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STUDIES OF CHELATION

VII *. DITHIOALKYNE COMPLEXES OF MOLYBDENUM, TUNGSTEN, IRON, RUTHENIUM AND COBALT CARBONYLS **

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Summary

The complexes formed by 2,5-dithiahex-3-yne (Z) with various metal carbonyls and their derivatives have been identified by analytical and spectroscopic (IR, NMR (^{1}H and ^{13}C), mass) methods as [M(CO)Z_3] (M = Mo, W), [CpMClZ_2] (M = Mo, W), [CpMo(CO)Cl(Z_2CO)], [M(CO)$_3$(Z_2CO)] (M = Fe, Ru), [Ru_2(CO)$_6$$Z_2$], [$Ru_3(CO)_9$Z] and [$Co_2(CO)_6$Z]. Comparisons are made with diphosphinoalkynes and it is concluded that the triple bond plays a dominant role in the coordination chemistry of Z.

Introduction

The complexes formed by alkynes with transition metals have attracted attention for thirty years because of their role as possible intermediates in metal-catalysed trimerisation or polymerisation reactions. Under suitable conditions the oligomerisation may proceed with the insertion of other reaction components, such as carbon monoxide. The factors responsible for the formation of specific types of complex are still poorly understood. One reason for this may be that relatively few attempts have been made to assess the influence of the nature of substituents at the triple bond upon the reactions of the alkynes.

Studies of the complexes formed by the acetylenic ditertiary phosphine $Ph_2PC{\equiv}CPPh_2$ have shown [2] that it behaves almost exclusively as a bridging ligand, bonding to two metal atoms through the two phosphorus atoms. Chelation is inhibited by the rigid triple bond. Even the more flexible $Ph_2PCH_2C{\equiv}CCH_2PPh_2$ behaves [3] exclusively as a bridging ligand through phosphorus only.

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Monotertiary acetylenic phosphines, $Ph_2PC{\equiv}CR$ on the other hand, form a remarkable variety of complex compounds [4], in which coordination can occur through either the triple bond or the phosphorus atom or both of these. More recently it was shown [5] that the P—C(*sp*) bond can be broken quite easily in reactions with iron carbonyls.

In the course of a comparative study [6] of the mechanism of the process by which molecules having the common structural unit [E—C—C—E] (E = S^{II} or P^{III}) chelate to transition metals we examined [7] the dithio-alkyne, 2,5-dithiahex-3-yne, Z. A detailed investigation [8] of the structure and spectra of Z provided no evidence of conjugation between the sulphur atoms and the triple bond, in contrast to the diphosphino-alkyne mentioned above in which $(C_p{\rightarrow}P_d)$ π-bonding is evident [9]. We were interested to know whether this difference in electronic structure combined with the slightly harder base character of sulphur(II) compared with phosphorus(III) would be manifest in the products of the reactions of Z with certain metal carbonyls and their derivatives.

Results and discussion

The complexes which we have prepared show no evidence of bonding of the dithio-alkyne ligand, Z, to a metal atom through sulphur, even when this might have been expected to be particularly advantageous. Thus we expected that 18-electron complexes $[CpMClZ_3]$, containing two π-bonded alkyne ligands and one alkyne ligand bonded to M through the sulphur lone pair would form instead of the 16-electron complexes [10] $[CpMClZ_2]$ (M = Mo, W) which we have isolated from the reaction between Z and $[CpM(CO)_3Cl]$.

There is no evidence of the S—C(*sp*) bond of Z being broken as a consequence of reactions with iron carbonyls; both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ gave, exclusively, the same cyclopentadienone complex $[Fe(CO)_3\{(MeS)_4C_5O\}]$. The μ-thiomethoxide complex [11] $[Fe_2(CO)_6(\mu\text{-SMe})_2]$ is not formed, neither is an analogue of the μ-phosphido, σ-, π-alkynyl complex $[Fe_2(CO)_6(PPh_2)(C{\equiv}CPh)]$ described by Carty [12], produced in these reactions.

All of the compounds we report are analogues of types of π-alkyne complexes which have been prepared by others in the past. However they show a number of features which bear closer attention.

Group VI elements. The tris-alkyne complexes $[M(CO)Z_3]$ (M = Mo, W) have been prepared in high yield from the reaction between *fac*-$[M(CO)_3(NCMe)_3]$ and Z in ethanol. When the same procedure is used with *fac*-$[Cr(CO)_3(NCMe)_3]$ at low temperature (195 K, warming to 223 K) an unusual, particularly photosensitive purple crystalline complex is formed [7], which has the empirical formula $[Cr(CO)_2Z_2]$. The action of daylight on the purple solid produces the brown complex *cis*-$[Cr(CO)_4\{C_6(SMe)_6\}]$ in high yield. The process by which such a trimerisation might occur has been exemplified for binuclear systems based on $[CpM(CO)_2]_2$ (M = Cr, Mo) [13]. We note that tetrakis(methylthio)cyclopentadienone is not formed in these reactions of Z, in marked contrast to the formation of tetraphenylcyclopentadienone as the only isolable product of the reaction between Ph_2C_2 and *fac*-$[Cr(CO)_3(NCMe)_3]$ [14].

The spectroscopic properties of $[M(CO)Z_3]$ (M = Mo, W) show many differences from those reported [14,15] for other alkyne complexes of this type. The shift of $\nu(C{\equiv}C)$ on complex formation is easily recognised by the appearance of two well defined bands of medium intensity (1593, 1568 cm^{-1} (M = Mo); 1572, 1516 cm^{-1} (M = W)) in a region where Z does not absorb [8]. The magnitude of the average shift (500 cm^{-1} (Mo), 538 cm^{-1} (W)) is greater than that reported (ca. 350 cm^{-1}) [14] for complexes such as $[W(CO)(Et_2C_2)_3]$. The carbonyl ligand is recognised by an intense absorption at 2081 (Mo), 2080 (W) cm^{-1}, which is at a slightly higher frequency to that (2034 cm^{-1}) [14] in $[W(CO)(Et_2C_2)_3]$. The ^1H and ^{13}C NMR spectra of $[M(CO)Z_3]$ (M = Mo, W) show only one signal for the six methyl groups and this is essentially unchanged (proton spectrum) in the temperature range 240—310 K. This is in contrast to the proton NMR spectra of complexes such as $[W(CO)(Et_2C_2)_3]$ which show that the two ethyl groups are inequivalent because of their disposition with respect to the carbonyl ligand, and suggests that there is rotation about the M—Z axis in $[M(CO)Z_3]$ which makes the two methyl groups equivalent. The mass spectrum of $[Mo(CO)Z_3]$ was not observed because the sample decomposed in the beam. In contrast, the tungsten analogue produces an intense molecular ion. Fragmentation of this ion occurs by loss of the CO ligand followed by successive loss of all six methyl groups to give $[W(SC_2S)_3]^+$ (*m/e* 448).

We have studied the reactions of $[M(CO)Z_3]$ and other $[M(CO)(R_2C_2)_3]$ (M = Mo, W) complexes with phosphines [7], and isonitriles (to give $M(CNR)_6$ and $[M(CO)(CNR)_5]$). These will be described in detail elsewhere.

The characterisation of the 16-electron bis-alkyne complexes $[CpMClZ_2]$ is unremarkable and is based principally upon satisfactory analysis. It is worth noting that the reaction between $[CpMo(CO)_3Cl]$ and Z in toluene produced a cyclopentadienone complex. Others have observed that hexafluorobut-2-yne forms a cyclopentadienone complex, but but-2-yne forms a duroquinone complex [10].

Group VIII elements. The alkyne, Z, behaves in a similar manner to alkynes, R_2C_2 bearing highly electronegative substituents (R = Cl, CF_3) [16] in producing only the cyclopentadienone complex $[Fe(CO)_3\{(R_2C_2)_2CO\}]$ in a reaction with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ under mild conditions. It is interesting to note that $Fe_2(CO)_9$ reacts with 2,5-dioxahex-3-yne, L, to produce a mixture of binuclear complexes $[Fe_2(CO)_6L_2]$ and $[Fe_2(CO)_6(L_2CO)]$; the mononuclear complex $[Fe(CO)_3(L_2CO)]$ is not formed at all [17].

The products isolated from the reaction between $Ru_3(CO)_{12}$ and Z are characterised by mass and infrared spectroscopy together with partial analyses. On the basis of this evidence it is suggested that in addition to the cyclopentadienone complex $[Ru(CO)_3\{(MeS)_4C_5O\}]$, the ruthenacyclopentadiene complex $[Ru_2(CO)_6Z_2]$ similar to other $[Ru_2(CO)_6(alkyne)_2]$ compounds which have been reported [18], and the trinuclear complex $[Ru_3(CO)_9Z]$ similar to $[Ru_3(CO)_9(Ph_2C_2)]$ [19], which may have been the same *closo*-trigonal bipyramid structure as its iron analogue [20], are formed in this reaction together with other compounds which we have not been able to isolate in a pure form.

The alkyne-bridged dicobalt complex $[Co_2(CO)_6Z]$ is formed in high yield at room temperature. Just as for the cyclopentadienoneiron complexes $[Fe(CO)_3(R_4C_5O)]$, the observed variation of $\nu(C{\equiv}O)$ for the carbonyl groups attached to the metal indicates [17,21] that the thiomethyl group acts as an electron donor. There is no evidence that the sulphur atoms participate in a polyhedral expansion of the Co_2C_2-*nido* trigonal bipyramid.

Experimental

The details of general procedures, methods and materials used in this work have been described elsewhere [6]. The metal carbonyls $Fe(CO)_5$ (Fluka), $Mo(CO)_6$, $W(CO)_6$ and $Ru_3(CO)_{12}$ (Strem) were purchased and $Fe_2(CO)_9$ and $Co_2(CO)_8$ were prepared by standard methods [22]. The metal carbonyl derivatives $[M(CO)_3(NCMe)_3]$ (M = Mo, W) [23] and $[CpMo(CO)_3Cl]$ (M = Mo, W) [24] were prepared by the methods cited and their purity was checked by analysis and spectroscopy. The alkyne 2,5-dithiahex-3-yne, Z, was prepared from the reaction between methyl thiocyanate and sodium acetylide in liquid ammonia [25] and fully characterised [8]. All manupulations were carried out in an atmosphere of oxygen-free dry nitrogen.

Preparation of monocarbonyltris(2,5-dithiahex-3-yne)molybdenum

A solution of $MeSC{\equiv}CSMe$ (1.10 g, 9.35 mmol) in ethanol (10 ml) was added dropwise to a stirred solution of $[Mo(CO)_3(NCMe)_3]$ (0.95 g, 3.12 mmol) in ethanol (50 ml) at 298 K. On adding the alkyne the pale yellow solution of $[Mo(CO)_3(NCMe)_3]$ darkened rapidly to brown and a yellow solid precipitated from the solution. These changes were accompanied by vigorous gas evolution. The mixture was heated to reflux briefly (10 min) to ensure complete reaction. The precipitate was isolated by filtration (G3) of the cooled solution, washed with ethanol until the washings were colourless, and then dissolved in warm toluene (30 ml). Addition of ethanol (60 ml) produced light-sensitive orange microcrystals of $[Mo(CO)(C_4H_6S_2)_3]$ (1.52 g, 3.1 mmol, 95%). M.p. 428 K (dec.) Found: C, 32.6; H, 3.8; S, 40.2; Mo, 20.1. $C_{13}H_{18}MoOS_6$ calcd.: C, 32.6; H, 3.8; S, 40.0; Mo, 20.0%. ν_{max} (Nujol/HCB) 2914, 2081, 1593, 1568 cm^{-1}. δ ($CDCl_3$) 2.75 ppm.

Preparation of monocarbonyltris(2,5-dithiahex-3-yne)tungsten

A solution of $MeSC{\equiv}CSMe$ (1.05 g, 8.9 mmol) in ethanol (10 ml) was added dropwise to a stirred solution of $[W(CO)_3(NCMe)_3]$ (1.16 g, 2.96 mmol) in ethanol (50 ml) at 298 K. The reaction proceeded as in the case just described, and the mixture was treated in a similar manner to give pale yellow crystals of $[W(CO)(C_4H_6S_2)_3]$ (1.59 g, 2.8 mmol, 95%). M.p. 453 K (dec.). Found: C, 27.6; H, 3.2; S, 33.5; W, 32.6. $C_{13}H_{18}OS_6W$ calcd.: C, 27.6; H, 3.2; S, 33.9; W, 32.6%. ν_{max} (Nujol/HCB) 2913, 2080, 1572, 1516 cm^{-1}. δ^1H ($CDCl_3$) 2.78. $\delta^{13}C$ ($CDCl_3$) 23.0, 116.8 ppm. *m/e* (*I*, %) 566 (100, M^+), 538 (94), 523 (39), 508 (19), 493 (60), 478 (17), 463 (43), 448 (34).

Reaction with $CpMo(CO)_3Cl$

(a) In hexane. $CpMo(CO)_3Cl$ (0.48 g, 1.7 mmol) and $MeSC{\equiv}CSMe$ (0.65 g, 5.1 mmol) were heated in hexane (50 ml) at reflux for 19 h. The reaction was allowed to cool and was then filtered (Celite). Concentration of the eluate gave yellow crystals of $[CpMoCl(C_4H_6S_2)_2]$ (0.12 g, 0.28 mmol, 16%). M.p. 394—397 K (dec.). Found: C, 36.3; H, 4.0; Cl, 7.9; Mo, 22.4; S, 29.3. $C_{13}H_{17}ClMoS_4$ calcd.: C, 36.1; H, 4.0; Cl, 8.2; Mo, 22.2; S, 29.6%. δ ($(CD_3)_2CO$) 2.43 ($C\underline{H}_3$), 5.89 ($C_5\underline{H}_5$) ppm.

(b) In toluene. $CpMo(CO)_3Cl$ (0.40 g, 1.4 mmol) and MeSC≡CSMe (0.90 g, 7.7 mmol) were stirred in toluene (50 ml) for 12 h. Treatment of the mixture as before gave red-yellow crystals (CH_2Cl_2/pentane) of $[CpMo(CO)Cl(C_9H_{12}OS_4)]$ (0.18 g, 0.38 mmol, 27%). M.p. 418—429 K (dec.). Found: C, 37.0; H, 3.8; Cl, 7.8; Mo, 19.1; S, 26.8. $C_{15}H_{17}ClMoO_2S_4$ calcd.: C, 36.8; H, 3.5; Cl, 7.2; Mo, 19.6; S, 26.2%. ν(CO): 2060, 2034; ν(C=O) 1630, 1618 cm^{-1}. δ ($CDCl_3$) 2.61, 2.76 ($C\underline{H}_3$), 6.21, 6.58 ($C_5\underline{H}_5$) ppm.

Reaction with $CpW(CO)_3Cl$

The alkyne (0.50 g, 4.25 mmol) and $CpW(CO)_3Cl$ (0.40 g, 1.1 mmol) were heated in heptane at reflux for 10 h. Treatment as in previous examples gave pale yellow crystals of $[CpWCl(C_4H_6S_2)_2]$ (0.19 g, 0.33 mmol, 30%). M.p. 416—420 K (dec.). Found: C, 30.0; H, 3.1; Cl, 6.3; S, 23.8; W, 35.9. $C_{13}H_{17}ClS_4W$ calcd.: C, 30.0; H, 3.3; Cl, 6.8; S, 24.6; W, 35.3%. δ ($(CD_3)_2CO$) 2.40 ($C\underline{H}_3$), 6.12 ($C_5\underline{H}_5$) ppm.

Reaction with $Fe_2(CO)_9$

A solution of MeSC≡CSMe (1.8 g, 15.3 mmol) in petroleum ether (60—80°C fraction) (20 ml) was added to $Fe_2(CO)_9$ (2.76 g, 7.6 mmol) in the same solvent (200 ml). The reaction mixture was heated at reflux for 12 h. On cooling to room temperature an amber coloured crystalline solid was deposited. Concentration of the solution produced further solid material which was recrystallised from boiling hexane to give bright amber needles of $[Fe(CO)_3(C_9H_{12}OS_4)]$ (2.5 g, 6.2 mmol, 82%). M.p. 398 K. Found: C, 35.8; H, 2.9; Fe, 14.0; S, 31.7. $C_{12}H_{12}FeO_4S_4$ calcd.: C, 35.8; H, 3.0; Fe, 13.9; S, 31.7%. ν(CS_2/$CHCl_3$): 2915, 2054, 2006, 1660, 1645, 1417, 1294, 1081, 967, 902; 798, 727 cm^{-1}. δ ^{1}H-($CDCl_3$): 2.60, 2.70; δ ^{13}C ($CDCl_3$): 11.0, 13.1, 104.1, 122.0, 200.0, 252.0 ppm. *m/e* (*I*, %) 404 (*I*, M^+), 376(3), 348(12), 320(15), 305(8), 290(13), 274(4), 264(100), λ_{max} (log ϵ) (95% EtOH) 263 (3.11) 340 (2.75) nm.

Reaction with $Ru_3(CO)_{12}$

A mixture of MeSC≡CSMe (0.12 g, 1.0 mmol) and $Ru_3(CO)_{12}$ (0.29, 0.33 mmol) in petroleum ether (100—120°C fraction) (50 ml) was heated at reflux for 2 h. Evaporation of volatiles left a brown solid residue, which was chromatographed (thin layer) with hexane, toluene, ether and CH_2Cl_2 as eluents. Three compounds were eventually isolated in pure form. Yields were low. A. $[Ru(CO)_3(C_9H_{12}OS_4)]$. Found: C, 32.8, H, 2.9; $C_{12}H_{12}O_4RuS_4$ calcd.: C, 32.1, H, 2.67%. ν(CH_2Cl_2/hexane) 2072, 2013, 2000, 1610 cm^{-1}; *m/e* 449 (M^+), 421, 393, 365. B. $[Ru_2(CO)_6(C_4H_{12}S_4)]$. Found: C, 28.1, H, 2.3. $C_{14}H_{12}O_6Ru_2S_4$ calcd.: C, 27.7; H, 2.0%. ν(hexane): 2080, 2053, 2019, 2008, 1996, 1948 cm^{-1}; *m/e*: 606 (M^+), 578, 550, 522, 494, 466, 438. C. $[Ru_3(CO)_9(C_4H_6S_2)]$. Found: C, 23.0; H, 1.0. $C_{13}H_6O_9Ru_3S_2$ calcd.: C, 23.2, H, 0.9%. ν(CH_2Cl_2): 2093, 2072, 2052, 2031, 2012, 2000, 1975 cm^{-1}; *m/e* 673 (M^+), 645, 617, 589, 561, 533, 505, 477, 449, 421.

Reaction with $Co_2(CO)_8$

A solution of MeSC≡CSMe (0.44 g, 3.7 mmol) in hexane (10 ml) was added dropwise to a stirred solution of freshly prepared $Co_2(CO)_8$ (1.26 g, 3.7 mmol) in hexane (50 ml). An immediate change of colour from brown to violet was observed. After 10 min stirring the mixture was filtered, concentrated and cooled to 195 K. Purple needles of $[Co_2(CO)_6(C_4H_6S_2)]$ (1.2 g, 98%) were obtained. M.p. 343 K. Found: C, 29.7; H, 1.5; Co, 28.8; S, 16.0. $C_{10}H_6Co_2O_6S_2$ calcd.: C, 29.7; H, 1.5; Co, 29.2; S, 15.8%. δ ($CHCl_3/CS_2$): 2910, 2085, 2044, 2025, 1430, 1308, 885 cm^{-1}. δ^1H ($CDCl_3$) 2.5; $\delta^{13}C$ ($CDCl_3$): 7.0, 113.0 ppm; m/e (I, %) 404(24, M^+), 376(50), 348(50), 320(21), 292(59), 264(110), 236(158), 221(24), 206(23), 118(100). λ_{max} (log ϵ) (95% EtOH) 290 (4.66), 317 (4.51), 468(2.54), 548(2.15) nm.

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