_2P(S)Ph_2$ in CH_2Cl_2 gave the acetonitrilereplaced complexes $[MI_2(CO)_3] Ph_2P(S)CH_2P(S)$ Ph_2-S,S'] (1 and 2) in good yield. Complexes 1 and 2 were characterized by elemental analysis, IR and ¹H NMR spectroscopy (Table 1). Complex 2 has also been characterized by ¹³C NMR spectroscopy. Complexes 1 and 2 are soluble in acetone, nitromethane and acetonitrile but insoluble in chlorinated solvents. They are, as expected, nonconducting in both acetone and nitromethane. They are air-sensitive, both in the solid state and in solution. The molybdenum complex (1) is less stable than the tungsten complex (2), as has often been observed with this type of complex.^{13,14}

The IR spectra of complexes 1 and 2 showed a decrease in the frequency of v(P=S) relative to the free ligand, indicating S-coordination. For example, complex 2 showed v(P=S) at 563 cm⁻¹, compared with the free ligand which has v(P=S) at 626 cm⁻¹. The CO stretching frequencies for the molybdenum complex 1 (2068, 2015 and 1930 cm⁻¹) are slightly higher than in the tungsten ana-

logue 2 (2066, 2011 and 1927 cm⁻¹), which is compatible with a more effective π -electron donation from the tungsten to the antibonding orbitals of the carbonyl ligands.

The ¹H NMR spectra of complexes 1 and 2 (Table 1) showed the expected downfield of the methylene proton signals, as well as a slight downfield shift of the phenyl protons, relative to those of the free ligand. The CH₂ resonance for uncoordinated Ph₂P(S)CH₂P(S)Ph₂ appears as a triplet at δ 3.9 and shifts to δ 4.3 for 1 and δ 4.4 for complex 2 respectively. Complex 2 is a CH₂Cl₂ solvate, which was confirmed by the ¹H NMR data (δ 5.6, s, 2H, CH₂Cl₂ in ((CD₃)₂CO)), and repeated elemental analyses of the complex.

The room temperature ¹³C NMR ((CD_3)₂CO) of complex **2** showed resonances at δ 210 (s, C=O), 135.4, 134.6, 132.2, 128.9 (m, Ph-*C*), 54.6 (m, CH₂Cl₂), 35.2 (t,CH₂); the observation of only one carbonyl resonance suggests that the complex is fluxional with a rapid exchange of carbonyl ligands at ambient temperature.

Attempts to grow single crystals of complexes 1 and 2 for X-ray crystallography were unsuccessful; however, the IR spectral properties of those complexes closesly resemble analogous seven-coordinate compounds^{15,16} with capped octahedral geometry. Therefore, it is likely that these complexes also have a capped octahedral geometry.

It is interesting to compare complexes 1 and 2 to the previously reported,¹⁷ analogous oxygen donor complexes [MI₂(CO)₃{Ph₂P(O)CH₂P(O)Ph₂-O,O'] (M = Mo or W). The IR spectrum of the tungsten complex [WI₂(CO)₃{Ph₂P(O)CH₂P(O) Ph₂-O,O'] has three carbonyl stretching bands at v(CO)(KBr) = 2072, 2014 and 1915 cm⁻¹ i.e. at similar positions to the *S,S'*—bonded complex, 2.

Reaction of complex 2 with one equivalent of $Ph_2PCH_2PPh_2$ in NCMe at room temperature afforded the previously reported¹² complex [WI₂ (CO)₃(Ph₂PCH₂PPh₂)] 3 in 70% yield. This complex was characterized by elemental analysis, IR and ¹H NMR spectroscopy (Table 1). This reaction occurs by displacment of the more weakly attached diphosphine disulfide ligand. We have previously observed that reaction of [WI₂(CO)₃ {PhS(CH₂)₂SPh}] with an equimolar quantity of Ph₂PCH₂PPh₂ in CH₂Cl₂ at room temperature gives the SS displaced complex [WI₂(CO)₃ (Ph₂PCH₂PPh₂)] in 62% yield.¹⁸

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Complex	Colour	Yield - (%)	Analysis (%) ^a				IR $(cm^{-1})^{b}$		
			С	Н	S	Mo or W	v(CO)	v(PS)	⁻ ¹ H (δ ,ppm)
1	Brown	66	38.2(38.1)	2.9(2.5)	7.0(7.3)	11.6(10.9)	2068 s, 2015 s, 1930 m	584(s)	^c 8.0 (m, 8H, Ph- <i>o</i>), 7.48 (m, 12H, Ph- <i>m</i> and - <i>p</i>) 4.3 (t, 2H, CH ₂)
2	Orange	67	32.8(33.0)	2.1(2.3)	5.7(6.1)	17.9(17.4)	2066 m, 2011 s, 1927 br	563(s)	^c 8.1 (m, 8H, Ph- <i>o</i>), 7.5 (m, 12H, Ph- <i>m</i> and - <i>p</i>) 5.6 (s, 2H, CH ₂ Cl ₂), 4.4 (t, 2H, CH ₂) ^d 7.4 (m, 20H, Ph), 3.1 (br s, 2H, PCH ₂)
3	Yellow	70	37.3(37.1)	2.5(2.4)	—		2031 s, 1970 br, 1905 br		

"Calculated values in parentheses.

^{*b*}Spectra recorded as $\hat{\mathbf{K}}\mathbf{B}\mathbf{r}$ discs; $\mathbf{b}\mathbf{r} = \mathbf{b}\mathbf{r}\mathbf{o}\mathbf{a}\mathbf{d}$, $\mathbf{s} = \mathbf{s}\mathbf{t}\mathbf{r}\mathbf{o}\mathbf{n}\mathbf{g}$, $\mathbf{m} = \mathbf{m}\mathbf{e}\mathbf{d}\mathbf{i}\mathbf{u}\mathbf{m}$.

^cSpectra recorded in $(CD_3)_2CO$; s = singlet, t = triplet, m = multiplet, br = broad.

^dSpectrum recorded in CDCl₃.

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