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PHOTOCHEMICAL SYNTHESIS AND REACTION OF d^6 METALLOCENES—TETRACYANOETHYLENE CHARGE-TRANSFER COMPLEXES

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Summary

Photolysis of tetracyanoethylene in the presence of $(\eta\text{-}C_5H_5)_2M$ (M = Ru, Os) gives the novel $(\eta\text{-}C_5H_5)_2M \cdot$ TCNE complexes. Charge transfer absorptions are identified for these compounds. Selective irradiation of the complexes gives metallocenium cations and $TCNE^{\overline{\cdot}}$ anion radicals as the primary photoproducts.

Introduction

The strong π-acid tetracyanoethylene (TCNE) reacts with iron metallocenes, commonly regarded as π-bases, to give charge transfer complexes, or in some cases, salts of the TCNE anion radical [1]. The nature of the product, is supposed to depend on the ease of oxidation of the basic substrate. It has been reported that neither ruthenocene nor osmocene form stable complexes with TCNE, since grinding the components together does not produce a color change [1]. As the ease of oxidation of $(\eta\text{-}C_5H_5)_2M$ is suggested to be $M = Fe > Ru > Os$ [2], TCNE is perhaps not a strong enough π-acid to form complexes with the more difficulty oxidized ruthenocene and osmocene.

Electronic excitation decreases the ionization potential and increases the electronic affinity of a molecule [3]. Consequently, those electronically excited states of an acceptor molecule which live long enough to encounter a donor species, can be involved in an intermolecular electron transfer process. Thus, the formation of charge-transfer complexes between TCNE and some d^6 metallocenes may be under photochemical activation. We report in this paper a study of the photoinduced addition of some metallocenes $(\eta\text{-}C_5H_4R)M(\eta\text{-}C_5H_5)$[M = Ru, Os; R = H or —COPh] to TCNE.

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Experimental

$(\eta\text{-}C_5H_5)_2Ru$ was obtained commercially. Sublimation or recrystallizations were carried out until the electronic spectrum and m.p. indicated that a pure sample had been obtained. $(\eta\text{-}C_5H_5)_2Os$ and $(\eta\text{-}C_5H_4COPh)Ru(\eta\text{-}C_5H_5)$ were prepared by known routes [2]. TCNE was always freshly resublimed under vacuum. Spectroquality solvents were used, and dried before use. $CDCl_3$ was a Merck product, and used as received.

Irradiation procedure

Irradiation at 254 nm was carried out with a PGQ immersion Hg lamp with a UV power supply unit, model Mineral light SCT4. The irradiation vessel was a Pyrex condenser sealed with a greaseless joint. Irradiations were carried out at room temperature. Monochromatic light of λ 334, 366 and 436 nm was obtained from a Hg vapor lamp (HANAU Q 400) by means of the appropriate Baush and Lomb interference filters. Radiations > 580 nm were obtained from a tungsten incandescent lamp (Philips Attralux Spot 150 W) by means of a filter solution (7 cm $Fe(O\text{-}phen)_3SO_4$: the concentration was adjusted until the absorbance at 580 nm was 2.0).

Since the metallocenes—TCNE adducts are extremely sensitive to light, oxygen and moisture, all handling procedures were carried out under red light in a dry-box with an atmosphere of argon dried over Na—K alloy.

Apparatus

The IR spectra were recorded with a Perkin—Elmer 577 instrument and the electronic spectra with a Perkin—Elmer 323 recording spectrophotometer. NMR spectra were recorded on a Hitachi—Perkin—Elmer R 24A instrument. ESR spectra were recorded at room temperature with a JES - 3BQ JEOL spectrometer.

Synthesis of $(\eta\text{-}C_5H_5)_2Ru \cdot TCNE$ (I)

A cyclohexane solution of TCNE and $(\eta\text{-}C_5H_5)_2Ru$ in 2/1 molar ratio with 0.2 *M* total concentration was irradiated under argon for 4 h with a PGQ immersion lamp. The green solution was evaporated under vacuum and the crude residue, which consisted of a mixture of I and unchanged starting material, was crystallized from chloroform/hexane to give pure I as pale green needles, soluble in chloroform and insoluble in hexane. Analysis found: C, 53.50; N, 15.55; H, 2.82; Ru, 28.13. $C_{16}H_{10}N_4Ru$ calcd.: C, 53.48; N, 15.59; H, 2.80; Ru, 28.13%.

Synthesis of $(\eta\text{-}C_5H_4COC_6H_5)Ru(\eta\text{-}C_5H_5) \cdot TCNE$ (II) and of $(\eta\text{-}C_5H_5)_2Os \cdot TCNE$ (III)

The method used for preparing I was used also to give II and III starting from solutions of TCNE and $(\eta\text{-}C_5H_4COC_6H_5)Ru(\eta\text{-}C_5H_5)$ or $(\eta\text{-}C_5H_5)_2Os$ in a 2/1 molar ratio. Analysis for II: found: C, 59.65; N, 12.1; H, 3.00; O, 3.45; Ru, 21.80. $C_{25}H_{14}N_4ORu$ calcd.: C, 59.63; N, 12.08; H, 3.04; O, 3.45; Ru, 21.80%. Analysis for III: found: C, 42.90; N, 12.45; H, 2.23; Os, 42.42. $C_{16}H_{10}N_4Os$ calcd.: C, 42.85; N, 12.49; H, 2.25; Os. 42.41%.

No reaction occurred between TCNE and metallocenes in cyclohexane at 20°C in the dark.

Photolysis of $(\eta\text{-}C_5H_5)_2M \cdot TCNE$ *CT complexes*

The photoreactions were monitored by observing the increase in absorbance of the bands near 400 nm typical of $TCNE^{\overline{\cdot}}$ [4]. The incident light intensity was measured by means of the ferric oxalate actinometer [5]. Alternatively, deoxygenated solutions of the samples were directly irradiated in a 4 mm cyclindrical quartz ESR tube. Irradiation of I, II and III in the ESR cavity generated a signal centered at g 2.006 within a few seconds. The g value and the presence of a nine-line spectrum show the signal to be that of the $TCNE^{\overline{\cdot}}$ anion radical [6]. Solutions of I, II and III in degassed cyclohexane were photolysed for 30 min in a quartz vessel. Removal of the solvent resulted in a residue consisting of a mixture of TCNE, $TCNE^{\overline{\cdot}}$, metallocenes and metallocenium cations. These compounds were identified by IR and electronic spectra [2,4].

Results and discussion

Irradiation of cyclohexane solutions of TCNE and $(\eta\text{-}C_5H_4R)M(\eta\text{-}C_5H_5)$ [M = Ru; R = H, —COPh; M = Os, R = H] in a 2/1 molar ratio gave the adducts I, II and III. The rate of formation of the adducts was increased by increasing the TCNE concentration. This observation is consistent with a mechanism in which the cyanoolefin is photochemically excited and attacks the other component in the reaction:

$$\text{TCNE} \xrightarrow{h\nu} [\text{TCNE}]^*$$

$$[\text{TCNE}]^* + (\eta\text{-}C_5H_5)_2M \rightarrow (\eta\text{-}C_5H_5)_2M \cdot \text{TCNE}$$

The view that photoexcited TCNE is trapped by metallocenes to yield I, II and III seems plausible when it is appreciated that the light absorbed by the $(\eta\text{-}C_5H_5)_2M$ is <10% of the total light absorbed. Even if the reactions were not exclusively those of the TCNE excited state [3], the increase in electronic affinity due to a change in electron distribution, should influence the reaction rates and also the positions of equilibria compared with the corresponding ground state reactions.

TABLE 1

INFRARED DATA (cm^{-1}) FOR METALLOCENE—TETRACYANOETHYLENE COMPLEXES [a]

$(\eta\text{-}C_5H_5)_2Ru \cdot TCNE$	$(\eta\text{-}C_5H_4COPh)Ru(\eta\text{-}C_5H_5) \cdot TCNE$	$(\eta\text{-}C_5H_5)_2Os \cdot TCNE$
3098s	3100s	3095s
2185s	2190s	2200s
	1640	
	1605	
	1588	
	1458	
1415m	1415m	1405m
1105vs	1105vs	1100s
1002s	1000s	995s
810s	810s	820s
440s	440s	430s
370m	370m	370m

[a] Determined in KBr pelietts.

Experimental

(η-C_5H_5)$_2$Ru was obtained commercially. Sublimation or recrystallizations were carried out until the electronic spectrum and m.p. indicated that a pure sample had been obtained. (η-C_5H_5)$_2$Os and (η-C_5H_4COPh)Ru(η-C_5H_5) were prepared by known routes [2]. TCNE was always freshly resublimed under vacuum. Spectroquality solvents were used, and dried before use. $CDCl_3$ was a Merck product, and used as received.

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2185s	2190s	2200s
	1640	
	1605	
	1588	
	1458	
1415m	1415m	1405m
1105vs	1105vs	1100s
1002s	1000s	995s
810s	810s	820s
440s	440s	430s
370m	370m	370m

[a] Determined in KBr pelletts.

The IR spectra of the adducts are reported in Table 1. The spectra show only one sharp C≡N stretching vibration in the 2200—2180 cm^{-1} range, somewhat lower than the corresponding stretching frequencies at 2228 and 2260 cm^{-1} for TCNE [7]. This indicates the filling of antibonding orbitals in the cyano groups, and is in accord with the occurrence of back-bonding from metal to ligand, as established for other TCNE—π-complexes [8]. There is a shift of the 806 and 819 cm^{-1} metallocene bands, associated with a C—H out-of-plane bending mode [2], to 810 and 820 cm^{-1} in ruthenocene and osmocene complexes, respectively. The failure to observe the strong band in the 850—860 cm^{-1} region characteristic of metallocenium cations [9], indicates that oxidation did not occur upon complex formation. This point is confirmed by the lack of the bands at 2190 and 1360 cm^{-1}, characteristic of TNCE$^{\overline{\cdot}}$ ion radical [7]. These IR observations are consistent with the formulation of the I, II and III as π complexes.

In the ^{1}H NMR spectra, the signal assigned to the five-membered ring protons [2] is not substantially changed (δ 0.30 and 0.35 ppm downfield for Ru and Os complexes, respectively) over the values for $(\eta\text{-}C_5H_5)_2Ru$ and $(\eta\text{-}C_5H_5)_2Os$. This indicates that the interaction between TCNE and metallocenes does not appreciably affect the π-orbital ring current associated with each cyclopentadienyl ring [2]. An electron flow from metal atoms towards TCNE must instead cause the observed deshielding of the ring protons [9], on the assumption that there is metal participation in the bonding to the cyanoolefin. This is consistent also with the electronic data, which indicates the participation of metal *d* electrons in the coordination with TCNE.

The electronic spectra of solid complexes are reported in Fig. 1. The spectra contain new bands which are absent in the spectra of either component, and which can be referred to as charge-transfer bands (CT) since they are generated by energy uptake in transferring an electron from donor metallocene to accep-

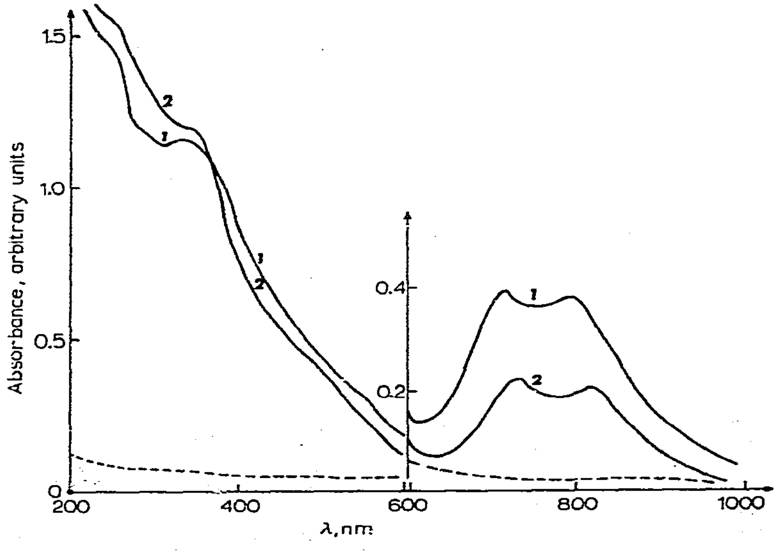

Fig. 1. Electronic spectra of tetracyanoethylene complexes in KBr; 1, $(\eta\text{-}C_5H_5)_2Ru$ · TCNE; 2, $(\eta\text{-}C_5H_5)_2Os$ · TCNE.

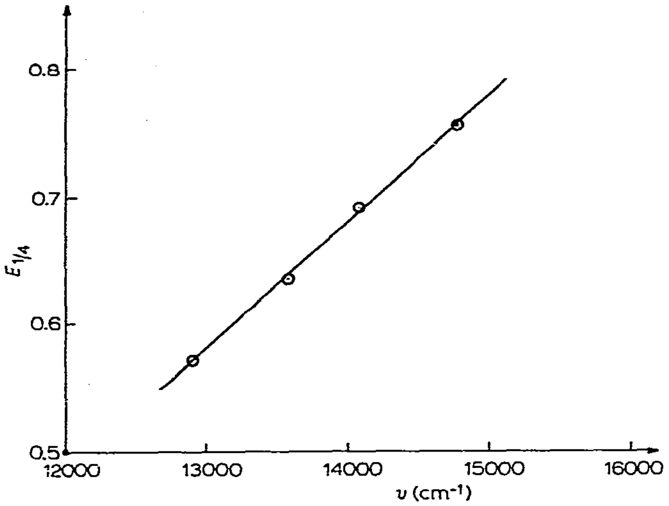

Fig. 2. Correlation of oxidation potentials of metallocenes and the energy of their TCNE charge-transfer complexes.

tor TCNE. The energies of these electronic transitions relate to the metallocene oxidation potentials, as determined by the chronopotentiometric $E_{1/4}$ values.

The observation of a linear relationship between the CT transition energies and the metallocene oxidation potentials (Fig. 2) is in conformity with the behaviour found in some substituted ferrocenes [1]. This strongly supports the view that charge-transfer complexes are formed by means of a TCNE interaction with metal atoms. The appearance of two absorptions in the low energy region can be explained by assuming the existence of two closely located occupied orbitals in the metal [10]. On this basis one would expect the difference in energy between the two charge-transfer absorption maxima to be close to that between the two highest occupied metal orbitals. The data in Table 2 confirm this prediction. The difference is also in conformity with the $a_1(d)$ and $e_2(d)$ ionization energies orbital difference (1452 cm^{-1}) indicated by the He photoelectronic spectra of ruthenocene and osmocene [11]. Thus, the results are in agreement with a direct metal participation in the bonding with TCNE, e.g., the chemically active electron pairs are localized mainly on the metal.

The stability of I, II and III in solution shows a strong dependence on solvent polarity. Solvents having high dielectric constants favour complete electron

TABLE 2

ELECTRONIC DATA FOR THE CT ABSORPTIONS OF TETRACYANOETHYLENE COMPLEXES IN CYCLOHEXANE

Donor	λ_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	ϵ_{max}
$(\eta\text{-}C_5H_4COC_6H_5)Ru(\eta\text{-}C_5H_5)$	14780 13325	1445	395
$(\eta\text{-}C_5H_5)_2Ru$	14084 12636	1458	400
$(\eta\text{-}C_5H_5)_2Os$	13550 12100	1450	230

transfer, giving metallocenium cations and $TCNE^{\overline{\cdot}}$. In solvents of relatively low dielectric constants (cyclohexane, chloroform), the complexes are quite stable in the dark, as evidenced by the presence of the characteristic charge transfer absorptions (Table 2) and by the lack of absorptions of the respective ions. This indicates that the form of association between TCNE and metallocenes in solution is probably closer to that found for the crystalline state. The extinction coefficients for the I, II and III complexes (Table 2) vary in the order $(\eta\text{-}C_5H_5)_2Ru > (\eta\text{-}C_5H_5)_2Os$. It is not clear whether this effect will be related to the equilibrium process:

$$(\eta\text{-}C_5H_5)_2M \cdot TCNE \rightleftharpoons (\eta\text{-}C_5H_5)_2M + TCNE$$

or reflects the difference in metallocene ionization potentials, as proposed for other charge transfer complexes [1].

Photolysis of the $(\eta\text{-}C_5H_5)_2M \cdot TCNE$ CT complexes

The I, II and III complexes were selectively excited in the ligand field bands and in the metal—TCNE CT transitions, using filtered light (Table 2). Metallocenium cations, $TCNE^{\overline{\cdot}}$, metallocenes and TCNE are the observed photoproducts. The electronic spin resonance spectra of the photoreaction mixtures show the characteristic transitions of the $TCNE^{\overline{\cdot}}$; the intensity ratio and the g value are in agreement with that reported [6]. The electronic spectra of the irradiated solutions also indicate that in each case an electron transfer process has occurred to form $(\eta\text{-}C_5H_5)M^+$ cations and $TCNE^{\overline{\cdot}}$.

The quantum yield values for the formation of $TCNE^{\overline{\cdot}}$ (0.75 and 0.68 for ruthenocene and osmocene complexes, respectively) are wavelength-independent. Such relatively efficient reactions indicate that CT states are populated both by decay of ligand field excited states and by direct excitation. Thus, the excited CT complexes must breakdown by a non diffusive collapse K_d, to $(\eta\text{-}C_5H_5)_2M$ and TCNE, and by an electron transfer, K_{rp}, to give a radical pair (Scheme 1). Diffusive separation of this radical pair would give $(\eta\text{-}C_5H_5)_2M^+$ and $TCNE^{\overline{\cdot}}$.

SCHEME 1

$$(\eta\text{-}C_5H_5)_2M \cdot TCNE \xrightarrow{h\nu} [(\eta\text{-}C_5H_5)_2M \cdot TCNE]^*$$

$$[(\eta\text{-}C_5H_5)_2M \cdot TCNE]^* \begin{cases} \xrightarrow{K_d} (\eta\text{-}C_5H_5)_2M + TCNE \\ \xrightarrow{K_{rp}} [\eta\text{-}C_5H_5M^+ \cdot TCNE^{\overline{\cdot}}]_{rp} \end{cases}$$

$$[\eta\text{-}C_5H_5M^+ \cdot TCNE^{\overline{\cdot}}]_{rp} \rightarrow \eta\text{-}C_5H_5M^+ + TCNE^{\overline{\cdot}}$$

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References

1 M. Rosenblum, R.W. Fish and C. Bennett, J. Amer. Chem. Soc., 86 (1964) 5166.
2 M. Rosenblum, Chemistry of the Iron Group Metallocenes, Interscience Publishers, John Wiley, New York, 1965.
3 H. Gerischer, Disc. Faraday Soc., 58 (1974) 219.
4 O.W. Webster, W. Mahler and R.E. Benzon, J. Amer. Chem. Soc., 84 (1962) 3678.
5 C.G. Hatchard and C.A. Parker, Proc. Roy. Soc. (London), Ser. A, 235 (1956) 518.
6 R. Vars, L.A. Tripp and L.W. Pichett, J. Phys. Chem., 66 (1962) 1754.
7 J. Stanley, D. Smith, B. Latimer and J.P. Devlin, J. Phys. Chem., 70 (1966) 2011.
8 W.H. Baddley, J. Amer. Chem. Soc., 88 (1966) 4545.
9 O. Traverso, C. Chiorboli, U. Mazzi and G.L. Zucchini, Gazz. Chim. Ital., 107 (1977) 181.
10 J.N. Murell, J. Amer. Chem. Soc., 81 (1959) 5037.
11 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, J. Chem. Soc., Faraday II, (1972) 1847.