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REACTIONS OF MOLYBDENUM AND TUNGSTEN HALIDES WITH ACETYLENIC HYDROCARBONS: AN APPROACH TO THE STRUCTURE AND PATHWAYS OF FORMATION OF METATHESIS CATALYSTS

A. GRECO, F. PIRINOLI and G. DALL'ASTA
Centro Ricerche di Milano, Montecatini Edison, Via G. Colombo 81, Milano (Italy)
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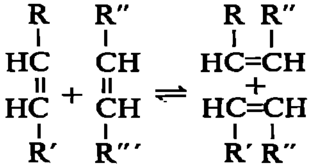
SUMMARY

A number of acetylene and mixed acetylene–nitrile complexes of tungsten and molybdenum halides have been prepared and investigated. Depending on the acetylene and the reaction conditions, one or more acetylene molecules may be coordinated to the metal. In the latter case acetylenes are coordinated not as single molecules but in systems of conjugated non-aromatic double bonds. On the basis of the supposed structure of such species and on their pyrolysis products a decomposition scheme is proposed, which considers the formation of apparent metathesis products as a side reaction of the cyclotrimerization of acetylenes to aromatic hydrocarbons.

INTRODUCTION

The metathesis of unsaturated hydrocarbons, illustrated by the following scheme



$$\begin{matrix} R & & R'' & & R\ \ R'' \\ | & & | & & |\ \ \ | \\ HC & & CH & & HC{=}CH \\ \| & + & \| & \rightleftharpoons & + \\ HC & & CH & & HC{=}CH \\ | & & | & & |\ \ \ | \\ R' & & R''' & & R'\ R'' \end{matrix}$$

is a comparatively new class of reactions hitherto applied to acyclic, cyclic, and bicyclic mono- and poly-olefins as well as to acetylenes. The two most important reactions of this type, the basis of scientific and industrial development over the last decade, are the ring-opening polymerization of cycloolefins[1–7] and the disproportionation of acyclic monoolefins[8–10].

Many mechanistic features of metathesis reactions, comprising aspects of the transalkylidenation process and its transition state, chain growth via macrocycles, enthalpy and entropy requirements, thermodynamic or kinetic control, stereochemistry and selectivity, have been elucidated in the last six years thanks to contributions of several laboratories[11–25]. Far less is known about the structure of the metathesis catalysts and the reactions involved in their formation.

Three main classes of metathesis catalysts are known: (1) Ziegler–Natta type systems, (2) supported transition metal oxides or carbonyls, and (3) Group VIII transition metal compounds. The first class, especially with tungsten or molybdenum halides as the transition metal component, is the most attractive for study. This preference is justified not only by their high activity and versatility in various metathesis reactions, but especially because they generally appear to act in the homogeneous phase. Catalysts of this class are the reaction products of tungsten or molybdenum halides with organometallic compounds[3–4] preferably of aluminium, or with Lewis acids,[26,27] such as aluminium trihalides. Their catalytic activity is strongly enhanced by stoichiometric amounts of an oxygen-containing activator[28,29], such as O_2, peroxides, alcohols, etc., and their selectivity is increased by stoichiometric amounts of Lewis bases[24,25,30] such as triphenylphosphine, pyridine, and thiophene.

This paper is the first of a series discussing possible formation pathways and the structure of Ziegler–Natta type metathesis catalysts.

Our early attempts to isolate catalytic species containing olefin molecules complexed to tungsten or molybdenum failed, primarily because of the instability of such compounds. It is known, on the other hand, that acetylenic hydrocarbons are also able to yield metathesis products[31], even if high temperatures are required, and with 1-alkynes[32,33], the main products are cyclooligomers and polymers. The stability of the coordination complexes containing acetylenic ligands, which is generally much higher than that of corresponding olefin complexes, induced us to try to obtain information on the mechanism of catalyst formation by studying reactions of acetylenes with tungsten and molybdenum halides.

RESULTS

The investigations reported in this paper are mainly confined to the pentahalides of tungsten and molybdenum because of the poor reactivity of the hexahalides towards acetylenic hydrocarbons.

(*A*). *1-Alkyne complexes*

When tungsten or molybdenum pentachlorides were reacted in benzene at different temperatures with variable excess of propyne, oligomerization products were generally obtained. The resulting insoluble powders exhibited indefinite composition corresponding to $MX_m(C_3H_4)_n$, where the number of halogen atoms m varied between three and four and $n \leqslant 7$, depending on the reaction conditions. Two IR bands, at 1350 and 1380 cm^{-1}, attributed to methyl groups, and different bands assigned to acetylenic (1760 cm^{-1}) and conjugated (1580 and 787 cm^{-1}) double bonds indicated that propyne was coordinated in at least two different ways.

However, in one case, when carrying out the reaction of $MoCl_5$ was reacted with a sixfold excess of propyne at room temperature, a well-defined product of formula $MoCl_4(C_3H_4)_3$ (I) was obtained as a quite insoluble, non-volatile, strongly paramagnetic, crystalline brown powder. Its IR spectrum showed no evidence for the presence of complexed propyne monomer, but broad absorptions at 1583 and 787 cm^{-1}, attributable to a system of non-aromatic conjugated double bonds. In addition, the methyl absorption, which appears at 1350 cm^{-1} in complexes containing monomeric acetylenes, was shifted to 1380 cm^{-1}.

Several attempts to hydrolyse (I) did not yield free propyne or, surprisingly, any other organic material. However, pyrolysis under vacuum at 250° yielded a mixture of allene, propyne, 2-butyne, 1,2,4- and 1,3,5-trimethylbenzene, along with minor products including a chlorinated dimer: its structure could be either dimethyldichlorocyclobutene or dimethyldichlorobutadiene; ethyne could not be detected. 2-Butyne could be considered as a metathesis product; however, its amount varied widely depending upon the reaction conditions and was in any case much lower than was to be expected for a pure metathesis.

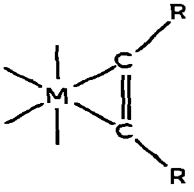
(*B*). *Complexes with internal acetylenes*

Significantly different results were obtained with 2-alkynes or 2-arynes instead of 1-alkynes.

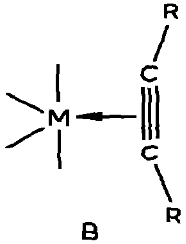
When $MoCl_5$ or WBr_5* was treated in CCl_4 or benzene under mild conditions with excess 2-butyne or diphenylacetylene, partial dehalogenation of the metal halides occurred, and crystalline products corresponding to the formula $MX_4(C_2R_2)$ were obtained in high yield: (II): $M=Mo$, $X=Cl$, $R=CH_3$; (III): $M=Mo$, $X=Cl$, $R=C_6H_5$; (IV): $M=W$, $X=Br$, $R=CH_3$; (V): $M=W$, $X=Br$, $R=C_6H_5$.

The excess of acetylene acts as scavenger for halogen. In the reaction of $MoCl_5$ with 2-butyne, *cis* and *trans* isomers of 2,3-dichloro-2-butene and 2-chloro-2-butene were detected in significant amounts in the reaction mixture. This finding indicates that alkynes may act as dehalogenating agents for high valency tungsten or molybdenum halides, thus lowering the oxidation state of the metal and/or providing the vacant coordination sites necessary for complexation of the ligands to be metathesized or cyclooligomerized. On the basis of analogous observations made with olefins we believe that this behaviour is likely to be general.

The above transition metal–acetylene complexes were either brown [(II), (IV)] or greenish [(III), (V)] crystalline powders, barely soluble in CH_2Cl_2, or CCl_4, and quite insoluble in benzene. They dissolved in acetone and other polar compounds, from which they could not be recovered unchanged. Complexed 2-butyne showed sharp IR bands at 1755 and 1730 cm^{-1} in (II) and (IV), respectively. The bands of complexed diphenylacetylene in (III) and (V) were observed at 1695 and 1678 cm^{-1}, respectively. These frequencies suggest that in these complexes the structure of the metal–acetylene bond is closer in accord with A than with B:



A



B

both generally considered[34-36] for transition metal–alkyne complexes. The assignment of a *quasi* A structure is supported by the finding that all four complexes are

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* WCl_5 also readily reacts at −5° with 2-butyne, but unfortunately the elemental product analysis did not accord with the expected $WCl_4 \cdot C_4H_6$. The mass spectrum confirmed the presence of this species with a clear fragmentation pattern.

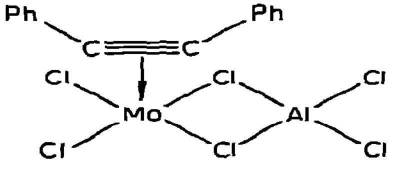
converted by alkyl cyanides into the known[37] $MX_4(RCN)_2$ complexes.

Similarly, an excess of 2-butyne slowly reacted with $WOCl_4$ in CH_2Cl_2 to yield an analogous $WOCl_3 \cdot C_4H_6$ complex as an olive green crystalline solid (VI). A product close to (VI), but of ill-defined composition, was obtained from the reaction of equimolecular amounts of WCl_6 and ethanol with excess 2-butyne in CCl_4. (VI) showed the IR bands of complexed acetylene at 1745 and a broad absorption in the 840–750 cm^{-1} region, indicating a strong intermolecular metal–oxygen interaction in the solid, similar to that found in $MoOCl_3 \cdot L$ complexes[38]. Poor solubility prevented molecular weight determination of (VI). However, the mass spectra of (II) and (IV) agreed with monomeric species, at least in the vapour phase.

^1H NMR spectra of (IV) and (VI) (acetone-d_6/benzene) showed a singlet due to methyl protons at τ 5.6 ppm, assigned to complexed 2-butyne. The intensity of the signal diminished during recording of the spectrum, and two additional singlets of increasing intensity appeared. The first, at τ 7.2, is assigned to a methyl group in a complex solvated by acetone; the second, at τ 8.5, corresponding to the signal for free 2-butyne. (II) was very unstable in acetone, and only free 2-butyne was detected by NMR.

Pyrolysis of (II) under vacuum gave nearly quantitative yields of free 2-butyne, always accompanied by small amounts of 2-chloro-2-butene, 2,2- and 2,3-dichlorobutane.

Reaction of (III) with 1.5 moles of $EtAlCl_2$ in benzene at 0° yielded a barely soluble, black, crystalline compound, whose elemental analysis corresponded with $MoAlCl_6(C_6H_5C{\equiv}CC_6H_5)$ (VII). The IR spectrum exhibited a band at 1695 cm^{-1}, already observed in (III) and attributed to diphenylacetylene complexed to Mo, and three absorptions at 674 and 360–300 cm^{-1}, assigned respectively to Mo–Cl–Al and to Mo–Cl. On the basis of this evidence we may tentatively propose a bimetallic, alkyl-free structure incorporating trivalent molybdenum and aluminium bridged together by two chlorine atoms:



(C). Complexes containing 2-alkyne and alkyl cyanide ligands

The conversion of 2-acetylene complexes into bis (alkyl cyanide) complexes induced us to further examine the behaviour of 2-alkynes and alkyl cyanides in complexation and replacement reactions involving molybdenum halide compounds.

If (II) was treated with equimolecular amounts, instead of excess alkyl cyanide, brown crystals were isolated in good yields, which were soluble in conventional organic solvents and could be recrystallized from CH_2Cl_2. Elemental analysis indicated the $MoCl_4(C_4H_6)(RCN)$ structure, where $R = CH_3$ (VIII) or C_2H_5 (IX), depending upon the cyanide employed. The ^1H NMR spectrum of (IX) showed two signals at τ 5.9 (butyne CH_3) and 8.5 ppm (nitrile C_2H_5), in accordance with the assigned structure.

The IR spectrum of all three complexes exhibited the typical absorptions of complexed nitrile in the 2300 cm^{-1} region and a band at 1770 cm^{-1}, attributed to the Mo-coordinated alkyne. The shift, by ca. 15 cm^{-1}, of this band to higher frequencies, if compared to those of the cyanide-free complexes (1755 cm^{-1}), indicated weakening of the bond.

Mixtures of (IX) and (II) were obtained from $MoCl_5$ and 2-butyne in the presence of less than equimolecular amounts of propionitrile. On the contrary, when operating under the same conditions with oxygen-containing solvents, (II) was obtained together with a compound (X) of formula $MoOCl_3(C_2H_5CN)$.

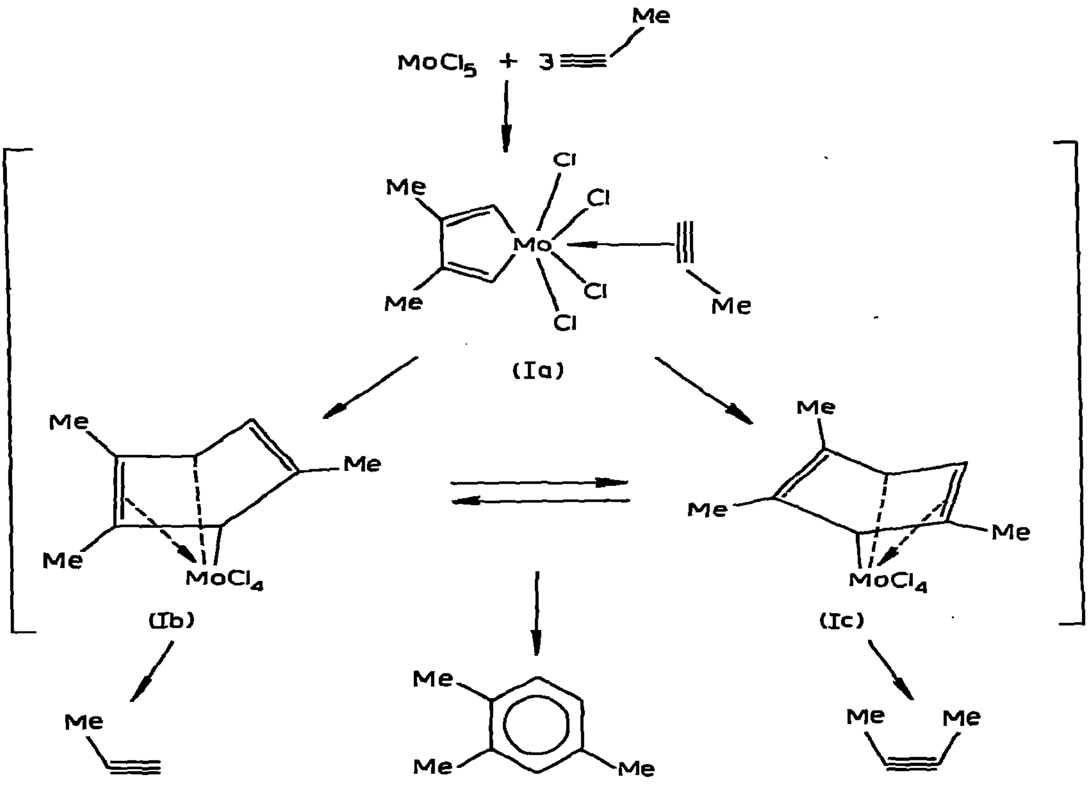
Mixed alkyne cyanide complexes, which are characterized by weakened Mo–alkyne bond, appeared to us as a favourable starting point for the synthesis of complexes containing two 2-butyne ligands, which were thought to be intermediates in a possible alkyne metathesis. However, the reaction of $MoCl_4(C_2H_5CN)_2$ with excess 2-butyne, did not yield defined alkyne complexes, but an uncrystallizable violet product (either solid or oily) in low yield. Elemental analysis and IR evidence indicated the presence of species containing more than one 2-butyne molecule. IR bands at 1595 and 788 cm^{-1}, attributed to a system of conjugated but non-aromatic double bonds (in the same position as in complex (I), containing three propyne units), suggested that 2-butyne molecules are not present as isolated alkynes, but are linked with consequent loss of the triple bond structure.

DISCUSSION

Formation of 2-butyne during pyrolysis of the propyne complex (I) posed the question whether a metathesis reaction was involved. It is not surprising that 2-butyne is not formed in the preparation of (I) from $MoCl_5$ and propyne and that severe pyrolysis is conditions were necessary to obtain it; in fact alkyne metatheses reported in literature always required high temperatures. However, the structure of (I), in which three propyne units are linked together in a system having conjugated double bonds, cannot account for the type of transition states generally postulated[11,15,16] in olefin metatheses. On the contrary, the composition of the pyrolysis products leads us to consider cyclotrimerization and formation of apparent metathesis products as different aspects of the same process. The decomposition scheme on the following page accounts for the formation of the observed pyrolysis products.

Complex (I) may decompose either *via* aromatization or *via* splitting of different alkynes (*retro*-Diels–Alder process). Obviously formation of 1,3,5-trimethylbenzene would require that one of the two propyne units of the five-membered molybdenum-cyclopentadiene ring (Ia) has one methyl group α to the metal. If both methyl groups of this ring were α of the metal, splitting of ethyne should be expected. However, the latter could not be detected among the pyrolysis products. This could indicate that a ring having both methyls α was not formed due to steric hindrance, or that evolved ethyne readily polymerized.

Structures such as those proposed for (Ia) were actually found in arene complexes of transition metals[39]. Metallocyclopentadiene complexes of type (Ib) or (Ic) were more recently postulated[40,41] as intermediates the cyclotrimerization of disubstituted acetylenes, induced by iridium, rhodium, and palladium catalysts moreover, metallocyclopentanes were proposed as intermediates in olefin metathesis[42].



The proposed scheme is in agreement with the aromatization mechanism of diphenylacetylene proposed by Nesmeyanov[43,44] and experimentally well supported. In this case the carbonyl groups of V, Nb, and Ta complexes are replaced in successive steps by diphenylacetylene, yielding isolable mono-, bi- and triacetylene species.

Internal alkynes generally exhibit a much lower cyclotrimerization tendency than 1-alkynes, thus favouring the formation of metathesis products[31]. However, our results with mixed 2-alkyne cyanide complexes showed the absence of intermediates suggested for metathesis reactions, *e.g.* species having coordinated two single alkyne molecules or cyclobutadiene. On the contrary, they indicate that also in this case entrance of a second alkyne gives rise to intermediates with conjugated double bonds, most likely of the type suggested for (Ib) and (Ic).

Therefore it is reasonable to conclude that, at least with our halide complexes, apparent metathesis products are not formed in a typical transalkylidenation process, but in a side reaction of cyclotrimerization to aromatic compounds. This view is supported by the following observations:

(1) the formation of apparent metathesis products is not catalytic;

(2) the statistical 1/2/1 ratio of the three possible alkynes, required by the metathesis equilibrium and experimentally verified for olefins[12,45,46] has never been observed by us;

(3) the generally accepted olefin metathesis scheme requires coordination of two unsaturated groups, unlike the three propyne molecules coordinated in (I).

Observations 1 and 2 are similar to those made by Moulijn *et al.*[32] with 1-alkynes in the presence of silica-supported MoO_3 catalysts. They differ, however, from those made by Pennella *et al.*[31] in the reaction of 2-pentyne over analogous supported catalysts, which resulted in the catalytic formation of metathesis products in the statistical 2-butyne/2-pentyne/2-hexyne = 1/2/1 equilibrium ratio. Therefore our conclusions cannot be generalized to all alkyne metatheses, but only to those involving formation of a considerable quantity of aromatic products.

The catalytic activity of all the above acetylene complexes in olefin metathesis, even in the presence of organometallic cocatalysts, is very poor. This may be ascribed to their stability or to the difficulty in replacing the triple by a double bond.

One further comment may be made with regard to the reaction of the molybdenum halide–acetylene complex (III) with $EtAlCl_2$, which does not lead to decomplexation of the acetylene ligand, even if reduction of the transition metal is involved. The first reduction step from penta to tetravalent molybdenum, induced by acetylenes acting as halogen scavengers as well as ligands, is followed by further reduction from tetra to tri-valency, by the action of the organometallic cocatalyst. This may indicate that the metathesis-active species, obtained from high valency transition metals, could also be below the tetravalent state, recently postulated by Pampus *et al.*[47].

EXPERIMENTAL

All experiments were carried out under nitrogen. Solvents were purified in the conventional manner. $MoCl_5$, WCl_6, $WOCl_4$, and WBr_5 (Schuchardt) were used as supplied. WCl_5 was prepared according to literature procedure[48].

^1H NMR spectra were recorded on a C60 HL Jeol spectrometer, and IR spectra with a Perkin–Elmer 221 spectrophotometer using Nujol or hexafluoro butadiene mulls.

Reaction of $MoCl_5$ with propyne

$MoCl_5$ (1.5 g; 5.5 mmol) and propyne (1.5 g; 37.5 mmol) in benzene (100 ml) were stirred for 1 h. The precipitated microcrystalline brown powder (I) was filtered off, washed with benzene, and dried under vacuum. Yield 1,4 g (70%). (Found: C, 29.6; H, 3.6; Cl, 39.4. $MoC_9H_{12}Cl_4$ calcd.: C, 30.1; H, 3.4; Cl, 39.7%.) IR max, 3020 w, 2960 w, 1755 w, 1580 m (br), 1445 m (br), 1380 m, 1000 w, 787 s, 765 m (br) cm^{-1}. On heating, the product decomposes before melting.

Pyrolysis of (I)

(I) (1.5 g; 4.2 mmol) was heated under vacuum to 250°. The volatile material was passed through solid KOH and trapped with liquid nitrogen. Yield 0.3g, corresponding to 60% of the organic material contained in (I). Combined GLC–mass spectrometry revealed the presence of propyne, 2-butyne, allene, 1,2,4- and 1,3,5-trimethylbenzene, and minor products, among which was a compound having molecular weight of 150 (dimethyldichlorocyclobutene or dimethyldichlorobutadiene). The propyne/2-butyne ratio widely varied depending on the yield of trimethylbenzene. Considerable amounts of organic material were retained by molybdenum.

Preparation of complexes with internal acetylenes

The acetylenic compound (20 mmol) was added at room temperature (unless otherwise indicated) with stirring to 4 mmol of the tungsten or molybdenum halide suspended in 25 ml of a diluent. Stirring was continued for 20 h (unless otherwise indicated). The precipitate was filtered, washed with the same solvent used as the diluent (in the case of diphenylacetylene, complexes were diluted 1/1 with light petroleum), and dried under vacuum at room temperature. The 2-butyne complexes were barely soluble in chlorinated solvents, and virtually insoluble in hydrocarbons. The diphenylacetylene complexes were somewhat more soluble. On heating all complexes decomposed before melting, they were air-instable, and diamagnetic.

In the case of the $MoCl_5$/2-butyne reaction, the liquid phase after removal of the precipitate by filtration, was examined by GLC–mass spectroscopy which revelaed the presence of *cis*- and *trans*-2,3-dichloro-2-butene and 2-chloro-2-butene in amounts roughly corresponding to the stoichiometry of the $MoCl_5$ dehalogenation.

(*a*). *$MoCl_5$ + 2-butyne* (*II*). Diluent CCl_4. Reaction time 1 h at 10°. Microcrystalline, brown powder; yield 97%. (Found: C, 16.0; H, 2.0; Cl, 48.0. $MoC_4H_6Cl_4$ calcd.: C, 16.4; H, 2.0; Cl, 48.7%.) IR max. 2920 w, 1755 s (C–C), 1405 w, 1350 m, 1157 w, 1000 w, 787 w, 335 m (br), 290 m (br) cm^{-1}. Mass spectrum (35 and 70 eV), 288 (mol.wt.), 253 ($-$Cl), 234 ($-C_4H_6$), 199 ($-C_4H_6$, $-$Cl).

(*b*). *WBr_5 + 2-butyne* (*IV*). Diluent benzene. Microcrystalline, brown powder; yield 77%. (Found: C, 8.4; H, 1.3; Br, 57.2. $WC_4H_6Br_4$ calcd.: C, 8.6; H, 1.1; Br, 57.4%.) IR max, 2920 w, 1730 s (C≡C); 1410 m, 1350 m, 1180 w, 830 s (br) cm^{-1}. Mass spectrum (30 and 70 eV), 554 (mol. wt.), 500 ($-C_4H_6$), 475 ($-$Br), 421 ($-C_4H_6$, $-$Br) ^{1}H NMR (acetone-d_6/benzene mixture) τ (ppm) 5.4 (CH_3 of 2-butyne in original complex; decreasing); 7.1 (idem, as solvated species; increasing); 8.5 (CH_3 of free 2-butyne; increasing).

(*c*). *WCl_5 + 2-butyne*. Diluent CCl_4; time 15 min.; temperature -5°. Microcrystalline, greenish powder; yield 77%. (Found: C, 10.7; H, 1.7; Cl, 38.9; W, 48.0. $WC_4H_6Cl_4$ calcd.: C, 12.6; H, 1.6; Cl, 37.4; W, 48.4%.) IR max, 1745 (C≡C) cm^{-1}. Mass spectrum (35 and 70 eV), 380 (mol. wt.), 345 ($-$Cl), 326 ($-C_4H_6$), 310 ($-$2 Cl), 291 ($-C_4H_6$, $-$Cl), 252 ($-C_4H_6$, $-$2 Cl).

(*d*). *$MoCl_5$ + diphenylacetylene* (*III*). Diluent CCl_4. Microcrystalline, dark brown powder; yield 90%. (Found: C, 40.0; H, 2.8; Cl, 34.5. $MoC_{14}H_{10}Cl_4$ calcd.: C, 40.3; H, 2.4; Cl, 34.1%.) IR max, 3060 w, 1695 s (C≡C), 1595 m, 1494 w, 1448 m, 1400 m, 1275 s, 1177 m, 1000 m, 913 m, 768 m, 760 s, 714 m, 674 s, 355 s (br) cm^{-1}. ^{1}H NMR (acetone-d_6/benzene mixture) τ 2.6 ppm (m, aromatic protons).

(*e*). *WBr_5 + diphenylacetylene* (*V*). Diluent benzene. Microcrystalline, dark brown powder; yield 86%. (Found: C, 24.4; H, 1.7; Br, 46.9. $WC_{14}H_{10}Br_4$ calcd.: C, 24.6; H, 1.5; Br 46.9%.) IR max, 3060 w, 1678 s (C≡C), 1600 m, 1495 w, 1448 m, 1277 m, 1176 w, 1075 w, 1000 w, 936 w, 833 s (br), 768 s, 757 w, 720 m, 680 s cm^{-1}.

(*f*). *$WOCl_4$ + 2-butyne* (*VI*). Diluent CH_2Cl_2. Time 48 h. Microcrystalline, greenish powder; yield 56%. (Found: C, 13.7; H, 1.8; Cl, 30.2; W, 51.8. $WOC_4H_6Cl_3$ calcd.: C, 13.3; H, 1.7; Cl, 29.6; W, 51.1%.) IR max, 2930 w, 1745 s (C≡C), 1415 w, 1353 m, 1176 w, 835 s (v br) cm^{-1}. ^{1}H NMR (acetone-d_6/benzene), very similar to case (V).

(*g*). *WCl_6 + ethanol + 2-butyne*. WCl_6 (2 mmol) in 25 ml CCl_4 was treated at 0° with 2 mmol of ethanol in 5 ml CCl_4. The red solution was stirred for a further 2 h at room temperature and 8.5 mmol of 2-butyne were added. Stirring was discontinued after 5 h more, and the solution was then cooled to 0°. The precipitated greenish powder (27% yield) showed spectroscopic properties very similar to those of (VI). However, the elemental analysis indicated the composition $WO_{1.6}C_{3.9}H_{6.8}Cl_3$.

Pyrolysis of (II)

(II) (1.1 g) was heated under vacuum to 250°. The volatile material [0.18 g = 90% of the organic material of (II)] was trapped with liquid nitrogen. GLC–mass spectroscopy indicated essentially 2-butyne, together with small amounts of 2-chloro-2-butene and *cis*- and *trans*-2,3-dichlorobutane.

Reaction of (III) with $EtAlCl_2$

To a stirred suspension of (III) (4 mmol) in benzene (15 ml) at 0° were slowly added 6–8 mol of $EtAlCl_2$, dissolved in 5 ml benzene. The product which separated after 20 min was filtered off, washed with benzene/light petroleum (1/1) and dried under vacuum. A microcrystalline, brown powder, obtained in 52% yield (VII), was scarcely soluble in benzene. (Found: C, 32.8; H, 1.8; Cl, 41.2; Al, 5.1; Mo, 19.0. $MoAlCl_6C_{14}H_{10}$ calcd.: C, 32.7; H, 1.9; Cl, 41.4; Al, 5.3; Mo, 18.7%) IR max, 3080 w, 1695 s ($C\equiv C$), 1595 s, 1482 m, 1448 m, 1397 m, 1274 s, 1178 m, 1130 w, 1000 m, 912 m, 763 s, 715 m, 674 s (br), 360 s, 200 s cm^{-1}.

Preparation of cyanide complexes

(*a*). *$MoCl_4(C_4H_6)$ + excess acetonitrile.* (II) (0.5 g; 1.72 mmol) was dissolved in 3 ml acetonitrile. Upon standing at room temperature a brown product precipitated which was filtered off, washed with light petroleum, and dried. Yield 0.38 g (68%). Elemental analysis and IR spectrum indicated the known[37] $MoCl_4(CH_3CN)_2$ structure.

(*b*). *$MoCl_4(C_4H_6)$ + equimolecular amounts of alkyl cyanides.* (II) (0.92 g; 3.15 mmol) in 20 ml CH_2Cl_2 was treated at −78° with acetonitrile (0.1 g; 2.8 mmol) with stirring. The reaction mixture was maintained for 1 h at 0°. On cooling the filtered solution to −78°, brown crystals precipitated; they were recrystallized from CH_2Cl_2 and dried under vacuum. Yield 0.58 g (55%). Soluble in chlorinated and aromatic solvents. Elemental analysis and IR spectrum showed the $MoCl_4(C_4H_6)(CH_3CN)$ structure (VIII). (Found: C, 21.1; H, 2.7; N, 4.5; Cl, 42.4; Mo, 28.9. $MoCl_4C_6H_9N$ calcd.; C, 21.6; H, 2.7; N, 4.2; Cl, 42.6; Mo, 28.8%.) IR max, 2320 s, 2300 s (CN), 1770 s ($C\equiv C$), 1408 m, 1370 m, 1350 s, 1165 m, 1114 w, 1028 m, 967 w, 938 m, 805 w, 767 w cm^{-1}.

The analogous reaction of (II) with proprionitrile yielded brown crystals, which were recrystallized from CH_2Cl_2/light petroleum (5/1) at −78°. Yield 35%. Soluble in chlorinated and aromatic solvents. Assigned structure $MoCl_4(C_4H_6)(C_2H_5CN)$ (IX). (Found: C, 21.7; H, 3.0; N, 3.9; Cl, 40.4; Mo, 28.6. $MoCl_4C_7H_{11}N$ calcd.: C, 24.2; H, 3.2; N, 4.0; Cl, 40.9; Mo, 27.7%.) IR max, 2300 s (CN), 1770 s ($C\equiv C$), 1460 m, 1414 m, 1357 m, 1306 m, 1160 s, 1070 w, 1026 w, 855 w, 778 w, 757 w cm^{-1}. ${}^1H$ NMR ($CHCl_3$) τ 5.9 ppm (s, 6H, CH_3 of 2-butyne); 8.5 (s, broad, 5H, C_2H_5).

(*c*). *$MoCl_5$ + 2-butyne + C_2H_5CN.* A stirred suspension of $MoCl_5$ (7.0 g; 25.6 mmol) in CH_2Cl_2 (75 ml) was treated at −78° with proprionitrile (0.78 g; 14.3 mmol) and 2-butyne (3.5 g; 65.0 mmol), added in this order. The suspension was then stirred for 1 h at 0°. The separated crystals of (II) (3.8 g; 40%) were filtered off, and the dark solution cooled to −78° overnight. 1.6 g (18%) of (IX) were isolated as brown crystals.

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