Journal of Organometallic Chemistry, 97 (1975) C43—C45

Preliminary communication

ALKYNYL THIOETHER COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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(Received July 18th, 1975)

Summary

Treatment of MeSC≡CSMe (L) with $[M(CO)_3(MeCN)_3]$ (M = Cr, Mo, W) has given $[M(CO)L_3]$ (M = Mo, W) and $[Cr(CO)_2L_2]$ and the reactions of these π-acetylene complexes with ditertiary phosphines are described, it is suggested that trimerisation of L on chromium proceeds through a [4+2] π cycloaddition.

Very few π-acetylene complexes of the Group VI metals are known [1]. In particular, no simple π-acetylene derivative of $Cr(CO)_6$ has been described, although $[(\eta\text{-arene})Cr(CO)_2(R_2C_2)]$ and $[\eta\text{-}C_5H_5Cr(CO)(NO)(R_2C_2)]$ are well known [2]. Most of the work on acetylene complexes of the transition metals has concerned a relatively restricted range of alkyl and aryl acetylenes, particularly where the organic group is electron attracting (e.g. CF_3, CO_2R). Apart from some recent work on alkynyl phosphines [3] and silanes [4], very little attention has been given to the organometallic chemistry of other hetero-substituted acetylenes. Despite the rapid development of the chemistry of alkynyl ethers and thioethers and their extensive application in organic synthesis [5], almost nothing [6] is known of their reactions with transition metals.

Reaction between $[M(CO)_3(MeCN)_3]$ (M = Mo, W) and 2,5-dithia-3-hexyne, MeSC≡CSMe (L), in ethanol produces the yellow crystalline complexes, $[M(CO)L_3]$ in high yield (90-95%). These new compounds, which have been fully characterised by microanalysis and spectroscopy (for M = W, m.p. 448-452 K (dec.); ν(CO) 2081 (CH_2Cl_2 solution) cm^{-1}; $\delta(C\underline{H}_3)$ 2.78, $\delta(\underline{C}H_3)$ 23.0 ppm; *m/e* 566 (100%)), most probably have structure I (M = Mo, W) similar to that [1] of $[W(CO)(Ph_2C_2)_3]$; there is no evidence of sulphur coordination. The addition of the ditertiary phosphine $Me_2PCH_2CH_2$-PMe_2 (dmpe) to an equimolar quantity of $[W(CO)L_3]$ in CH_2Cl_2 solution

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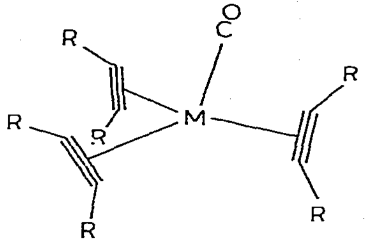
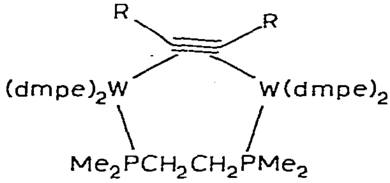
at room temperature rapidly produces the salmon pink complex [W(CO)(dmpe)L_2] (ν(CO) 1903 cm^{-1}; λ_{max} 488 nm). With excess dmpe, an insoluble white solid complex [W_2 L(dmpe)$_5$] is formed which may have the structure indicated by II. Hexakis(methylthio)benzene is not formed in these displacement reactions. Under similar conditions there is no detectable reaction between $Ph_2PCH_2CH_2PPh_2$ and [W(CO)L_3]. A similar distinction in reactivity arises in the case of [W(CO)(Ph_2C_2)].

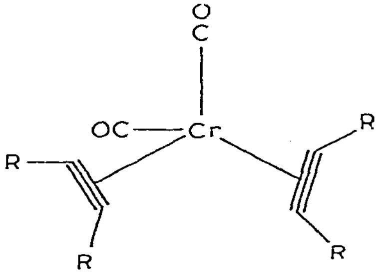


(I)

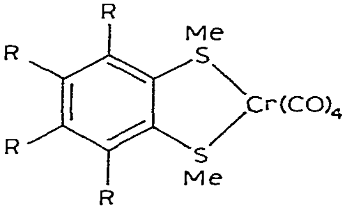


(II)

R = SMe



(III)



(IV)

The dropwise addition of a cooled solution of L in ether to [Cr(CO)$_3$(MeCN)$_3$] stirred in ether at 195 K and warming to allow reaction at 230 K in the dark, followed by removal of the volatile materials in the dark gives violet needles of [Cr(CO)$_2$ L_2] (III) (Found: C, 35.0; H, 3.5; Cr, 14.8; S,37.0. $C_{10}H_{12}CrO_2S_4$ calcd.: C, 34.9; H, 3.4; Cr, 15.0; S, 37.2%). This photosensitive compound is easily converted both in the solid state and, more rapidly, in solution to a mixture of products of which by far the major constituent is a brown crystalline solid complex *cis*-[Cr(CO)$_4$ (L_3)] (IV) (ν(CO) 2023m, 1910s, 1879s (CH_2Cl_2 solution) cm^{-1}), in which the chelating ligand is hexakis(methylthio)benzene obtained by trimerisation of the acetylene, L. Destruction of IV gives pure C_6(SMe)$_6$ (*m/e* 354). Addition of dmpe to III gave IV and, subsequently, *cis*-[Cr(CO)$_4$ (dmpe)].

The surprising contrast in the constitution of I and III, with the observation that trimerisation of L occurs from III but not from I under comparable conditions, may suggest that trimerisation occurs as a result of a [4 + 2] π-cycloaddition, as in the case [7] of [η-$C_5H_5Nb(CO)(Ph_4C_4)(Ph_2C_2)$], rather than as a result of a [2 + 2 + 2] π-cycloaddition [8].

The reactions of L and other alkynyl thioethers with a variety of organometallic compounds have been examined and the results will be reported in due course.

We thank the S.R.C. for support.

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