

*Journal of Organometallic Chemistry*, 280 (1985) 81–85  
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

## COMPLEX FORMATION OF ARENETRICARBONYL DERIVATIVES OF GROUP VI METALS WITH PHENYL- AND DIPHENYL-ACETYLENE AT LOW TEMPERATURES

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(Received May 29th, 1984)

### Summary

The intermolecular interactions of arenetricarbonyl-chromium, -molybdenum and -tungsten derivatives with phenyl- and diphenyl-acetylene have been studied by electronic emission spectroscopy (static luminescence quenching ( $T$  77 K) of the first order in methylene chloride matrices). Donor-acceptor complexes in the electronic ground state are formed, in which the organometallic compounds act as electron acceptors. The strength of the complexes changes proportionally with the catalytic activity of arenetricarbonyl metals in the phenylacetylene polymerization reaction.

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### Introduction

From investigation of the mechanisms of catalytic alkyne transformations on organic compounds of transition metals [1,2] it can be concluded that alkyne-organometallic (OMC) complexes are formed in the initial stages of the process. The further transformations of these complexes depend on the nature and valence state of the central atom, its ligand arrangement, and the type of acetylene compound [1]. Among the great number of compounds catalysing the polymerization of acetylene derivatives, carbonyl compounds of Groups VI–VIII form a substantial part.

In the past decade there has been some work in the literature dealing with the investigation of the catalytic properties of transition metal  $\pi$ -complexes, in particular, arenetricarbonyl-chromium, -molybdenum and -tungsten compounds. Farona et al. [3–5] have shown that arenetricarbonyl compounds of Group VI elements catalyse phenylacetylene polymerization at elevated temperatures. This reaction also proceeds at lower temperatures on UV-irradiation of the reaction mixture [6,7]. Two mechanisms of polymerization have been suggested for these reactions. Yet, in none

of the papers has the complex of arenetricarbonyl metal with phenylacetylene been investigated. This complex may even be formed by mixing the reagents and its properties may play a leading role in polymerization processes.

The present study examines the results of diphenylacetylene (DPhA) and phenylacetylene (PhA) interaction with arenetricarbonyl-chromium, -molybdenum and -tungsten derivatives in very dilute solutions at low temperatures. The electron-donor-acceptor complex, in which the organometallic compound acts as an electron acceptor, seems to be formed in the first stage of the reaction of acetylene derivatives with arenetricarbonyl metals (ATCM) under these conditions. The interaction occurs at the expense of increasing coordination number of the central metal atom. Electronic emission spectroscopy was used to investigate the complex formation.

### Results and discussion

Intensive DPhA phosphorescence has been observed in the region of 330–400 nm ( $\lambda$  313 nm,  $c[\text{DPhA}] 9 \times 10^{-5} \text{ mol l}^{-1}$ ) at 77 K in frozen methylene chloride solution [8]. The intensity of PhA phosphorescence (in the 360–450 nm region) is extremely weak under the same conditions, yet it increases slightly with increasing solution concentration ( $c[\text{PhA}] 2.7 \times 10^{-2} \text{ mol l}^{-1}$ ). The addition of small quantities of arenetricarbonylchromium to the solution results in DPhA and PhA phosphorescence quenching without variation of the type of spectrum (Fig. 1). In the region of quencher concentration  $10^{-6}$ – $1.2 \times 10^{-5} \text{ mol l}^{-1}$  for DPhA and  $3 \times 10^{-6}$ – $1.3 \times 10^{-5} \text{ mol l}^{-1}$  for PhA, a linear relationship in  $I_0/I - Q$  coordinates is obtained in all cases, where  $I_0$  and  $I$  are the DPhA or PhA phosphorescence intensities in relative units, in the absence ( $I_0$ ) and presence ( $I$ ) of quenchers and  $Q$  is the quencher concentration in  $\text{mol l}^{-1}$ .

$$\frac{I_0}{I} = 1 + K_Q[Q] \quad (1)$$

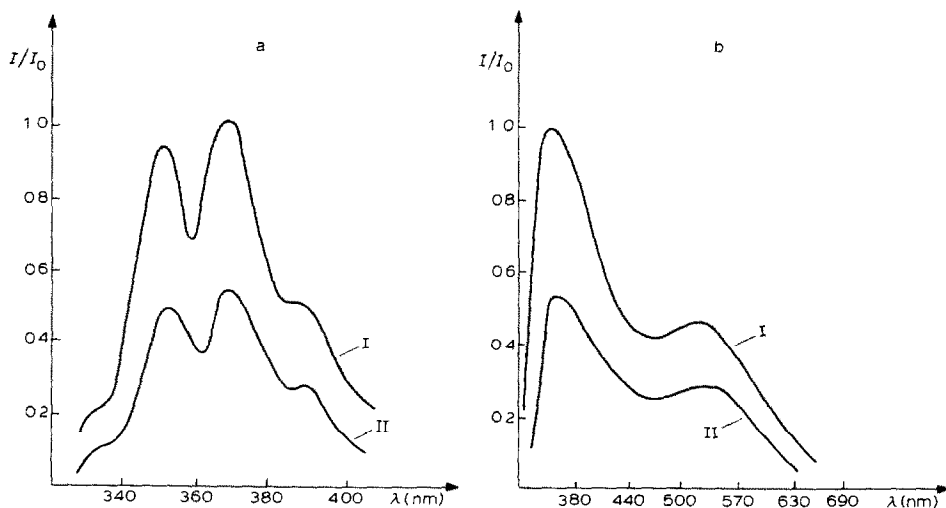


Fig. 1. Influence of the organometallic quencher on the phosphorescence spectra of diphenylacetylene and phenylacetylene ( $\text{CH}_2\text{Cl}_2$  solution). (a) I, DPhA ( $c[\text{DPhA}] 0.9 \times 10^{-4} \text{ mol l}^{-1}$ ); II, DPhA +  $\text{CH}_3\text{OCC}_6\text{H}_5\text{Cr}(\text{CO})_3$   $c = 1.2 \times 10^{-6} \text{ mol l}^{-1}$ . (b) I, PhA ( $c[\text{PhA}] 2.7 \times 10^{-2} \text{ mol l}^{-1}$ ); II, PhA +  $\text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$  ( $c_Q = 1.2 \times 10^{-5} \text{ mol l}^{-1}$ ).

The slope of equation 1 represents the quenching constant,  $K_Q$ , of DPhA and PhA phosphorescence by arenetricarbonylchromiums. In this case, the fact that equation 1 could be used to a rather high accuracy (correlation coefficients of straight lines were not less than 0.985; number of experimental points 5–7) under static quenching conditions [9–12] indicates the ability of non-luminescent DPhA and PhA complexes with arenetricarbonylchromium (ATCCh) in the electronic ground state to form. Due to the small quantum yield of PhA phosphorescence and the larger error in  $K_Q$  determination associated with this, as well as the weaker  $\pi$ -donor-ability of the latter in comparison to DPhA (PhA and DPhA ionization potentials are 8.75 and 8.00 eV, respectively [13]), diphenylacetylene was chosen as the model compound to investigate the regularities of static phosphorescence quenching by arenetricarbonylchromiums. The values of DPhA phosphorescence quenching constants for some ATCCh complexes at 77 K are listed in Table 1. The  $\sigma$ -constant values of the substituents in the aromatic ATCCh ligand [15] and the CT frequencies,  $\nu_{CT}$ , determined earlier [14] from electronic absorption spectra of the investigated ATCCh complexes with the  $\pi$ -acceptor tetracyanoethylene (TCNE) ( $T$  298 K,  $\text{CH}_2\text{Cl}_2$  solution) are also shown.

CT frequencies are known to characterize the donor ability of arenetricarbonylmetals with respect to the  $\pi$ -acceptor TCNE. With increasing donor ability of the organometallic compound,  $\nu_{CT}$  rises [14].

Analysis of the  $K_{QI}$  values (Table 1) shows that  $\ln K_{QI}$  and  $\nu_{CT}$  are related by the linear correlation

$$\ln K_{QI} = -4.99 \times 10^{-4} \nu_{CT} + 19.63 \quad (\gamma = 0.95) \quad (2)$$

Thus the quenching process of DPhA phosphorescence by arenetricarbonylchromiums is mainly due to the donor-acceptor interaction between these compounds in the ground state.

TABLE 1

VALUES OF DIPHENYLACETYLENE ( $K_{QI}$ ) AND PHENYLACETYLENE ( $K_{QII}$ ) LUMINESCENCE QUENCHING CONSTANTS FOR SOME ARENETRICARBONYL METALS; CT FREQUENCIES,  $\nu_{CT}$ , FROM THE ABSORPTION SPECTRA OF ATCM COMPLEXES WITH TCNE; AND  $\sigma_p$ -CONSTANTS OF THE SUBSTITUENTS IN ATCM

No.	Compound	$K_{QI} \times 10^{-5}$ ( $l^{-1}$ mol)	$K_{QII} \times 10^{-5}$ ( $l^{-1}$ mol)	$\nu_{CT} \times 10^{-3}$ $\text{cm}^{-1}$ [14]	$\Sigma \sigma_p$ [15]
1	$\text{CH}_3\text{OOC}_6\text{H}_5\text{Cr}(\text{CO})_3$	7.85		12.1	+0.44
2	$\text{C}_2\text{H}_5\text{OOC}_6\text{H}_5\text{Cr}(\text{CO})_3$	7.50			+0.42
3	$\text{ClC}_6\text{H}_5\text{Cr}(\text{CO})_3$	5.26	1.70	12.8	+0.23
4	$\text{FC}_6\text{H}_5\text{Cr}(\text{CO})_3$	4.99		12.7	+0.06
5	$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$	4.78	1.38	13.6	0.00
6*	$\text{CH}_3\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$	4.54			-0.17
7	$(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Cr}(\text{CO})_3$	3.34		13.9	-0.34
8	$(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$	2.11		14.3	-0.51
9	$(\text{CH}_3)_4\text{C}_6\text{H}_2\text{Cr}(\text{CO})_3$	1.64		15.0	-0.68
10	$(\text{CH}_3)_6\text{C}_6\text{Cr}(\text{CO})_3$	1.24	0.30	15.7	-1.02
11	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$	3.68	0.70	14.4	-0.15
12	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{Mo}(\text{CO})_3$	4.92			-0.15
13	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{W}(\text{CO})_3$	2.72			-0.15

Yet the opposite tendencies are observed when complexing ATCCh with TCNE and DPhA, as follows from the reverse relationship (eq. 2) between  $\ln K_{QI}$  and  $\nu_{CT}$ . The increase of donor arenetricarbonylmolybdenum (ATCM) ability with reference to TCNE causes the  $\nu_{CT}$  value to rise in the course of successive passing from compound **1** to **10**. Yet with such passing of the value  $\ln K_{QI}$  does not increase, but in contrast decreases. The latter indicates the increase of stability of ATCM complexes with DPhA with decreasing donor ATCM properties. As DPhA is a typical  $\pi$ -donor, the above-mentioned stability increase of its ATCM complexes may be related to the electron-acceptor ATCCh character with respect to DPhA. The electron-acceptor ATCCh character increases regularly with decreasing donor ability of the substituents in the aromatic ring from compound **10** to **1**. From the examples of the systems, naphthalene derivatives with TCNE and benzene derivatives with TCNE [10,12], the first-order luminescence (fluorescence or phosphorescence) quenching constants under static conditions are shown to be proportional to the equilibrium constants of complex formation processes at the solvent's freezing point. This is demonstrated by the linear relationship between  $\ln K_{QI}$  (which is proportional to Gibbs free energy of complex formation process) and the  $\sigma_p$ -constants of the substituents in the ATCCh-benzene ring in the DPhA-arenetricarbonylchromium system studied:

$$\ln K_{QI} = 1.18 \Sigma \sigma_p + 13.01 \quad (\gamma = 0.96) \quad (3)$$

Consequently, in the series of organometallic compounds (from Table 1), the strength of the complexes with DPhA rises with increasing electron-acceptor ability of the substituents in the ring. This is further confirmation of the ATCCh electron-acceptor character in complexes with DPhA.

We have also studied the variation of DPhA phosphorescence quenching efficiency with the nature of the central metal atom in the arenetricarbonyl metal (for example, ethyl derivatives, compounds **11**–**13**, Table 1). As can be seen from the  $K_{QI}$ -constant values, the strength of the complexes decreases in the series: Mo > Cr > W.

The phosphorescence quenching process of PhA by some of the ATCCh complexes studied is characterized by similar regularities (Table 1). Yet in this case, because of the lower accuracy in the determination of the quenching constant (see above), only a symbatic dependence in the change of  $K_{QII}$  ( $\ln K_{QII}$ ) and  $\nu_{CT}$  ( $\sigma_p$ -constants) may be seen.

Comparison of the quenching efficiencies of DPhA and PhA phosphorescence by compounds **3**, **5**, **10** and **11** indicates that phenylacetylene, according to already mentioned weaker  $\pi$ -donor ability, does not form as strong electron-donor-acceptor complexes with ATCCh in the ground state.

From literature data [6,7], the catalytic activity of ATCM in the PhA polymerization reaction is dictated by the character of the central metal atom and by the donor-acceptor properties of the substituents in the aromatic ring. The following series of decreasing catalytic activity [7] were found for arenetricarbonyl metals with any central metal atom: Mo > Cr > W; for substituted benzenetricarbonylchromium derivatives:  $\text{ClC}_6\text{H}_5\text{Cr}(\text{CO})_3 > \text{CH}_3\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3 > \text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3 > (\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3 > \text{CH}_3\text{OC}_6\text{H}_5\text{Cr}(\text{CO})_3$ .

Comparing these series with the change order of the appropriate  $K_{QII}$  or  $K_{QI}$  values (Table 1), it is easy to see the symbatic change of catalytic ATCM activity

characterized by the PhA polymerization rate constant [7] and that of the strength of ATCM complexes with PhA (or DPhA) characterized by  $K_Q$  quenching constant.

The data obtained allow us to conclude that ATCM-alkyne complex formation even in the electronic ground state really determines catalytic ATCM activity in the polymerization reactions of alkynes, the catalytic activity increasing with a rise of complex strength. In its turn, the luminescence quenching method of alkynes in the presence of arenetricarbonyl metal compounds may be used for predicting the catalytic activity of the latter in polymerization reactions of alkynes.

## Experimental

The luminescence spectra were measured by the methods described previously [16]. The determination error of quenching constant  $K_Q$  was within 10%. Arenetricarbonyl-chromium, -molybdenum and -tungsten complexes were synthesized by known methods [17], recrystallized from toluene/heptane (1/1) and sublimed under high vacuum. DPhA was purified under vacuum; PhA was purified by rectification under reduced pressure prior to testing. Methylene chloride was purified by known methods [18].

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