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STUDIES OF CHELATION

VIII *. SUBSTITUTION REACTIONS OF TRIS-(η-ALKYNE)MONOCARBONYLTUNGSTEN COMPLEXES WITH PHOSPHORUS AND SULPHUR LIGANDS. INFLUENCE OF THE ALKYNE LIGAND

J.A. CONNOR and G.A. HUDSON

Department of Chemistry, The University, Manchester M13 9PL, (Great Britain)

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Summary

The η-alkyne complexes $[W(CO)(RC{\equiv}CR)_3]$ (R = Ph, SMe) react with the ditertiary alkylphosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) in dichloromethane solution at ambient temperature. $[W(CO)(MeSC{\equiv}CSMe)_3]$ produces $[W(CO)(dmpe)(MeSC{\equiv}CSMe)_2]$ and eventually $[W(dmpe)(MeSC{\equiv}CSMe)_2]$; with excess dmpe, $[W_2(dmpe)_5(MeSC{\equiv}CSMe)]$ is formed. All of the alkyne ligands are rapidly displaced from $[W(CO)(PhC{\equiv}CPh)_3]$ to give *cis*-$[W(CO)_2(dmpe)_2]$ as the principal product. Other phosphorus (Ph_3P, $Ph_2PCH_2CH_2PPh_2$) and sulphur ligands ($PhSCH_2CH_2SPh$, $Me_3CSCH_2CH_2CMe_3$) have no detectable reaction with $[W(CO)(RC{\equiv}CR)_3]$ (R = Ph, SMe) under the same conditions.

Introduction

Alkyne complexes of the type $[M(CO)(RC{\equiv}CR)_3]$ (M = Mo, W) have been known for many years [1]. The structure of $[W(CO)(PhC{\equiv}CPh)_3]$ shows that the complex has C_{3v} local symmetry at the tungsten atom, so that only 10 of the 12 π-electrons provided by the three alkyne ligands are available for bonding to the metal. The geometry of the alkyne ligands approaches that of *cis*-1,2-diphenylethene in that the interbond angle (C≡C—C) is 138° [2]. Recently, the substitution of the carbonyl ligand in $[W(CO)\{PhC{\equiv}C \cdot C_6H_3(OMe)_2\text{-}3,4\}_3]$ by PMe_2Ph was reported [3]. Apart from this, nothing is known of the substitution reactions of these unusual complexes. We were particularly interested in the possibility of replacing the formal 4-electron donor alkyne ligand in these

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* Part VII, ref. 4. No reprints available.

complexes by chelating (2 + 2) electron heteroatom donor ligands. The question also arose of whether the substituent R in $[W(CO)(RC{\equiv}CR)_3]$ might influence the reactions. Our previous work had shown that there are small but significant differences between $[W(CO)(MeSC{\equiv}CSMe)_3]$, in which the six methyl groups are magnetically equivalent at ambient temperature [4], and $[W(CO)(EtC{\equiv}CEt)_3]$ where this is not the case [1].

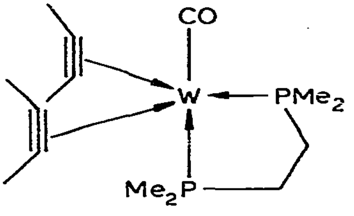
Results

We have investigated reactions of two tungsten complexes containing different alkyne ligands $[W(CO)(RC{\equiv}CR)_3]$ (R = Ph [1,2], SMe [4]) with both monodentate and bidentate phosphine, and bidentate sulphide ligands. In general, both of these tungsten complexes are remarkably resistant to substitution. Reactions were attempted with 3 : 1 and 1 : 1 mole ratios of ligand to $[W(CO)(RC{\equiv}CR)_3]$, initially at room temperature and, in those cases where no reaction was detected by IR or NMR spectroscopy, at the reflux temperature of dichloromethane and of tetrahydrofuran. There was no detectable reaction between the disecondary sulphides $QSCH_2CH_2SQ$ (Q = CMe_3, Ph) and either of the alkyne complexes $[W(CO)(RC{\equiv}CR)_3]$. Likewise, triphenylphosphine and $Ph_2PCH_2CH_2PPh_2$ failed to react with either of the alkyne complexes under the conditions outlined above. Under more forcing conditions (di-n-butylether at reflux) thermal decomposition of the alkyne complex was observed in preference to substitution by the aforementioned ligands. However, a ditertiary *alkyl*-phosphine reacts with each of the alkyne complexes under mild conditions.

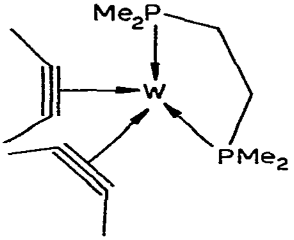
Addition of $Me_2PCH_2CH_2PMe_2$ (dmpe) to $[W(CO)(MeSC{\equiv}CSMe)_3]$ (equimolar proportions) in dichloromethane solution at ambient temperature produced a bright pink (λ_{max} 480 nm) air stable solid complex which was shown to be $[W(CO)(dmpe)(MeSC{\equiv}CSMe)_2]$ (I) by microanalysis and spectroscopy ($\nu(CO)$ 1902 cm^{-1}). The proton NMR spectrum showed signals which were assigned to both coordinated dithiahex-3-yne (δ 2.86 ppm) and coordinated dmpe (δ 1.70 ppm). The complex is sparingly soluble in acetone and diethylether, and readily soluble in chloroform and dichloromethane. Solutions of the pink complex I in dichloromethane darken in colour in the course of an hour and this is accompanied by a progressive diminution in the intensity of the IR absorption at 1902 cm^{-1}. When this absorption has disappeared completely, a yellow-amber air stable solid complex can be isolated from the otherwise clear solution. The yellow-amber solid was shown to be $[W(dmpe)(MeSC{\equiv}CSMe)_2]$ (II), by microanalysis and spectroscopy. The IR and ^1H NMR spectra of II were indistinguishable from those of I, with the exception of the absorption at 1902 cm^{-1} already mentioned. The decarbonylation reaction by which I is converted into II might be understood as being assisted by urge of both of the alkyne ligands which remain coordinated to tungsten to function as 4-electron donors in II. There was no evidence of monodentate coordination of th dmpe ligand [5] in the proton NMR spectrum of I.

The reaction between equimolar quantities of dmpe and $[W(CO)(MeSC{\equiv}CSMe)_3]$ in acetone solution produces another pink air stable complex III, which is insoluble in common organic solvents. Microanalysis indicated that, like I, this complex III has the composition [W(CO)(dmpe)-

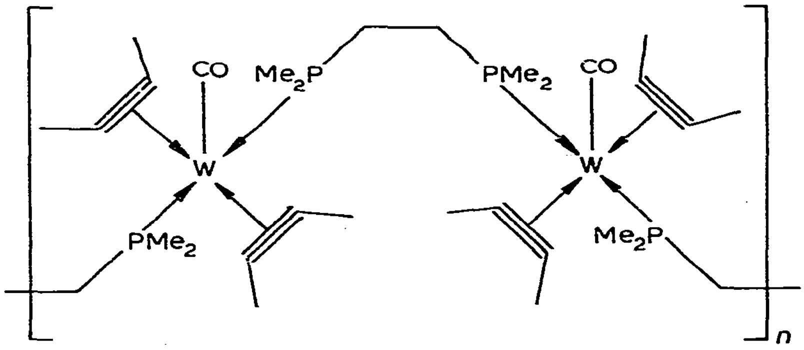
$(MeSC{\equiv}CSMe)_2]$. However, the decomposition points of I (418 K) and III (464 K) are different. The infrared (KBr disc) of I and III are very similar. A polymeric structure of the type represented below is suggested for III.



(I)

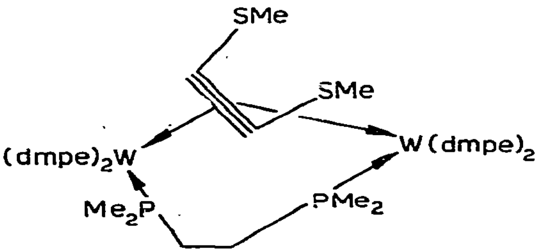


(II)



(III)

The reaction between $[W(CO)(MeSC{\equiv}CSMe)_3]$ and excess dmpe (4 mol) in dichloromethane solution at reflux produced a colourless, air sensitive complex IV, which was shown by microanalysis to have the composition $[W_2(dmpe)_5(MeSC{\equiv}CSMe)]$. The infrared spectrum shows absorptions which can be assigned to both dmpe and 2,5-dithiahex-3-yne. The ^1H NMR spectrum (CD_3OD solution) shows signals at δ 1.91, 2.20 (dmpe) and δ 2.77 ($MeSC{\equiv}CSMe$). Integration of these signals confirms the ratio 5 dmpe : 1alkyne. A structure consistent with these observations would indicate a bridging alkyne and also bridging dmpe as in



(IV)

Alkyne ligands bridging two metal atoms are well known, for example in

$[Co_2(CO)_6(alkyne)]$ complexes [4]. In contrast to the reaction of $[W(CO)(MeSC{\equiv}CSMe)_3]$ with dmpe in dichloromethane to give I, and with excess dmpe to produce IV, the reaction of $[W(CO)(PhC{\equiv}CPh)_3]$ with dmpe (3 mol), which also proceeds under mild conditions (on mixing at room temperature), results in complete displacement of diphenylethyne and transfer of carbonyl ligands between tungsten atoms. We did not succeed in separating the many products of this reaction. The ^1H NMR spectrum of the mixture was not helpful in identifying the products, consisting of many signals in the region δ 0.8—2.0 ppm. However, the use of infrared spectroscopy in the 2200—1600 cm^{-1} region together with mass spectrometry [6] permitted adequate identification of some of the various tungsten-containing compounds formed in the reaction.

The principal product of the reaction between $[W(CO)(PhC{\equiv}CPh)_3]$ and dmpe (3 mol) on dichloromethane solution at ambient temperature is *cis*-$[W(CO)_2(dmpe)_2]$ (ν(CO) 1827, 1760 cm^{-1} (CH_2Cl_2); 1868, 1810 cm^{-1} (hexane) [6]; *m/e* 540). Other compounds formed include $[W(CO)(dmpe)_3]$ (ν(CO) 1905 cm^{-1}; *m/e* 662), and $[W(dmpe)_3]$ [7] (*m/e* 634). Observation of the infrared spectrum of the reaction mixture at intervals of 3 minutes over a period of an hour showed that the carbonyl complexes were formed in the following sequence:

$$\begin{tikzcd}
{[W(CO)(PhC{\equiv}CPh)_3]} \arrow[r] & {[W(CO)(dmpe)_3]} \arrow[r] \arrow[d] & cis\text{-}{[W(CO)_2(dmpe)_2]} \\
 & {[W(dmpe)_3]} &
\end{tikzcd}$$

The formation of $[W(dmpe)_3]$ from $[W(CO)(dmpe)_3]$ was established by observing the disappearance of the latter whilst *m/e* 634 remained in the mass spectrum. It is important to emphasize that other compounds may have been formed in the reaction which could not be identified by means of infrared and mass spectrometry because of their low concentrations. The process by which *cis*-$[W(CO)_2(dmpe)_2]$ is formed from $[W(CO)(dmpe)_3]$ is a matter of speculation: it is possible that a binuclear complex is involved. Previous work [6] has shown that $[W_2(CO)_6(dmpe)_3]$ reacts with dmpe at elevated temperature (above 400 K) to form *cis*-$[W(CO)_2(dmpe)_2]$: a coordinatively unsaturated monomer $[W(CO)(dmpe)_2]$ may be a suitable precursor for the formation of *cis*-$[W(CO)_2(dmpe)_2]$ and $[W(CO)(dmpe)_3]$ under the mild conditions which exist in the reaction between dmpe and $[W(CO)(PhC{\equiv}CPh)_3]$.

Experimental

All preparations were carried out in an atmosphere of oxygen-free dry nitrogen. Solvents were dried, deaerated and distilled under nitrogen immediately prior to use. Decomposition points were recorded on a hot stage block. IR spectra were recorded in solution in hexane, CH_2Cl_2 and $CHCl_3$ using 1.0 mm solution cells and as mull spectra with Nujol and hexachlorobutadiene on a PE 257 grating spectrometer. UV and visible spectra were recorded on a Unicam SP800 spectrometer. Proton NMR spectra were recorded in $CDCl_3$ solution using tetramethylsilane as an internal standard at 60 MHz on a PE 12 instrument. Mass spectra were recorded on an AEI MS 12 spectrometer. Microanalysis were carried out by Mr. M. Hart and his staff in this Department. The preparation of $[W(CO)(PhC{\equiv}CPh)_3]$ [1], of $[W(CO)(MeSC{\equiv}CSMe)_3]$ [4] was as described in the literature.

Reaction between $[W(CO)(MeSC{\equiv}CSMe)_3]$ *and dmpe*

a. A solution of dmpe (0.125 ml, 0.08 g, 0.53 mmol) in dichloromethane (10 ml) was added dropwise to a stirred solution of $[W(CO)(MeSC{\equiv}CSMe)_3]$ (0.30 g, 0.53 mmol) in dichloromethane (10 ml). The yellow solution rapidly changed to a deep wine red colour. When the addition was complete (5 minutes), the solution was concentrated to approximately 10 ml under reduced pressure and hexane (50 ml) added to precipitate a pink solid. The solid was isolated by filtration, washed with diethylether (3 × 15 ml) to remove any unreacted starting material, reprecipitated from CH_2Cl_2/hexane and dried in vacuo. The complex I (0.22 g) was obtained as a bright pink powdery solid, soluble in chlorinated solvents and sparingly soluble in acetone or ether. M.p. 418 K (dec). Found: C, 29.8; H, 5.0; P, 10.0; S, 21.4; W, 31.1. $C_{15}H_{28}OP_2S_4W$ calcd.: C, 30.1; H, 4.7; P, 10.4; S, 21.4; W, 30.8%. λ_{max}nm (log ϵ) (CH_2Cl_2) 480(1.8); 380(2.33), 330(2.64). ν_{max} (Nujol/HCB) 2950w, 2895m, 1913s(sh), 1902vs, 1570m, 1550m, 1445m, 1418m, 1290w, 1130w, 1108m, 964m, 940s, 925m, 900s, 738m, 662m. $\delta(CDCl_3)$ 2.86, 1.70 ppm. The solid failed to give a mass spectrum.

A solution of complex I (0.1 g) in dichloromethane (20 ml) was stirred at room temperature for 1 hour. During this time the pink solution turned to a deep yellow-amber colour. This solution was filtered, concentrated under reduced pressure and then diluted with hexane and set aside at 273 K. A yellow-amber solid II (0.04 g) was deposited from the solution. This powdery solid was isolated by filtration, washed with hexane and dried in vacuo. M.p. 485 K (dec). Found: C, 28.9; H, 4.8; P, 10.7; S, 22.8. $C_{14}H_{28}P_2S_4W$ calcd.: C, 29.5; H, 4.9; P, 10.9; S, 22.6%.

b. A solution of dmpe (0.13 ml, 0.101 g, 0.665 mmol) in acetone (10 ml) was added dropwise to a stirred solution of $[W(CO)(MeSC{\equiv}CSMe)_3]$ (0.375 g, 0.665 mmol) in acetone (20 ml). A pink solid was deposited from the solution during the addition. The solid was isolated from the colourless solution by filtration, washed with acetone (4 × 10 ml) and dried in vacuo. The compound, III (0.356 g) was obtained as a bright pink powder which is insoluble in the common organic solvents. M.p. 464 K (dec.). Found: C, 30.2; H, 4.9; P, 9.7; S, 23.3; W, 31.7. $C_{15}H_{28}OP_2S_4W$ calcd.: C, 30.1; H, 4.7; P, 10.4; S, 21.4; W, 30.8%. ν_{max} (Nujol/HCB) 2890m, 1912s(sh), 1903vs, 1632m, 1495w, 1461m, 1430m, 1417s, 1305m, 1300m, 1290m, 1280m, 1106m, 900s, 738m, 690w.

c. A solution of dmpe (0.62 ml, 0.484 g, 3.22 mmol) in dichloromethane (15 ml) was added to a stirred solution of $[W(CO)(MeSC{\equiv}CSMe)_3]$ (0.456 g, 0.81 mmol) in dichloromethane (20 ml). The solution became deep wine red in colour within a few minutes (see (a)). The mixture was then heated at reflux for 24 hours, during which time a white solid precipitate formed and the solution became pale yellow. At the end of this time the air sensitive white solid was isolated by filtration, washed with dichloromethane until the washings were colourless (ca. 50 ml) and dried in vacuo. The solid was dissolved in ethanol, filtered and reprecipitated with hexane, isolated and dried in vacuo. The white solid, IV, (0.35 g), air sensitive, hygroscopic complex is insoluble in chlorinated or hydrocarbon solvents and soluble in polar solvents. M.p. 528–532 K (dec.). Found: C, 33.0; H, 7.6; P, 24.9; S, 5.5; W, 29.0. $C_{34}H_{86}P_{10}S_2W_2$ calcd.: C, 33.0; H, 7.0; P, 25.0; S, 5.2; W, 29.8%. λ_{max}(EtOH) 265 nm. ν_{max}-

(Nujol/HCB) 2960m, 2890s, 2870m, 2820m, 2720w, 1580m, 1421s, 1300s, 1260s, 1174m, 1012m, 980vs, 940s, 920m, 885s, 819m, 795m, 784s, 725m.

Reaction between [W(CO)(PhC=CPh)₃] and dmpe

A cold (195 K, CO_2/acetone) solution of dmpe (0.33 ml, 0.273 g, 1.82 mmol) in dichloromethane (5 ml) was added dropwise to a stirred solution of [W(CO)(PhC≡CPh)$_3$] (0.45 g, 0.6 mmol) in dichloromethane (30 ml) also at 195 K (CO_2/acetone). At this temperature reaction was perceptible as indicated by the darkening of the yellow solution of the tungsten complex. The reaction mixture was allowed to warm to ambient temperature, in the course of which the colour changed to greenish brown. After stirring for a few minutes at room temperature the reaction solution was evaporated to dryness under reduced pressure. The residue was extracted with hexane (10 × 5 ml), concentrated to ca. 20 ml and cooled to 195 K which yielded an oily solid. The oily solid was isolated by filtration, washed with cold pentane and reprecipitated from CH_2Cl_2/hexane. Found: C, 30.6; H, 6.2; P, 22.4. $C_{14}H_{32}O_2P_4W$ calcd.: C, 31.1; H, 5.9; P, 23.0%. ν(CO)(CH_2Cl_2) 1827s, 1760s; (hexane) 1868s, 1810s cm^{-1}. *m/e* (*I*, %) 540(100), 512(60), 484(43). These served to identify *cis*-[W(CO)$_2$(dmpe)$_2$] [6].

The hexane insoluble residue was redissolved in dichloromethane (15 ml) and filtered. An excess of hexane (50 ml) was added to the solution which was then stored in the refrigerator to induce crystallisation. An oily amber coloured solid was obtained which was washed with cold hexane (2 × 10 ml), triturated to induce crystallisation, and dried in vacuo. Infrared and mass spectra of this solid indicated that it was a mixture. ν(CO) (CH_2Cl_2) 1905, 1827, 1760 cm^{-1}; *m/e* (*I*, %) 662(1), 634(4), 540(100), 512(65), 484(40); δ($CDCl_3$) 1.7—0.8 ppm (broad) 7.25—7.65 (Ph_2C_2). Similar spectra were recorded when the dichloromethane/hexane mother liquor was evaporated leaving a brown solid. Attempts to purify this fraction either by crystallisation, sublimation or chromatography were not successful.

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