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HOMOGENEOUS ACETYLENE METATHESIS. NATURE OF THE CATALYTICALLY ACTIVE SPECIES IN THE [Mo(CO)₆]/PHENOL SYSTEM *

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Summary

p-TolylC≡CPh is converted efficiently into PhC≡CPh and *p*-tolylC≡Ctolyl-*p* (metathesis) by $[Mo(CO)_3(PhOH)]$ in n-octane at the reflux temperature. Other molybdenum complexes, e.g. $[Mo(CO)_3(NH_3)_3]$, $[Mo(CO)_3(MeCN)_3]$, *trans*-$[Mo(CO)_4(PPh_3)_2]$ and *cis*-$[Mo(CO)_2(Ph_2PCH_2PPh_2)_2]$ also catalyse metathesis, the first two in the absence of phenol. Coordinatively unsaturated species such as "$Mo(CO)_3$" are considered to be active in promoting metathesis, the role of phenol being to provide an unstable intermediate complex, rather than to assist in removal of complexed acetylene from molybdenum as envisaged hitherto.

Introduction

In 1974, Mortreux and Blanchard and their associates published the first [1] of a series [2—4] of papers describing the metathesis of unsymmetrical acetylenes, RC≡CR′, under homogeneous conditions, viz.:

$$2\ RC{\equiv}CR' \rightleftharpoons RC{\equiv}CR + R'C{\equiv}CR'$$

$[Mo(CO)_6]$ was employed as a catalyst, but reaction took place with any degree of efficiency only in the presence of a large excess ** of a phenol and at the reflux temperature (110° C) of the toluene solvent. Arguing by analogy with metathesis obtained using heterogeneous catalysts, the authors proposed a mechanism involving initial rapid reversible formation of an acetylene-molybdenum complex which reacted with the excess of phenol to give an "acetylene-phenol species"; the latter then decomposed irreversibly to give metathesis

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* Dedicated to Joseph Chatt on the occasion of his 65th birthday.

** E.g. $[Mo(CO)_6]$/PhOH/Acetylene = 1/100/10.

products, viz.:

$$\begin{tikzcd}
{[\mathrm{Mo(CO)_6}] + \text{acetylene}} \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Mo(CO)}_x(\text{acetylene})_y]\,(y = 1 \text{ or } 2)} \arrow[d, "\mathrm{ArOH}"] \\
\text{metathesis products} & {[\text{ArOH-acetylene}]} \arrow[l]
\end{tikzcd}$$

We describe here experiments designed to gain further insight into the reaction mechanism(s), particularly with regard to the intriguing role of phenol in the homogeneous metathesis process.

Results and discussion

In a preliminary study, p-tolylC≡CPh (a substrate chosen by Mortreux and Blanchard) was subjected to homogeneous metathesis in toluene in the presence of $[\mathrm{Mo(CO)_6}]$/PhOH. The results, presented in Table 1, confirm the observations of the French workers and are as follows:

(i) Both $[\mathrm{Mo(CO)_6}]$ and PhOH are required for metathesis.

(ii) The reaction is catalytic with respect to $[\mathrm{Mo(CO)_6}]$ since a molybdenum/substrate ratio of 1/10 was effective. A minimum $[\mathrm{Mo(CO)_6}]$/PhOH ratio of 1/60 was necessary to achieve equilibrium * during 1 h in refluxing toluene under dinitrogen at atmospheric pressure. Recovery of acetylene is high (ca. 96%).

(iii) The function of PhOH is also probably catalytic since additional aliquots of 10 parts of p-tolylC≡CPh (up to a total acetylene/$[\mathrm{Mo(CO)_6}]$/PhOH of 80/1/60) were converted efficiently during 1 h.

(iv) A minimum temperature (ca. 110°C) is required if metathesis equilibrium is to be achieved within 1 h. Preheating the $[\mathrm{Mo(CO)_6}]$/PhOH mixture to 110°C in toluene before addition of the substrate leads to a slight diminution in the reaction time. However equilibrium can be achieved at 80°C provided the contact time is prolonged. This period can also be slightly reduced if the $[\mathrm{Mo(CO)_6}]$/PhOH mixture is first heated to 110°C in toluene before addition of the acetylene.

At this stage and still using toluene as solvent, phenol was replaced by a series of hydroxy compounds in order to determine whether or not metathesis could be catalysed by other species. The details, given in Table 2, show that resorcinol (also used successfully by Mortreux and Blanchard), p-t-$\mathrm{BuC_6H_4OH}$ and PhOH-d_6 lead to metathesis, whereas thiophenol, benzoic acid and acetic acid did not. Use of catechol or quinol resulted in destruction of the p-tolylC≡CPh (without metathesis in the case of catechol) and, significantly, yellow solutions were obtained in these experiments. Replacement of $[\mathrm{Mo(CO)_6}]$ by *fac*-$[\mathrm{Mo(CO)_3(PMe_2Ph)_3}]$, *trans*-$[\mathrm{Mo(CO)_4(PPh_3)_2}]$ or *cis*-$[\mathrm{Mo(CO)_2(dppm)_2}]$ ** using an hundred-fold excess of PhOH resulted in efficient metathesis with the latter two complexes but not with the *fac*-compound. Somewhat lower PhOH/[Mo] ratios were effective in these examples.

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* PhC≡CPh/p-tolylC≡CPh/p-tolylC≡Ctolyl-p = 1/2/1.

** Dppm = $\mathrm{Ph_2PCH_2PPh_2}$.

TABLE 1

EFFECT OF CATALYST RATIO, TEMPERATURE AND REACTION TIME ON THE ACETYLENE METATHESIS: *p*-tolylC≡CPh(A) ⇌ PhC≡CPh(B) + *p*-tolylC≡Ctolyl-*p*(C), IN PhMe SOLUTION

$[Mo(CO)_6]$/PhOH [a]	B/A/C [b]	Reaction temperature (°)	Reaction time (h)
1/100	1/26/1	80	1
1/100	1/ 9/1	100	1
1/100	1/ 2/1	110	1
1/100	1/13/1	80	2
1/100	1/ 8/1	80	4
1/100	1/ 6/1	80	6
1/100	1/ 5/1	80 [c]	4
1/100	1/ 3/1	80 [c]	6
1/ 80	1/ 2/1	110	1
1/ 60	1/ 2/1	110	1
1/ 20	1/ 4/1	110	1
1/ 10	1/ 4/1	110	1
1/ 5	1/ 5/1	110	1

[a] $[Mo(CO)_6]$/A = 1/10; [b] At equilibrium, B/A/C = 1/2/1; [c] $[Mo(CO)_6]$/PhOH mixture heated briefly to 110°C, then cooled to 80°C before addition of A.

Nature of the catalyst

In an attempt to isolate a catalytically active species, $[Mo(CO)_6]$ (1 mol) and phenol (3 mol) were heated in an excess of toluene under reflux. A bright yellow crystalline solid was isolated and characterised as $[Mo(CO)_3(PhMe)]$ on the basis of comparison with an authentic specimen. Efforts to prepare an analogous phenol complex were not entirely satisfactory. Thus heating $[Mo(CO)_6]$ (1 mol) with phenol (2 mol) in refluxing n-octane for 4 h gave a yellow-brown oily solution. Removal of starting materials by filtration, followed by evaporation of solvent in vacuo, left a brown air-sensitive solid which decomposed at

TABLE 2

EFFECT ON *p*-tolylC≡CPh(A)-METATHESIS [a] OF REPLACING (i) PHENOL BY OTHER HYDROXY COMPOUNDS (COCATALYST) AND (ii) $[Mo(CO)_6]$ BY OTHER MOLYBDENUM COMPLEXES

Cocatalyst (X) [b]	B/A/C	Mo complex (Y)	B/A/C	Y/PhOH [c]
Resorcinol	1/ 2/1	*fac*-$[Mo(CO)_3(PMe_2Ph)_3]$	1/6/1	1/100
Quinol	1/14/1 [d]	*cis*-$[Mo(CO)_3(dppm)_2]$	1/2/1	1/100
Catechol	— [e]	*trans*-$[Mo(CO)_4(PPh_3)_2]$	1/2/1	1/100
p-t-Bu-C_6H_4OH	1/ 6/1		1/2/1	1/20
p-$O_2NC_6H_4OH$	— [f]		1/3/1	1/10
PhOH-d_6	1/ 2/1		1/5/1	1/5
PhOMe	— [f]		1/2/1	1/5 [g]
$PhOSiMe_3$	— [f]			
H_2O_2	— [f]			
$PhCO_2H$	— [f]			
$MeCO_2H$	— [f]			

[a] Reactions conducted for 1 h (unless stated otherwise) in PhMe at 110°C. [b] $[Mo(CO)_6]$/X/A = 1/100/10. [c] Y/A = 1/10. [d] Acetylenes partly destroyed. [e] Acetylenes completely destroyed. [f] No metathesis. (A) recovery good. [g] Reaction time = 1.5 h.

ca. 78° C, when phenol sublimed away leaving a black residue. Efforts to purify the brown solid were unsuccessful, however, we tentatively assign it the formula of $[Mo(CO)_3(PhOH)]$ on the basis of mass and IR spectra and elemental analysis. When the brown solid (1 mol) and *p*-tolylC≡CPh (10 mol) were heated together in refluxing n-octane, equilibrium metathesis was achieved within 1 h with a high recovery (96%) of acetylenes. By contrast, when $[Mo(CO)_3(PhOH)]$ was replaced by $[Mo(CO)_3(PhMe)]$, methathesis did not take place and *p*-tolylC≡CPh was recovered unchanged after 1 h. Neither complex catalysed metathesis when solvent n-octane was replaced by toluene, but catalytic activity could be restored to the $[Mo(CO)_3(PhMe)]$/n-octane or $[Mo(CO)_3(PhMe)]$/toluene system provided a five- or ten-fold excess of phenol, respectively, was present. Finally, a mixture of $[Mo(CO)_6]$ (1 mol) and phenol (1 mol) brought about efficient metathesis in refluxing n-octane during 1 h.

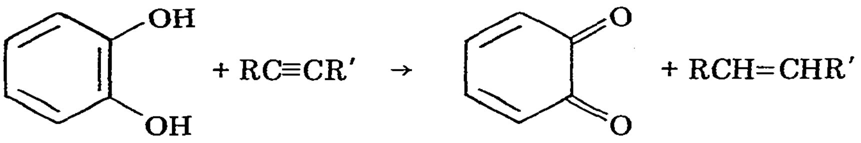
From these experiments, we conclude that the large excess of phenol required to achieve metathesis in toluene solution is necessary primarily to maintain a significant concentration of $[Mo(CO)_3(PhOH)]$, rather than to assist removal of the acetylene from an initial molybdenum complex as proposed by Mortreux and Blanchard. In the light of the difficulties experienced in isolating $[Mo(CO)_3(PhOH)]$, it seems highly likely that it is the precursor to the active catalyst, possibly the coordinatively unsaturated "$Mo(CO)_3$", whereas $[Mo(CO)_3(PhMe)]$ is too stable to provide a significant concentration of such a species, viz.:

$$\begin{tikzcd} {[Mo(CO)_6] + PhMe} \arrow[r] & {[Mo(CO)_3(PhMe)]\ \text{(inactive precursor)}} \arrow[d, "\text{PhOH (excess)}"] \\ {\text{"}Mo(CO)_3\text{"}} & {[Mo(CO)_3(PhOH)]} \arrow[l] \end{tikzcd}$$

When a mixture of *p*-tolylC≡CPh, $[Mo(CO)_6]$ and phenol was heated to the reflux temperature with passage of CO through the solution no metathesis occurred even after 6 h. Discontinuation of CO and replacement by N_2 restored the necessary conditions for metathesis. This cycle could be repeated and is consistent with some species such as "$Mo(CO)_3$" being involved in the catalyst.

If the foregoing argument is correct, other $[Mo(CO)_3L_3]$ complexes should catalyse metathesis, provided L is labile and that toluene or other "strongly binding" ligands are excluded. Both $[Mo(CO)_3(NH_3)_3]$ and $[Mo(CO)_3(MeCN)_3]$ were found to catalyse metathesis of *p*-tolylC≡CPh in the absence of phenol in n-octane at the reflux temperature although the equilibrium distribution of products could not be attained, even after 6 h. Strong metal-to-phosphorus bonding probably accounts for the catalytic inactivity of *fac*-$[Mo(CO)_3(PMe_2Ph)_2]$, whereas *trans*-$[Mo(CO)_4(PPh_3)_2]$ and *cis*-$[Mo(CO)_2(dppm)_2]$ dissociate sufficiently (assisted possibly by the phenol) to provide for catalysis.

Given the delicate balance of electronic and steric effects which influence the stability of π-arene-metal complexes, the range of substituents on the arene which would permit sufficient dissociation and, therefore, catalysis might be expected to be restricted. Nevertheless, it is surprising that anisole and phenoxy(trimethyl)silane proved to be completely inactive as catalysts since, at least on electronic grounds, the MeO and Me_3SiO substituents do not differ greatly from hydroxyl. The role of phenol may conceivably be wider therefore. The destruction of p tolylC≡CPh in the presence of quinol (accompanied by partial metathesis) and of catechol (no metathesis) and concomitant development of yellow solutions is instructive in this context. Both diols could conceivably be converted into quinones and the acetylene into an alkene; the latter was not detected however, viz.:



We have, as yet, no further evidence as to the reaction path for metathesis. By analogy with olefin metathesis, carbyne complexes should be considered. Cyclobutadiene, metallocyclopentadiene or acetylene complexes may also play a role. Our work sheds no light on these possibilities, since neither $[Mo(CO)_2(Ph_4C_4)_2]$, $[Mo_2(Ph_4C_4O)(Ph_4C_4)(Ph_2C_2)(CO)_3]$ nor [Mo(CO)-(MeSC≡CSMe)$_3$] catalysed metathesis in the absence of phenol. The molybdenum thioacetylene complex may be atypical since substituents on olefins are known to hinder olefin metathesis and might be expected to do the same in acetylene metathesis. Unfortunately, $[W(CO_6]$/PhOH/PhMe is not a catalyst, so we did not investigate the activity of $[W(CO)(Ph_2C_2)_3]$. Since dicarbonyl complexes can also give rise to catalysis, the formulation "$Mo(CO)_3$" must be considered as indicating a maximum CO content. Work is in hand to elucidate these details.

Experimental

Starting materials and products

Diphenylacetylene (Aldrich) was used as supplied and the following compounds were prepared by literature procedures: *p*-tolylC≡CPh [5], *p*-tolylC≡Ctolyl-*p* [6], $[Mo(CO)_3(PhMe)]$ [7], $[Mo(CO)_3(MeCN)_3)]$ [8], *fac*-$[Mo(CO)_3(PMe_2Ph)_3]$ [9], *cis*-$[Mo(CO)_2(dppm)_2]$, *trans*-$[Mo(CO)_4(PPh_3)_2]$ [10], $[Mo(CO)_2(Ph_4C_4)_2]$ [11] and $[Mo_2(Ph_4C_4O)(Ph_4C_4)(Ph_2C_2)(CO)_3]$ [12].

[Mo(CO)$_3$(PhOH)]

A mixture of PhOH (1.90 g, 20 mmol) and $[Mo(CO)_6)]$ (2.65 g, 10.mmol) was heated in n-octane (20 cm^3) at the reflux temperature under N_2 for 4 h. The resulting yellow-brown oily solution was filtered under N_2 and solvent was removed in vacuo (10^{-3} mmHg) to leave a brown oil which was freed from the excess of PhOH by sublimation. Attempts to recrystallise the residual brown solid were unsuccessful. (Yield ca. 4%) (Found: C, 41.0, H, 3.5, $C_9H_6MoO_4$ calcd.: C, 39.1; H, 2.2%) IR (CH_2Cl_2): ν(C≡O) 1970s, 1880s cm^{-1}; ν(O—H) 3510ms cm^{-1}; other bands 1600w, 1525w, 1505m, 1495(sh), 1160—1000(br)m, 800—750(br)w cm^{-1}. Mass spectrum: P^+(276), $(P-CO)^+$(248), $(P-2CO)^+$(220), $(P-3CO)^+$(192), $(P-4CO)^+$(164, additional loss of CO from PhOH). The compound is a non-conductor in nitromethane solution.

Metathesis

In a typical experiment, a 25 cm^3 flask fitted with a condenser, gas inlet and contact thermomenter was flushed with N_2 and charged with *p*-tolylC≡CPh (0.192 g, 1.0 mmol), PhOH (0.095 g, 0.1 mmol), $[Mo(CO)_6]$ (0.026 g, 0.1 mmol), n-octane (10 cm^3) and pentadecane (80 mg) as internal standard for GLC analysis. The mixture was heated on an oil bath whose temperature was controlled by an immersion coil connected via a relay to the thermometer. Samples of the mixture were removed with a microsyringe against a positive N_2 pressure and were injected into a gas chromatograph (Pye Unicam GCD Instrument fitted with a FID detector). Analyses were made on a 7′ 5% OV17 column held at 200°C with the injector port and detector maintained at 250°C. For programmed runs, the column temperature was increased by 2—4^0 min^{-1}. Experimental results were evaluated by comparing chromatograms with those of standard mixtures of reactants and products.

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