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CHELATE CYCLOPENTADIENYLMANGANESE DICARBONYL COMPLEXES

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Summary

Cyclopentadienylmanganese tricarbonyl complexes with allyloxymethyl- and propargyloxymethyl substituents have been synthesized. Under UV irradiation, they give new chelate cyclopentadienylmanganese dicarbonyl complexes with coordinated vinyl and ethinyl groups. In the case of cyclopentadienylmanganese-tricarbonyl complexes having two such substituents, only mono-bridged chelate dicarbonyl compounds have been obtained. α-Oxo-ω-cyanoalkyl derivatives of cyclopentadienylmanganese tricarbonyl give under UV irradiation new chelate complexes with σ-coordination between the metal and the nitrogen atom of cyano groups. An attempt to obtain chelate complexes by the same method from ω-cyanoalkyl derivatives of cyclopentadienylmanganese tricarbonyl failed.

Many papers have been devoted to the study of trends in the formation of chelates in the series of inorganic compounds. However, this problem has not been investigated for organometallic chelates in which the ligand is bonded to the metal either completely or partially through the carbon atoms. The only direction developed rather intensively in this field was stipulated by the wish to obtain percyclophanes of the ferrocene series. Under the guidance of A.N. Nesmeyanov we have undertaken the first steps to clarify the trends in the formation of chelates in the series of arenechromiumtricarbonyl complexes [1]. This report is a continuation of investigations undertaken to find out whether the trends discovered by us are common for other similar chelates prepared on the basis of the cyclopentadienylmanganese dicarbonyl system.

In the case of arenechromiumdicarbonyl complexes [2] it was shown that stable chelate arene-olefin dicarbonyl complexes of chromium are formed in the case of two- and three-atom bridges. In studying the formation of chelates in the series of organometallic compounds we obtained a stable manganese dicarbonyl complex (II) with cyclopentadienylmethyl allyl ether [3] used as a ligand [4]. The structure of complex II is confirmed by elemental analysis and

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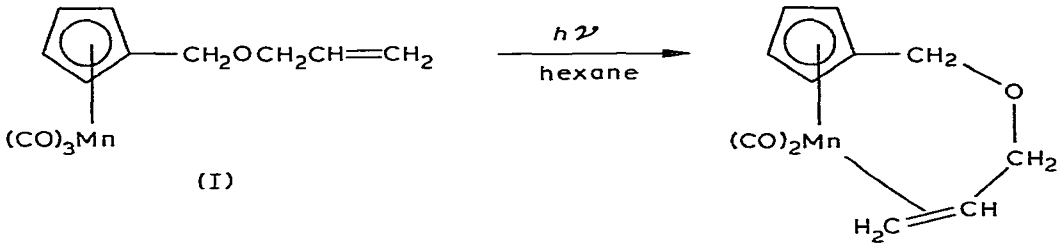
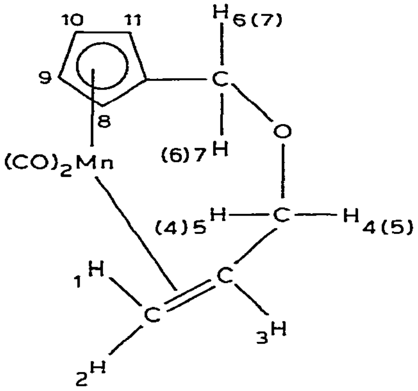
IR, PMR and mass spectra.

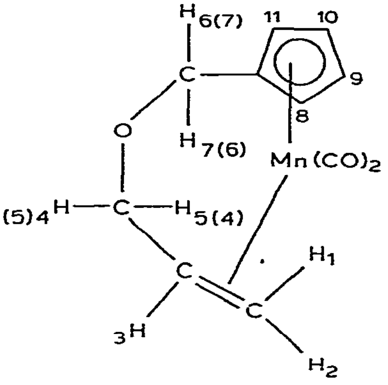


(I) (II)

In the mass-spectrum of complex II there is a molecular ion ($M^{+}246$), which confirms its monomeric structure. The IR spectrum of the initial allyloxymethylcymantrene * (I) [3] contains two absorption bands at 2030 and 1950 cm^{-1} in the valance stretching frequency region of the carbonyl ligands. A decrease in the ν(C≡O) frequencies by a few dozens of cm^{-1} (1980 and 1920 cm^{-1}, respectively) is observed in the IR spectrum on going from the tricarbonyl complex I to the dicarbonyl complex II.



(II′)



(II″)

TABLE 1

DATA ON THE PMR SPECTRUM OF COMPLEX II

Proton	Chemical shift (ppm)	Spin—spin coupling constants J (Hz)
H(1)	2.40	$J(1,2) \leq 1$
H(2)	1.79	$J(2,3) = 8.2$
H(3)	2.94	$J(3,4) = J(3,5) = 2.1$
H(4 or 5)	3.29	$J(4,5) = 14$
H(5 or 4)	4.22	
H(6 or 7)	3.35	$J(6,7) = 12.8$
H(7 or 6)	4.28	
H(8—11)	4.05, 4.15, 4.84, 5.18	

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* Cymantrene is a short name for cyclopentadienyltricarbonylmanganese.

TABLE 2

ANALYTICAL DATA FOR COMPLEXES III—VI

Complex	Yield (%)	M.p. (°C)	Found (%)			Calcd. (%)			Empirical formula
			C	H	Mn	C	H	Mn	
III	70	oil	52.52	3.31	19.76	52.94	3.38	20.22	$C_{12}H_9O_4Mn$
IV	52	oil	57.15	3.86	15.76	57.47	3.86	16.17	$C_{16}H_{13}O_5Mn$
V	51	oil	51.86	3.19	18.57	52.00	3.00	18.33	$C_{13}H_9O_5Mn$
VI	33	75—76	53.78	3.56	23.82	54.10	3.69	22.54	$C_{11}H_9O_3Mn$

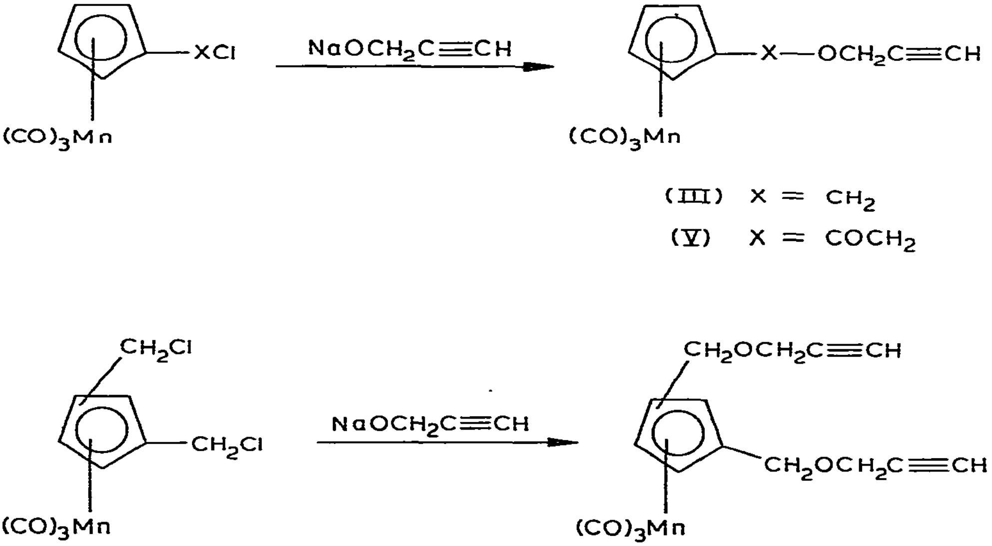
Complex II is a chiral molecule and exists in the form of an enantiomeric pair (II′) and (II″) and therefore the C_5H_5 ring protons as well as bridge CH_2 protons should be diastereotopic. Indeed, the protons mentioned show different chemical shifts in the PMR spectrum (Table 1).

Thus, the use of the three-atom bridge in the case of cyclopentadienylmanganese tricarbonyl led to success. An attempt to obtain a two-bridge chelate on the basis of bis(allyloxymethyl)cymantrene [3] failed. In this case the formation of only one bridge was observed [4].

The starting compounds for the synthesis of one-bridge chelates with acetylene groups were the previously unknown cymantrenylmethylpropargyl ester (III), its propargyloxymethyl derivative (IV) and cymantrenoylmethylpropargyl ester (V) (Tables 2 and 3).

Compounds III and IV were obtained by us from the corresponding chloromethyl derivatives [3], and complex V was obtained from the chloroacetyl derivative of cymantrene [5] (Scheme 1).

SCHEME 1



(III) X = CH_2
(V) X = $COCH_2$

(IV)

TABLE 3

DATA OF THE IR AND PMR SPECTRA FOR COMPOUNDS III–VII

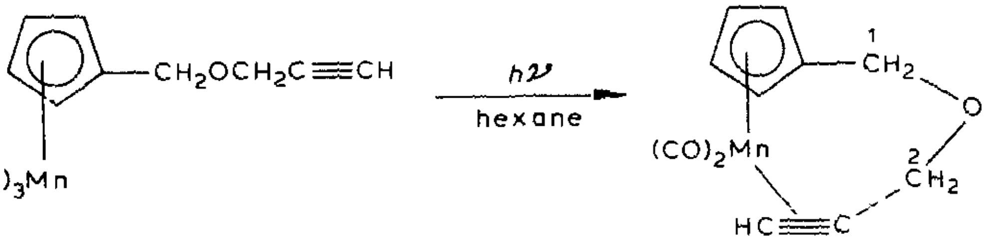
Complex	IR spectra (cm^{-1}) (in film)					PMR spectra (ppm)				
	$C\equiv O$ $\equiv CH$	CH_2	Cp	$C\equiv C$	$C=O$	Cp		$\overset{1}{C}H_2-O-\overset{2}{C}H_2-C\equiv CH$		
						H_α	H_β	$\overset{1}{C}H_2$	$\overset{2}{C}H_2$	CH
III	1930, 3300 2030	2850	3120	2130w	–	4.75 $J(H_\alpha, H_\beta) = 2.0$ Hz	4.81	4.28 $J(CH_2, CH) = 2.5$ Hz	4.28	2.57
IV	1950, 3300 2030	2860	3110	2130m	–	4.73		4.13 $J(CH_2, CH) = 2.50$ Hz	4.13	2.48
V	1950, 3310 2030	2880	3120	2130s	1700					
VI	1880, 3150 1960	2850	3170	1700w	—	4.22 $J(H_\alpha, H_\beta) = 2.2$ Hz	4.53	4.38 $J(CH_2, CH) = 2.7$ Hz	4.69	4.32
VII	1890, 3170 1970	2850	3100	1700m						

TABLE 4

DATA ON THE IR SPECTRA OF COMPOUNDS VIII—X

Compound		ν(C=O) (cm^{-1})	ν(C≡N) (cm^{-1})	ν(C≡O) (cm^{-1})	Solvent
VIIIa	$(CO)_3Mn(C_5H_4)$—$CO(CH_2)_2CN$	1685	2250	1955, 2040	$CHCl_3$
VIIIb	$(CO)_3Mn(C_5H_4)$—$CO(CH_2)_3CN$	1685	2250	1955, 2040	$CHCl_3$
VIIIc	$(CO)_3Mn(C_5H_4)$—$CO(CH_2)_4CN$	1680	2250	1955, 2040	$CHCl_3$
VIIId	$(CO)_3Mn(C_5H_4)$—$CO(CH_2)_6CN$	1685	2250	1955, 1965, 2040	cyclohexane
IXa	$(CO)_3Mn(C_5H_4)$—$(CH_2)_3CN$	—	2250	1935, 2025	$CHCl_3$
IXb	$(CO)_3Mn(C_5H_4)$—$(CH_2)_4CN$	—	2250	1930, 2020	$CHCl_3$
IXc	$(CO)_3Mn(C_5H_4)$—$(CH_2)_5CN$	—	2250	1935, 2025	$CHCl_3$
IXd	$(CO)_3Mn(C_5H_4)$—$(CH_2)_7CN$	—	2250	1945, 2025	$CHCl_3$
Xa	$(CO)_2\underline{Mn(C_5H_4)\text{—}CO(CH_2)_2CN}$	1685	2270	1895, 1960	$CHCl_3$
Xb	$(CO)_2\underline{Mn(C_5H_4)\text{—}CO(CH_2)_3CN}$	1680	—	1880, 1950	$CHCl_3$
Xc	$(CO)_2\underline{Mn(C_5H_4)\text{—}CO(CH_2)_4CN}$	1685	2270	1900, 1960	$CHCl_3$
Xd	$(CO)_2\underline{Mn(C_5H_4)\text{—}CO(CH_2)_6CN}$	1685	2290	1895, 1960	$CHCl_3$
Xe	$(CO)_2\underline{Mn(C_5H_4)\text{—}(CH_2)_5CN}$	—	—	1885, 1935	$CHCl_3$

UV irradiation of III in hexane solution yielded a chelate of type VI:

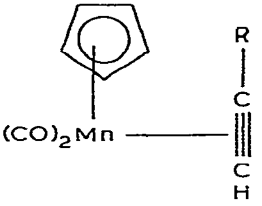


(VI)

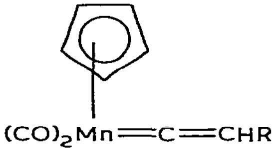
It is known from the literature that if the terminal hydrogen atom is present, the acetylene ligand is capable of forming either the usual complex of type A or the vinylidene complex of type B with cymantrene [6].

The structure of compounds VI obtained by us was established by elemental analysis, mass spectroscopy and IR, ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and

3). The mass spectrum of complex VI revealed the peak of the molecular ion M^+244; subsequent splitting of carbonyl ligands resulted in peaks $[M - CO]^+$ (*m/e* 216) and $[M - 2\ CO]^+$ (*m/e* 188).



(A)



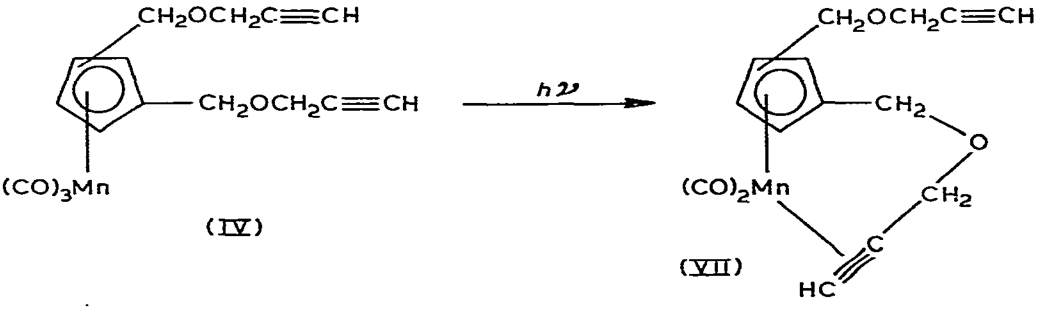
(B)

The IR spectrum of the initial complex III revealed a low intensity absorption band of the $C\equiv C$ bond at 2130 cm^{-1} and an absorption band of C—H valence stretching at the triple bond at 3300 cm^{-1}. In going from tricarbonyl complex III to the dicarbonyl one VI these bands shift to lower frequency regions by 430 and 150 cm^{-1}, respectively, which is typical of acetylene π-complexes of type A [7]. There is also a decrease in the valence stretching frequencies of the carbonyl ligands ($\nu(C\equiv O)$ 1880, 1970 cm^{-1}) as compared to $\nu(C\equiv O)$ in the initial complex III (1930 and 2030 cm^{-1}) (see Table 3). The absorption bands typical of the $C=C$ vibrations of the vinylidene ligand (Type B complexes) [6] are missing in the IR spectrum of VI. The PMR spectrum of VI (Table 3) shows a down-field shift of the ethynyl proton signal as compared to the corresponding signal in the spectrum of the initial complex III ($\Delta\delta$ 1.75 ppm). These data and the data from the IR spectra indicate the participation of the triple bond in the coordination with the Mn atom [7,8].

The acetylene structure of complex VI [8] agrees with the data from the ^{13}C NMR spectra, which reveal three signals of the carbon atoms of the cyclopentadienyl ring at 79.56, 88.52 (C_α, C_β) and 98.01 ppm (C key); two signals of the carbon atoms of two methylene groups at δ = 52.53 and 58.05 ppm; two signals of the carbon atoms of the ethynyl fragment at δ = 64.35 and 75.46 ppm and a singlet signal of the carbon atoms of two carbonyl groups at δ = 232.96 ppm.

It should be noted that the acetylene π-complexes of cymantrene reported in the literature are rather unstable and were in a number of cases characterised only by the IR spectra or as derivatives [6,8—13]. The acetylene complex VI obtained by us is quite stable, which may be due to the chelate effect.

UV irradiation of bis(propargyloxymethyl)cymantrene (IV) in benzene solution did not lead to a bischelate complex. In this case a monochelate complex VII is formed, i.e. as in the case of olefinic analogues [4] the ethynyl group is able to substitute only one CO molecule:

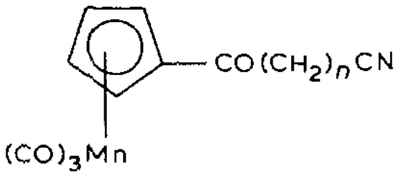


(IV)

(VII)

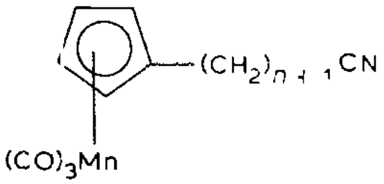
This may be due to the difficulty of substituting the second CO molecule, since in the formation of the one-unit bridge chelate complexes II and VI the CO group is substituted by either vinyl or ethynyl electron-donating groups, which strengthens the bonds of the metal with the remaining CO ligands, this being the result of an increase in the electron density on the metal atom (ν(C≡O) low frequency shift) [14,15]. Irradiation of the cymantrenoylpropargyl ester synthesized by us (V), both in benzene and THF solutions, did not lead to the formation of a chelate complex, which may be due to the length of the bridge, consisting of four atoms.

Nitryls can coordinate with transition metals in a way similar to acetylenes. Taking into consideration the fact that cyclopentadienylmanganese tricarbonyl can readily exchange a carbonyl ligand for a nitril one, α-oxo-ω-cyanalkyl and ω-cyanalkyl derivatives of cymantrene [16] (VIII and IX, respectively) obtained by us, can be regarded as convenient starting compounds to obtain chelate complexes.



(VIII)

$n = 2,3,4,6$



(IX)

$n = 2,3,4,6$

Coordination of the cyano group to the metal can be effected in two ways. σ type C≡N → M, and π-type $\underset{M}{C\equiv N}$, although it should be noted that the second type has so far been effected only in single cases and has been confirmed by X-ray analysis for only two examples [17,18].

Under UV irradiation of α-oxo-ω-cyanalkyl derivatives of cymantrene (VIII, n = 2, 3, 4, 6) in hexane, substitution of the CO ligand is accompanied by intramolecular cyclization with the formation of mono-bridge chelates for which structure X is proposed:

(X) a n = 2
b n = 3
c n = 4
d n = 6

Compounds Xa, Xb and Xd are orange oils, whereas Xc is a crystalline orange red solid. The IR spectra of these compounds (Table 4) reveal bands of the coordinated CN group in the 2270—2290 cm^{-1} region, which are shifted to higher frequency by 20—40 cm^{-1} as compared to the absorption of the free CN group (2250 cm^{-1}). This suggests that the coordination of the nitryl group with the metal is effected according to the σ-type by employing the unpaired electrons on the nitrogen atom [19]. It should be noted that the absorption band of the coordinated CN group in compounds Xb and Xe is missing (see below); however, this absence of ν(CN) in some σ-nitryl complexes has been observed previously [20].

Unfortunately, all compounds X appear to be unstable, and even the IR spectra of samples purified by chromatography revealed weak absorption bands of the free cyano group. Therefore it was possible to determine the molecular weight only for the most stable compound (Xc) (in the mass-spectrum M^+285, by ebullioscopy $M = 300$) which proves its monomeric structure. For complexes Xa, Xb and Xd, whose molecular weights were not determined, a dimeric structure is not excluded.

It should also be noted that the ketonic carbonyl group of all chelate complexes absorbs in the 1685 cm^{-1} region and its absorption is practically indistinguishable from that of the initial compound (VIII). This implies the absence of strain in the chelate complexes, since, if this were not the case, the twist of the ketonic group from the conjugation plane with the cyclopentadienyl ring would markedly influence its absorption.

In the absorption region of the carbonyl ligands these complexes contain two bands at 1885—1900 and 1950—1960 cm^{-1}, with some bands found at 2020—2030 cm^{-1} which belong to the initial non-chelate complexes.

An attempt to obtain chelate complexes by the same method from ω-cyanalkyl derivatives of cymantrene (IX) was a failure. In the case of compounds IX (irrespective of the n value) UV irradiation (6 hours) in THF or hexane even at high dilutions yielded dark-brown solids insoluble in conventional solvents; these may be coordination polymers. Only in the case of 5-cyanopentylcymantrene (IXc) was, besides the brown solid, a small amount of oil (Xe) isolated by chromatography (see Table 4). According to the IR spectra, this oil contained along with the initial compound (IXc) a substance with intense bands in the 1885 and 1935 cm^{-1} regions ($\nu(C\equiv O)$) which are seen in the more stable complex Xc where the cyano group takes part in coordination to the metal. However, the extreme instability of this compound made its more detailed study impossible.

Thus, the presence of the ketonic group near the cyclopentadienyl ring facilitates the formation of chelate nitryl complexes of manganese since the withdrawal of electron density off the metal strengthens its ability to coordinate with the CN group by employing the unpaired electron of the nitrogen atom.

In conclusion it should be noted that, like arenecarbonyl complexes of chromium, mono-bridge chelate cyclopentadienylcarbonyl complexes of manganese are formed with tris-atomic bridges. However, the possibility of the formation of chelate complexes with longer bridges may be influenced by the nature of the coordinated group. For example, the utilization of the cyano group as a coordinating one results in the formation of a five-atom bridge chelate which is more stable than the three-atom-bridge one.

Experimental

The IR spectra of the reported compounds were measured on a UR-20 spectrometer. The PMR spectra were obtained in deuterochloroform with TMS as an internal standard on a Perkin-Elmer R-12 spectrometer (60 MHz). The ^{13}C NMR spectra were recorded in CH_2Cl_2 on a Bruker HX-90 (22.635 MHz) spectrometer. The chemical shifts are given on the δ-scale with respect to TMS. The mass spectra were recorded on an MX-1303 spectrometer.

All the procedures for the synthesis of the reported organometallic compounds were performed in an argon atmosphere with the use of absolute solvents. Photochemical reactions were performed under irradiation with a PRK-4 mercury lamp (200 W) in a quartz flask with an inlet for internal cooling.

For chromatography (TLC) silica gel L100/160 was used.

Chelate complex II

A solution of I (0.2 g) in 200 ml hexane was irradiated for 5 hours with argon bubbling at 10—15°C. The bright-yellow solution was filtered and the solvent was removed under vacuo. The residue was chromatographed on silica. Eluent CH_2Cl_2/ether, 1/4. The crystalline yellow substance obtained was recrystallized from hexane by freezing out at —70°C. Melting point is 110°C. Yield 53% (0.9 g). Found: C, 53.68; H, 4.54; Mn, 21.61. $C_{11}H_{11}O_3Mn$ calcd.: C, 53.65; H, 4.47; Mn, 22.35%. IR spectrum: $\nu(C{\equiv}O)$ 1920, 1980 cm^{-1}.

Synthesis of III

1.5 g of Na was dissolved in 50 ml of propargyl alcohol; upon cooling and stirring 15 g of chloromethylcymantrene [3] was added dropwise to 15 ml of propargyl alcohol. The mixture was stirred at 50°C for 4 hours; then upon cooling it was decomposed with ice-cold water and extracted with ether. The extracts were dried over Na_2SO_4 and the solvent was removed under vacuo. The remaining dark-coloured oil was chromatographed on silica using acetone/ ether (1/3) as eluent. 11.3 g of III, a light yellow coloured oil was isolated (70%, as calculated from the initial chloromethylcymantrene) (Tables 2 and 3).

Synthesis of IV

Compound IV was obtained similarly to III from 18 g bis(chloromethyl)-cymantrene [3]. 8.84 g of IV as a yellow-coloured oil was isolated by TLC on silica (with acetone/ether 1/3 as eluent) (52% as calculated for the initial bis-(chloromethyl)cymantrene) (Tables 2 and 3).

Synthesis of V

1.5 g of Na was dissolved in 50 ml of propargyl alcohol and upon cooling and stirring 16.8 g of chloroacetylcymantrene [5] was added dropwise to 15 ml of propargyl alcohol. The mixture was stirred at 50°C for 8 hours and stored overnight. Then it was decomposed with ice-cold water and extracted with ether. The ether extracts were dried over Na_2SO_4 and the solvent was removed under vacuo. The residue was chromatographed on silica using methylene chloride/ petroleum ether (1/2) as eluent to give 9.18 g of V as an orange-coloured oil (51% as calculated for the initial chloroacetylcymantrene) (Tables 2 and 3).

Chelate complex VI

A solution of III (0.3 g) in 250 ml of hexane was irradiated for 5 hours with argon bubbling at 10—15°C. Upon removal of the solvent the orange needles were filtered from the initial oil (III). The residue was recrystallized from pentane by freezing out at —70°C to give 0.09 g of VI (33%) as an orange crystalline solid (see Tables 1 and 2).

Chelate complex VII

A solution of VI (0.3 g) in 250 ml of benzene was irradiated for 6 hours. After removal of the solvent under vacuo the residue was recrystallized from pentane by freezing out at —70°C to give 1.5 g of yellow-coloured oil which according to IR spectral data (see Table 3) contains a mixture of equal quantities of the initial compound IV and the chelate dicarbonyl complex VII. Attempts to isolate pure VII by chromatography were a failure because of decomposition of the compound.

Irradiation of cymantrenoylmethyl propargyl ether V

A solution of 0.3 g in 250 ml of benzene (or THF) was irradiated for 5—8 hours. The reaction was followed by IR spectroscopy. After 5 hours of irradiation the solution contained only a small amount of the initial V. After a prolonged irradiation (8 hours) V had completely decomposed.

Chelate complexes (Xa—e)

A 0.003 mol solution of α-oxo-ω-cyanalkylcymantrene (VIII) or ω-cyanalkylcymantrene (IX) [16] in 250 ml of hexane (or THF) was UV irradiated for 6 hours with argon bubbling. The solution was filtered and the solvent was removed under vacuo. The residue was purified by TLC on silica using acetone/hexane (1/3) as eluent (see Table 4). A stable chelate complex (Xc) was obtained in 30% yield (0.26 g) in the form of an orange-red crystalline solid, with a melting point of 45—46°C. Found: C, 55.97; H, 4.24; N, 5.03; Mn, 19.38. $C_{13}H_{12}O_3NMn$ calcd.: C, 55.73; H, 4.21; Mn, 19.29%.

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