Journal of Organometallic Chemistry, 137 (1977) 55—67

VINYLIDENE COMPLEXES OF TRANSITION METALS

II *. A NEW METHOD OF SYNTHESIS OF VINYLIDENE COMPLEXES. CYMANTRENE DERIVATIVES CONTAINING PHENYLVINYLIDENE LIGANDS

A.B. ANTONOVA *, N.E. KOLOBOVA, P.V. PETROVSKY, B.V. LOKSHIN and N.S. OBEZYUK

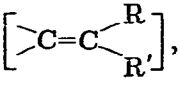
Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov Str. 28, Moscow, B-312 (U.S.S.R.)

(Received March 24th, 1977)

Summary

A rearrangement of transition metal acetylenic π-complexes into compounds with vinylidene n-ligands has been established. Compounds CpMn(C=CHPh)-$(CO)_2$ and $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ with terminal and bridging phenylvinylidene (benzylidenecarbene) ligands respectively were obtained from the π-complexes $CpMn(CO)_2(PhC{\equiv}CR)$ where R = H, Ph_3Ge or Ph_3Sn. Reactions leading to conversion of the terminal C=CHPh group into a bridging ligand and vice versa were studied. Under the action of L = Ph_3P, $(EtO)_3P$ or $(PhO)_3P$, substitution of CO groups in vinylidene complexes takes place and compounds CpMn(C=CHPh)-(CO)L are formed. IR, ^1H and ^{13}C NMR spectra of the novel complexes are discussed. The data obtained indicate an electron-withdrawing property of the C=CHPh ligand and stronger bonding of this ligand to the metal as compared with a CO group.

Introduction

Vinylidenes (methylenecarbenes),  $\left[\begin{smallmatrix}\\ \end{smallmatrix}\!>C=C<^{R}_{R'}\right]$, which are unstable in the free state, form stable complexes with transition metals. As carbonyl and isonitrile groups they are two-electron donors and may act as terminal and bridging ligands.

There have previously been reported only complexes of iron, molybdenum and tungsten with diphenylvinylidene [2] and dicyanovinylidene [3,4], obtained

---

* For Part I, see ref. [1].

respectively by the reactions of diphenylketene or dicyanodichloroethylene:

$$Ph_2C{=}C{=}O + Fe(CO)_5 \xrightarrow{h\nu} Fe_2(\mu\text{—}C{=}CPh_2)(CO)_8$$

$$(NC)_2C{=}CCl_2 + 2\ NaFe(CO)_2Cp \rightarrow Cp_2Fe_2[\mu\text{—}C{=}C(CN)_2](CO)_3$$

$$(NC)_2C{=}CCl_2 + NaM(CO)_3Cp \rightarrow (NC)_2C{=}C(Cl)M(CO)_3Cp \xrightarrow[-3\,CO]{+2\,L}$$

$$CpM[C{=}C(CN)_2](L_2)(Cl)$$

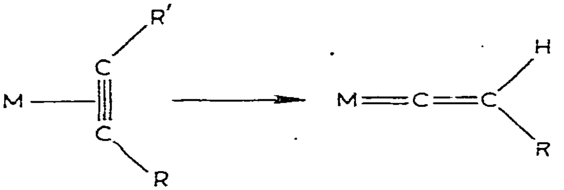
($M = Mo, W$; $L = Ph_3P, (RO)_3P, Ph_3As$, etc.)

In preliminary communications [1,5] we have described the formation of complexes $CpMn(C{=}CHPh)(CO)_2$ and $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ with a new phenylvinylidene ligand in the reaction of $CpMn(CO)_2(THF)$ with $PhC{\equiv}CH$ and determined their structure by X-ray study. In $CpMn(C{=}CHPh)(CO)_2$ the vinylidene carbon—metal bond has a double order and the practically linear $Mn{=}C{=}C$ fragment represents a metalallene system. Complex $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ contains a bridging vinylidene ligand supporting the Mn—Mn bond.

In the present paper we discuss in more detailed the preparation of cymantrene derivatives containing phenylvinylidene ligands, the properties of $CpMn(C{=}CHPh)(CO)_2$ and $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ and the reactions of these compounds with R_3P molecules where R = Ph, OEt or OPh.

Results and discussion

We first discovered the rearrangement of the π-acetylene system into a metalallene fragment while studying cymantrene derivatives containing π-acetylene ligands.



(1)

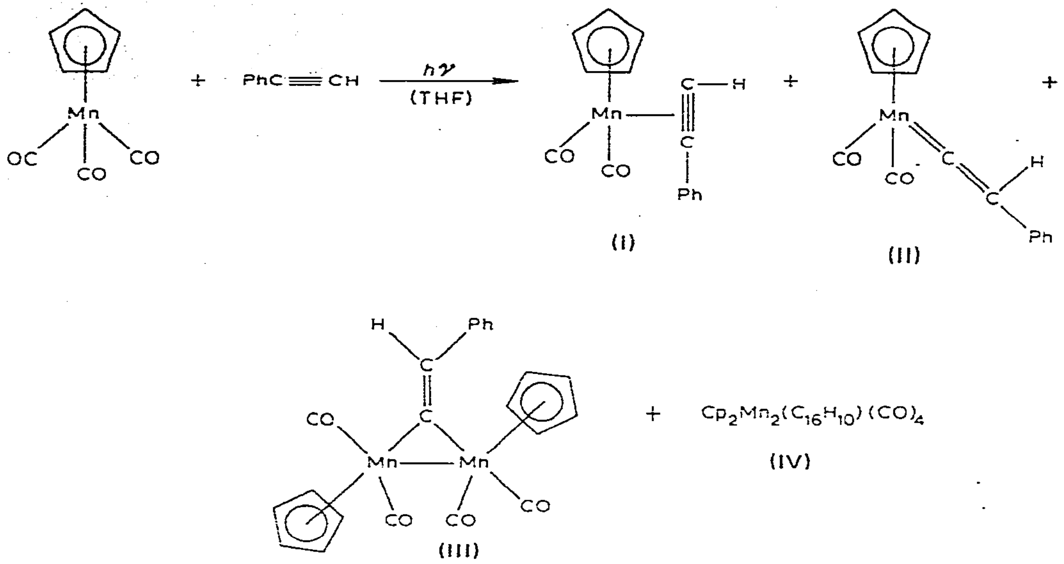
$M = CpMn(CO)_2$; R = Ph; R' = H, Ph_3Ge, Ph_3Sn

Formation of unstable $CpMn(CO)_2(HC{\equiv}CPh)$ (I) during the photochemical reaction of cymantrene with phenylacetylene in cyclohexane was reported in [6]. We studied the photochemical reaction of $CpMn(CO)_3$ with $PhC{\equiv}CH$ in THF and additionally obtained three novel stable manganese compounds that are formed according to Scheme 1.

The yields are relatively small and depend on reaction conditions and treatment of the reaction mixture. The amount of complex IV increases with the temperature and reaction period, whereas the ratio of compounds I and II mainly depends on the basicity of the aluminium oxide used for chromatography of the reaction mixture.

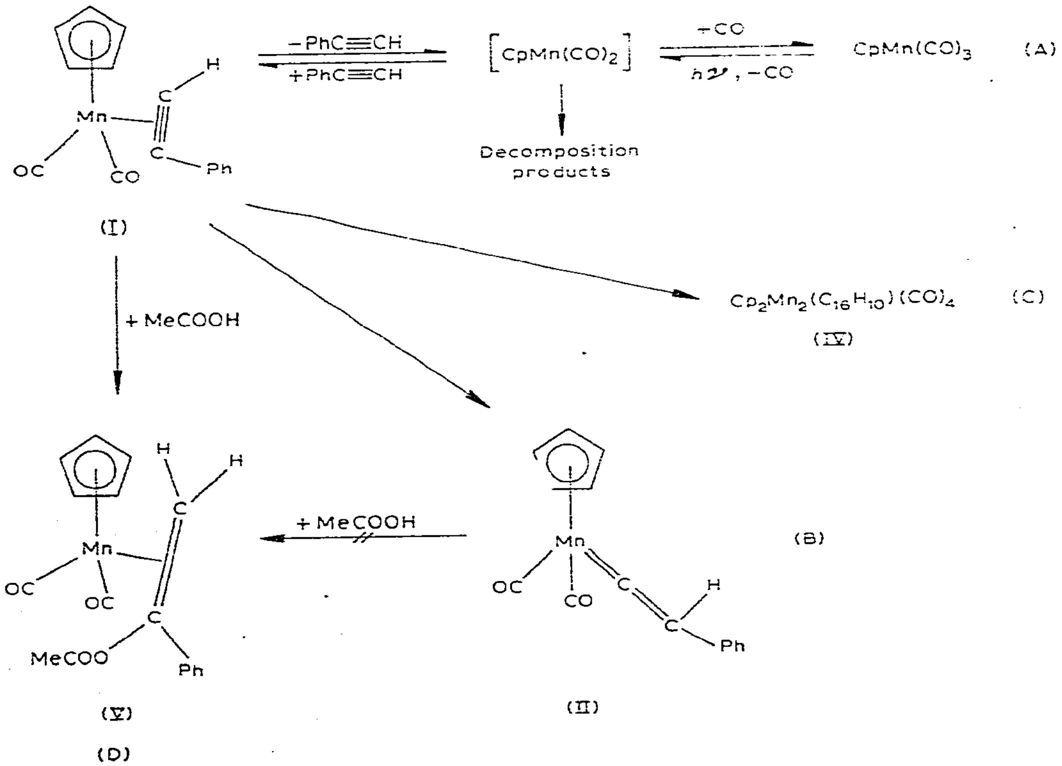
Irrespective of the reaction and separation conditions, the reaction mixture contains about 70% of the initial cymantrene. This apparently is due to decomposition of I under normal conditions with formation of coordination- and elec-

SCHEME 1



tron-deficient [$CpMn(CO)_2$] species and its reaction with CO, present in the reaction mixture (Scheme 2, reaction A). Similar formation of cymantrene with a considerable yield as a result of π-ligand elimination was observed for CpMn-$(CO)_2$(*cis*-cyclooctene) [7].

SCHEME 2



Complex II with a phenylvinylidene *n*-donor ligand is formed by rearrangement of the phenylacetylene π-complex I * (Scheme 2, reaction B) that proceeds mainly on Al_2O_3 at pH 9—10. It was established from IR spectra that in a neutral medium reactions A and B proceed simultaneously, rearrangement B however being much slower than the decomposition of I.

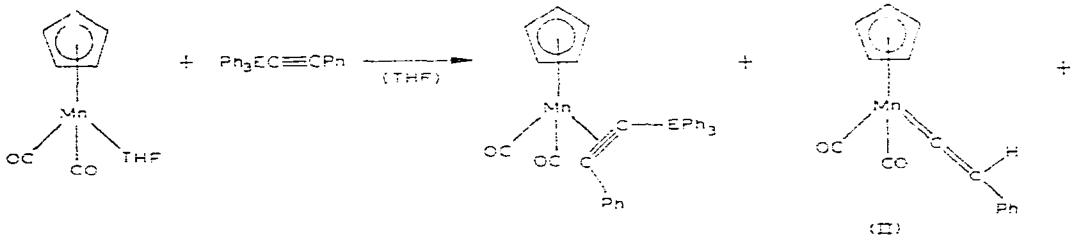
Complex III with a bridging C=CHPh ligand is a derivative of II but is not formed directly from I.

Binuclear compound IV can be obtained in good yield by treating I with a water/alcohol/alkaline mixture (Scheme 2, reaction C).

It is of interest that treatment of the irradiated $CpMn(CO)_3$ and PhC≡CH reaction mixture with acetic acid unexpectedly yielded complex V with a new olefine π-ligand (Scheme 2, reaction D). This compound is not formed by treating II with CH_3COOH. Presumably, V is formed from I, although addition of acetic acid to π-bonded acetylene without elimination of the ligand has not been previously observed, so far as is known [8].

The reaction of ethylcymantrene with phenylacetylene proceeds similar to Scheme 1. However, $EtC_5H_4Mn(CO)_2(HC{\equiv}CPh)$ (VI) and its vinylidene isomer $EtC_5H_4Mn(C{=}CHPh)(CO)_2$ (VII) are less stable than I and II respectively and, as yet, have been characterized only by their IR spectra.

We have shown previously [9] that in the reactions of $CpMn(CO)_2(THF)$ with $Ph_3EC{\equiv}CPh$ where E is an element of Group IVB, compounds (II) and (IV), along with acetylene complexes, are formed according to eq. 2.



(II)

(2)

(E = Si, Ge, Sn)

$Cp_2Mn_2(C_{16}H_{10})(CO)_4$

(IV)

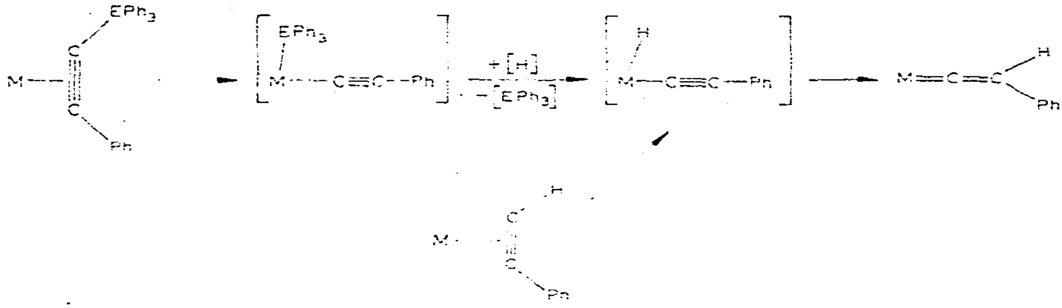
The stability of $CpMn(CO)_2(Ph_3EC{\equiv}CPh)$ π-complexes sharply decreases in the order E = Si > Ge >> Sn, while the yields of II in the reactions of the corresponding acetylenes with $CpMn(CO)_2$ (THF) increase in the reverse order. For E = Si complex II was not obtained, and for E = Ge and Sn the yields of II are 1% and 15% respectively.

The π-acetylenemetalallene rearrangement may proceed through intermediate formation of σ-phenylethynyl complexes, as in reactions of oxidative addition of PhC≡CH or $PhC{\equiv}CSnR_3$ to complexes of Group VIII metals [10], and with

---

[*] I was identified by the IR spectrum in the 2200—1600 cm^{-1} region, that exhibits a ν(C≡C) band at 1840 cm^{-1} and ν(CO) bands at 1981 and 1921 cm^{-1} in cyclohexane which are close to the ν(CO) bands of $CpMn(CO)_2(PhC{\equiv}CPh)$ at 1983 and 1922 cm^{-1}. We were unable to obtain the IR spectrum of pure I as samples of I always contain admixtures of II and $CpMn(CO)_3$.

subsequent addition of a hydrogen atom to the β-acetylenide carbon (eq. 3).



(3)

($M = CpMn(CO)_2$; E = Ge, Sn)

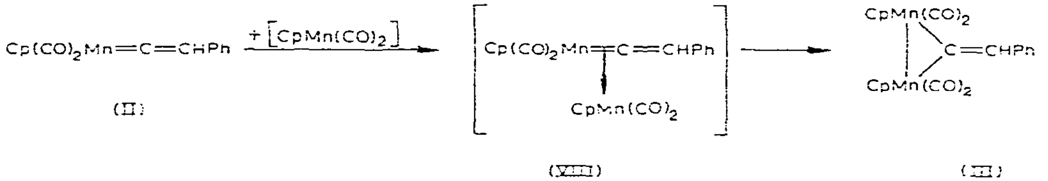
Hydrogen required for the formation of $CpMn(C{=}CHPh)(CO)_2$ from the $CpMn(CO)_2(Ph_3EC{\equiv}CPh)$ complexes is evidently provided by the solvent.

$Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ (III) is formed from $CpMn(C{=}CHPh)(CO)_2$ (II) both in solution and in the solid state. In solution of II at 20°C, after several hours admixtures of III and cymantrene are revealed by IR spectroscopy and TLG. Increase of temperature accelerates formation of III, and IV appears in the solution. The yields of III, however, are very small during decomposition of II due to slow abstraction of the C=CHPh ligand from II and to low concentrations of the intermediate $[CpMn(CO)_2]$ species in the reaction mixture.

Complex III can be obtained in good yield by the reaction

$$\underset{\text{(II)}}{CpMn(C{=}CHPh)(CO)_2} + CpMn(CO)_2(THF) \xrightarrow[20^\circ C,\ 5\ h]{(THF)} \underset{\text{(III)}}{Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO_4)}$$

Conversion of the terminal C=CHPh into a bridging ligand probably occurs via formation of the π-complex VIII (eq. 4).



(4)

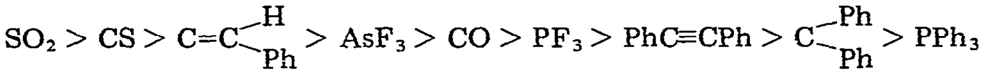
The suggested coordination of the Mn=C double bond with electron-deficient organometallic species is confirmed by synthesis of $[Cp(CO)_2MnC(CO)CHPh]\text{-}Fe(CO)_3$, in which the whole Mn=C=C fragment is incorporated into the π-ligand bonded to the iron atom [11].

Physico-chemical characteristics and analyses of the compounds obtained are given in Table 1. II readily dissolves in all organic solvents, and sublimates in vacuo (with partial decomposition). III hardly dissolves in aliphatic solvents, and dissolves readily in polar and aromatic solvents; it slowly sublimates at 120—140°C/1 × 10^{-2} mmHg. Binuclear complex IV is only slightly soluble in benzene, THF, and CH_2Cl_2, insoluble in CS_2, acetone, alcohols, etc. and is practically nonvolatile. III and IV gradually decompose in solution; in the crystalline state under normal conditions they are, unlike II, stable for a long period.

The structures of the compounds obtained were confirmed by IR and NMR spectroscopy, and interesting data about the novel phenylvinylidene ligand were obtained. IR and PMR data are also given in Table 1.

The IR spectra of $\mathrm{CpMn(C{=}CHPh)(CO)_2}$ (II) in solution reveal two absorbtion bands of CO stretching vibrations (A′ and A″) of equal intensity in accordance with local symmetry C_s of the $\mathrm{CpMn(CO)_2}$ group. On the basis of the IR spectrum of II and data published on other $\mathrm{CpMn(CO)_2L}$ cymantrene derivatives we were able to estimate the electronic effect of the new C=CHPh ligand. Table 2 presents ν(CO) frequencies of several $\mathrm{CpMn(CO)_2}$ L complexes and the force constants of the CO bonds calculated from these frequencies. Interaction of the CO modes with other molecular vibrations were neglected in the calculations.

On the basis of the K_{CO} values presented in Table 2 the ligands may be arranged in decreasing order of electron-withdrawing properties as follows:



$$\mathrm{SO_2 > CS > C{=}C}\begin{smallmatrix}\mathrm{H}\\ \mathrm{Ph}\end{smallmatrix} > \mathrm{AsF_3 > CO > PF_3 > PhC{\equiv}CPh > C}\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix} > \mathrm{PPh_3}$$

Thus, phenylvinylidene is among the ligands with the highest π-acceptor capacity.

X-ray study of $\mathrm{Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4}$ (III) established that ligands are *trans*-arranged in $\mathrm{CpMn(CO)_2}$ fragments in relation to the Mn—Mn bond [1]. According to the local symmetry C_{2h} of the $\mathrm{[CpMn(CO)_2]_2}$ fragment, with *trans*-arrangement of the ligands only two CO stretchings should be present in the IR spectrum corresponding to out-of-phase vibrations of the two $\mathrm{M(CO)_2}$ moieties (A_u and B_u). In the presence of a bridging C=CHPh ligand the local symmetry is lowered and the appearance of one or two more ν(CO) bands may be expected. Since they correspond to A_g and B_g vibrations forbidden for C_{2h} symmetry, their intensities should by considerably less than those of the A_u and B_u bands. Indeed, two strong bands at 1953 and 1928 $\mathrm{cm^{-1}}$ and a weak band at 1983 $\mathrm{cm^{-1}}$ were observed in the IR spectrum of III in cyclohexane, and this also confirms the retention of the *trans*-structure in solution.

Identification of ν(C=C) bands of phenylvinylidene is complicated by the additional presence in the 1650—1500 $\mathrm{cm^{-1}}$ region of phenyl absorption bands.

We were unable to record Raman spectra of II and III as they decompose in the laser beam. The Raman spectrum of $\mathrm{CpMn(C{=}CHPh)(CO)[P(OPh)_3]}$ (XI) shows a strong line at 1590 $\mathrm{cm^{-1}}$ that may be tentatively assigned to the vibrations of the C=C vinylidene bond. In the IR spectrum of $\mathrm{CpMn(C{=}CHPh)(CO)_2}$ (II) three intensive bands were observed in the same region at 1640, 1620 and 1592 $\mathrm{cm^{-1}}$, one of which apparently belongs to C=C vibrations of the vinylidene ligand while the others correspond to vibrations of the phenyl ring. The intensive band at 1550 $\mathrm{cm^{-1}}$ in the IR spectrum of III we assigned to C=C vibration.

The structure of II and III was also confirmed by ^{13}C NMR spectroscopy (Table 3). In the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of III two signals of Cp-ligand carbons and four carbonyl signals were observed, and in the ^{1}H NMR spectrum, two signals of cyclopentadienyl protons. This indicates asymmetrical arrangement of Cp and CO groups in relation to the C=CHPh ligand both in crystal form and in solution. The signal of the C^1-atom of C=CHPh is sharply shifted

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE NOVEL CYMANTRENE DERIVATIVES

Formula	Colour	M.p. (°C)	Analyses found (calcd.) (%)				Mol. wt.	IR spectra[c] ν(CO)	PMR[e] spectra δ (ppm)		
			C	H	Mn	P			C_5H_5	=CH	C_6H_5
$CpMn(C{=}CHPh)(CO)_2$ (II)	dark red	64–65	64.08 (64.76)	3.95 (3.98)	19.83 (19.75)		278[a,b]	2009s, 1955s	5.27	6.91	7.00– 7.40
$Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ (III)	violet	144	58.15 (58.17)	3.71 (3.55)	23.76 (24.18)		454[a,b]	1983w, 1953s, 1928s	4.72 4.70	8.46	7.00– 8.30
$Cp_2Mn_2(C_{16}H_{10})(CO_4)$ (IV)	light red	207 (dec. without melt.)	64.91 (64.99)	3.83 (3.64)	19.85 (19.83)		554[a]	2015 (sh)[d], 1998m, 1944s			
$CpMn(CO)_2[MeCO_2(Ph)C{=}CH_2]$ (V)	yellow	80–82	60.84 (60.37)	4.57 (4.47)	16.14 (16.25)		338[b]	1984s, 1927s			
$EtC_5H_4Mn(C{=}CHPh)(CO)_2$ (VII)	red	oil						2004s, 1943s			
$CpMn(C{=}CHPh)(CO)PPh_3$ (IX)	dark orange	175	74.78 (74.99)	5.40 (5.12)	10.52 (10.72)	5.93 (6.04)	512[a]	1920	4.69	7.04	7.00– 7.60
$CpMn(C{=}CHPh)(CO)P(OEt)_3$ (X)	red	oil						1914			
$CpMn(C{=}CHPh)(CO)P(OPh)_3$ (XI)	orange-red	114–115	68.71 (68.57)	4.71 (4.68)	9.80 (9.80)	5.53 (5.52)	560[a]	1946	4.32	6.98	7.00– 7.50

[a] Values were determined from mass spectra (30 eV) and correspond to calculated values. [b] Values were determined from X-ray diffraction data. [c] Cyclohexane solution. [d] CH_2Cl_2 solutions. [e] CS_2 solutions.

TABLE 2

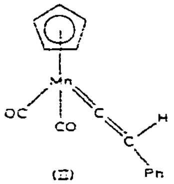
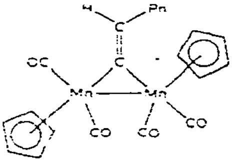
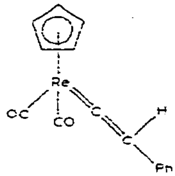
STRETCHING FREQUENCIES AND FORCE CONSTANTS OF CO GROUPS IN $CpMn(CO)_2L$ COMPLEXES

Ligand L	ν(CO) (cm^{-1}) (in cyclohexane)	Ref.	K_{CO} (mdn/Å)
SO_2	2028, 1969 [a]	12	16.15
CS	2012, 1962 [b]	7	15.96
$\mathrm{C{=}C}<^{\mathrm{H}}_{\mathrm{Ph}}$	2009, 1955	[c]	15.88
AsF_3	2006, 1953	13	15.84
CO	2034, 1949	14	15.81
PF_3	1996, 1938	13	15.64
PhC≡CPh	1983, 1929	[c]	15.41
$\mathrm{C}<^{\mathrm{Ph}}_{\mathrm{Ph}}$	1977, 1919 [b]	15	15.34
PPh_3	1946, 1880	14	14.80

[a] Benzene solution. [b] Hexane solution. [c] This work.

TABLE 3

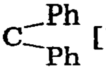
^{13}C NMR DATA [a] FOR PHENYLVINYLIDENE DERIVATIVES OF CYMANTRENE AND CpRe(C=CHPh)$(CO)_2$ [b]

Complex	C_5H_5	CO	$C^1{=}C^2<^{C_6H_5}_{H}$					
			C^1	C^2	C_6H_5			
					C_{key}	C_{ortho} and C_{meta}		C_{para}
 (II)	88.18 (179.4)	226.70	379.54	123.54	133.4	128.84 (158.7)	124.39 (159.7)	125.30 (159.9)
 (III)	88.98 (179.4) 88.65 (179.4)	235.53 234.07 232.41 229.16	284.16	125.22 (150.4)	140.4	128.48 (159.0)	126.08 (159.0)	147.00 (159.4)
	90.37 (180.7)	198.55	329.49	119.49 (155.6)	128.66	125.53 (160.0)	124.88 (158.7)	129.52 (158.7)

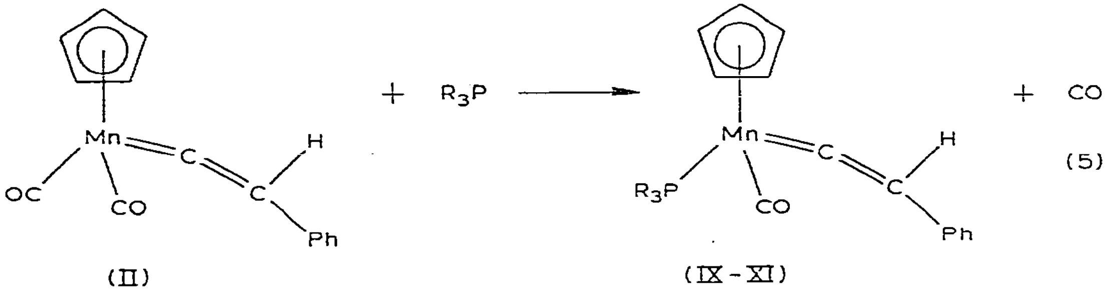
[a] ^{13}C chemical shift (δ(ppm)) downfield from internal TMS; in parantheses, the $J(^{13}C{-}^1H)$ coupling constants (Hz). [b] Ref. [16].

downfield in II and III thus providing reliable identification. In spectra recorded without ^{13}C—^{1}H spin decoupling the C^2 signal of vinylidene for both complexes is a doublet that does not show any widening due to long-range spin—spin interaction and, therefore, straightforward assignment of this signal is also possible.

NMR data for CpRe(C=CHPh)$(CO)_2$, an analog of II, are given for comparison. The signal of the Cp-ring carbons is shifted downfield by ~2 ppm in the case of the Re-complex as compared with II, whereas the CO and C^1 signals are strongly shifted upfield by ~28 and 50 ppm respectively.

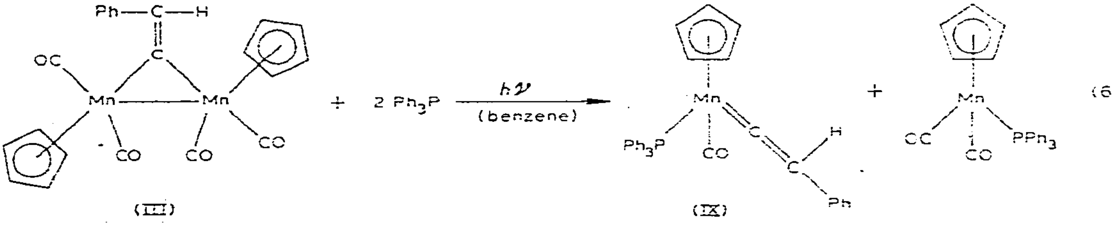
It was of interest to determine whether the reaction of phenylvinylidene derivatives of cymantrene with R_3P molecules proceeds with replacement of the C=CHPh or the CO group. It is known that in complexes $CpMn(CO)_2L$ such hydrocarbon ligands (L) as carbene  $C{\begin{smallmatrix}Ph\\Ph\end{smallmatrix}}$ [15], π-olefines [17] and π-acetylenes including PhC≡CH [6] are replaced by triphenylphosphine.

We established previously [18] that the reaction of II with R_3P (R = Ph, EtO, PhO) without UV irradiation proceeds in unusually mild conditions (pentane, 20°C, 5 h) with substitution of one of the carbonyl groups (eq. 5). This is explained by the effect of the electron-withdrawing C=CHPh ligand. UV irradiation noticeably accelerates the reaction (5°C, 1 h).



(IX : R = Ph; X: R = OEt ; XI : R = OPh)

Conversion of bridging vinylidene into a terminal ligand was first observed in the interaction of III with Ph_3P (eq. 6). This reaction proceeds only under UV irradiation and much more slowly (20°C, 5 h) than formation of IX from II in similar conditions. Presumably, in the first (slow) stage dissociation of the Mn—Mn bond and one of the μ-C—Mn bonds takes place with formation of CpMn(C=CHPh)$(CO)_2$ (II) and $[CpMn(CO)_2]$ which then rapidly interact with Ph_3P.



Formation of IX—XI in the reactions of phenylvinylidene compounds II and III with R_3P confirms the conclusion made from analysis of the mass spectra of II, III and IX that the Mn atom is more strongly bonded with the C=CHPh ligand than with CO. Elimination of C=ChPh in all cases occurs only from completely decarbonylated ions, $[CpMn(C{=}CHPh)]^+$, $[Cp_2Mn_2(C{=}CHPh)]^+$ and $[CpMn(C{=}CHPh)(PPh_3)]^+$ respectively.

Experimental

Argon-saturated dry solvents were used. All operations were carried out under argon. Photochemical reactions were run in a quartz apparatus equipped with a cooling jacket using a PRK-4 mercury lamp (200 W).

For column chromatography aluminum oxide, Brockmann II (Reanal, Hungary) was used. "Silufol" (Kavalier, Chechoslovakia) plates were used for TLC.

IR spectra were measured using a UR-20 (Zeiss) instrument. Raman spectra were obtained on a PHO Coderg spectrometer with He/Ne-laser excitation. Mass spectra were obtained on a MX 1303 instrument with a system of direct injection of samples into the ion source at an ionization chamber temperature of 130°C, and the energy of the electrons was 30 eV.

^1H NMR spectra in CS_2 solution were recorded with a Perkin-Elmer R-12 spectrometer (60 MHz), and ^{13}C NMR spectra in CH_2Cl_2 using a Brucker HX-90 spectrometer (22.635 MHz).

1. *Reaction of $CpMn(CO)_3$ with $PhC{\equiv}CH$*

(a) A mixture of 1.63 g (0.008 mol) of $CpMn(CO)_3$, 0.93 g (0.009 mol) of PhC_2H and 50 ml of THF was irradiated at 5°C for 6 h while bubbling through argon and stirring. The solvent was then removed at reduced pressure and 80 ml of petroleum ether (b.p. 35—40°C) was added to the dark red oil obtained. A light red precipitate was formed that was separated from the extract and recrystallized from CH_2Cl_2, to yield 0.14 g (3% with respect to cymantrene) of light red fine needles of IV that decomposes at 207°C without melting.

The orange extract was concentrated to 20 ml and chromatographed on a Al_2O_3 column (pH 9—10). Petroleum ether eluted a yellow band (1) and then a red band (2). A mixture of ether and petroleum ether (1 : 100) brought down a violet band (3). Fraction (1) yielded 0.99 g (61%) of $CpMn(CO)_3$. After removing the solvent from fraction (2) recrystallization of the solid residue from n-pentane afforded 0.27 g (10%) of II as dark red crystals, m.p. 64—65°C. Fraction (3) rendered, after evaporation and crystallization from an n-hexane/ether mixture (1 : 1) 0.07 g (2%) of violet crystalline III, m.p. 144°C.

(b) The orange extract obtained as described in *1.a* was chromatographed on neutral Al_2O_3. Petroleum ether (b.p. 35—40°C) eluted a yellow band that yielded 1.05 g (65%) of $CpMn(CO)_3$ and then an orange band that gave 0.31 g of an orange oil the IR spectrum of which (cyclohexane solution) exhibited six $\nu(CO)$ bands: 2034, 1949 ($CpMn(CO)_3$), 2009, 1955 (II), 1981, 1921 cm^{-1} ($CpMn(CO)_2(HC{\equiv}CPh)$ (I)). On the chromatogram of the orange oil ("Silufol" plate) three spots with close R_f values were observed: yellow (cymantrene), red (II) and orange (I).

(c) 0.31 g of the orange oil obtained in *1.b* were placed in a Al_2O_3 column (pH 9—10). The orange band during elution with petroleum ether gradually turned bright red. 0.02 g of $CpMn(CO)_3$, 0.19 g of red crystalline II, and traces of violet III, identified by TLC and IR, were obtained.

2. *Preparation of $Cp_2Mn_2(C_{16}H_{10})(CO)_4$ (IV)*

1 ml of 0.1% KOH solution in H_2O/EtOH mixture (1 : 10) was added at 20°C to 0.1 g of the orange oil (an mixture of $CpMn(CO)_3$, I and II) obtained in *1.b* dissolved in 20 ml of EtOH. After stirring, a light red precipitate was formed that was separated from the brown solution. Traces of $CpMn(CO)_3$ and of violet III were established in the solution by TLC. The residue was washed with 0.1% aqueous solution of acetic acid, then with alcohol, and dried to yield 0.04 g (40%) of light red fine crystalline IV, identified by the IR spectrum.

3. *Preparation of $CpMn(CO)_2[MeCO_2(Ph)C{=}CH_2]$ (V)*

After irradiation of a mixture of 1.63 g (0.008 mol) of $CpMn(CO)_3$, 0.93 g (0.009 mol) of $PhC{\equiv}CH$ and 50 ml of THF for 6 h at 5°C and evacuating the solvent under vacuum a dark red oil was obtained. To the solution of oil in 30 ml of ether a solution of 0.6 g (0.01 mol) of CH_3COOH in 20 ml of ether was added at 5°C. The mixture was stirred for 10 min, then evaporated and 50 ml of petroleum ether (b.p. 35—40°C) was added to the dark red oil formed. The extract was filtered and placed in a Al_2O_3 column and chromatographed as described in *1.a.* 0.59 g (36%) of $CpMn(CO)_3$, 0.04 g (1.7%) of II and 0.05 g (1.7%) of III were obtained. A bright yellow band was then eluted with an ether/petroleum ether mixture (1 : 1). Evacuation of the solvent, and recrystallization from n-hexane/ether mixture (1 : 1) yielded 0.14 g (5.2%) of V as yellow crystals, m.p. 80—82°C. IR spectrum (KBr pellets) (cm^{-1}): $\nu(C{\equiv}O)$ 1970, 1910; $\nu(C{=}O)$ 1743; $\delta(CH_3)$ 1440, 1361; $\nu({=}C{-}O{-}C)$ 1236 and 1180.

4. *$CpMn(C{=}CHPh)(CO)_2$ (II) conversion in a neutral medium*

(*a*) 50 ml of petroleum ether (b.p. 35—40°C) were added to 0.72 g of crystalline II stored for 3 months at +5°C, and after filtration 0.07 g of a pale brown insoluble precipitate was obtained in which IV was identified by IR spectroscopy. The filtrate was chromatographed on Al_2O_3 as described in *1.a* yielding 0.10 g (19% with respect to II) of $CpMn(CO)_3$, 0.37 g (51%) of II and 0.04 g (3.5%) of III.

(*b*) 0.30 g of freshly prepared crystalline II was placed in an apparatus for sublimation, and after 2 h 0.17 g (57%) of II was collected at 50°C/1×10^{-2} mmHg. The nonvolatile pink residue contained IV, identified from the IR spectrum.

(*c*) A solution of 0.10 g of II in 50 ml of cyclohexane was allowed to stand at 20°C. After 5 h traces of $CpMn(CO)_3$ and III were established by TLC and IR spectroscopy. After 5 days the II: $CpMn(CO)_3$ ratio was 1 : 1 (IR spectral data), and after 10 days only traces of $CpMn(CO)_3$ were found in the brown solution.

(*d*) A solution of 0.10 g of II in 50 ml of cyclohexane kept at 50°C for 2 h yielded a light red precipitate containing IV. The presence of $CpMn(CO)_3$, II and III in the solution was confirmed by TLC and IR spectroscopy.

5. *Preparation of $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ (III) in the reaction of $CpMn(C{=}CHPh)(CO)_2$ (II) with $CpMn(CO)_2(THF)$*

A solution of 0.20 g (0.001 mol) of $CpMn(CO)_3$ in 50 ml of THF was UV irradiated for 4 h. A solution of 0.14 g (0.0005 mol) of II in 20 ml of THF was then added, and the reaction mixture was mixed for 2 h at 20°C. After evaporation of the solvent at reduced pressure the dry residue was extracted with 30 ml of petroleum ether (b.p. 50—60°C), the extract chromatographed on a Al_2O_3 column yielding 0.05 g of $CpMn(CO)_3$, 0.03 g of unreacted II and 0.06 g (27% with respect to the initial II) of III as violet crystals.

6. Preparation of $CpMn(C{=}CHPh)(CO)(PR_3)$ complexes, where R = Ph (IX), OEt (X) or OPh (XI) from $CpMn(C{=}CHPh)(CO)_2$ (II)

(a) Interaction of II with Ph_3P without UV irradiation. 0.37 g (0.0013 mol) of II, 0.68 g (0.0026 mol) of Ph_3P and 80 ml of n-pentane were mixed for 5 h at 20°C, concentrated to 20 ml and placed in a column with neutral Al_2O_3. Petroleum ether (b.p. 35—40°C) elution brought down a colorless (1) and a red (2) band, eluation with ether/petroleum ether mixture (1 : 100) removed an orange band (3) and with ether/petroleum mixture (1 : 50), an orange-red (4) and then a dark orange (5) band. Evaporation of the eluates produced the following fractions: (1) unreacted Ph_3P; (2) 0.08 g of initial II; (3) traces of $CpMn(CO)_3PPh_3$; (5) traces of $CpMn(CO)(PPh_3)_2$, identified by IR spectra. Fraction (4) after recrystallization from ether yielded 0.11 g (17% with respect to initial II) of IX as dark orange crystals, m.p. 174°C (dec.).

(b) Reaction of II with $(PhO)_3P$. After stirring a solution of 0.56 g (0.002 mol) of II and 1.24 g (0.004 mol) of $(PhO)_3P$ in 50 ml of n-pentane at 20°C for 5 h the reaction mixture was treated as described in *6.a.* A light red band was eluted with an ether/petroleum ether mixture (1 : 50). Evaporation of the eluate and crystallization from n-hexane yielded 0.16 g (14%) of XI as orange-red crystals, m.p. 110—112°C.

(c) Photochemical reactions of II with R_3P (R = Ph, OEt or OPh). 0.56 g (0.002 mol) of II and 0.004 mols of R_3P in 50 ml of n-hexane were irradiated for 1.5 h. After treating the reaction mixtures as described in *6.a*, 0.25 g (24%) of dark orange crystals of IX for R = Ph; 0.20 g (24%) of X as a light red oil for R = EtO; or 0.24 g (21%) of orange-red crystals of XI for R = PhO were obtained.

7. Photochemical reaction of $Cp_2Mn_2(\mu\text{-}C{=}CHPh)(CO)_4$ (III) with Ph_3P.

A mixture of 0.30 g (0.0065 mol) of III, 0.35 g (0.0134 mol) of Ph_3P and 40 ml of benzene was irradiated for 4 h. The solvent was then evaporated, the dry residue dissolved in petroleum ether (b.p. 50—60°C) and the solution chromatographed on a column with neutral Al_2O_3 to yield 0.13 g (46%) of $CpMn(CO)_2PPh_3$ and 0.08 g (24%) of $CpMn(C{=}CHPh)(CO)(PPh_3)$ (IX).

Acknowledgement

The authors are grateful to Yu.S. Nekrasov and D.A. Zagorevsky for measurement and discussion of the mass spectra.

References

1 A.N. Nesmeyanov, G.G. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, J. Organometal. Chem., 110 (1976) C36.
2 O.S. Mills and A.D. Redhouse, Chem. Commun., (1966) 444.
3 R.B. King and M.S. Saran, J. Amer. Chem. Soc., 94 (1972) 1784.

4 R.B. King and M.S. Saran, J. Amer. Chem. Soc., 95 (1973) 1817.
5 A.N. Nesmeyanov, A.B. Antonova, N.E. Kolobova and K.N. Anisimov, Izv. AN SSSR, Ser. Khim., (1974) 2873.
6 W. Strohmeier and H. Hellmann, Chem. Ber., 98 (1965) 1598.
7 I.S. Butler and A.E. Fenster, J. Organometal. Chem., 51 (1973) 307.
8 L.P. Yur'eva, in A.N. Nesmeyanov and K.A. Kocheshkov (Eds.), Metody elementoorganicheskoy khimii. Tipy metalloorganicheskikh soedineniy perekhodnykh metallov (Methods of organoelement chemistry. Types of organometallic compounds of transition metals), Nauka, Moscow, 1975, p. 440.
9 A.N. Nesmeyanov, N.E. Kolobova, A.B. Antonova and K.N. Anisimov, Dokl. Akad. Nauk SSSR, 220 (1975) 105.
10 B. Cetinkaya, M.F. Lappert, J. McMeeking and D.E. Palmer, J. Chem. Soc. Dalton, 1202 (1973).
11 V.G. Andrianov, Yu.T. Struchkov, N.E. Kolobova, A.B. Antonova and N.S. Obezyuk, J. Organometal. Chem., 122 (1976) C33.
12 W. Strohmeier, J.F. Guttenberger and H. Hellmann, Z. Naturforsch., 19b (1964) 353.
13 J. Müller and K. Ferendi, Angew. Chem., Int. Ed. Engl., 10 (1971) 418.
14 E.O. Fischer and M. Herberhold, Essays in Coordination Chemistry, Exper. Suppl. IX. Basel, Birkhäuser Verlag, 1964, p. 259.
15 W.A. Herrmann, Chem. Ber., 108 (1975) 486.
16 N.E. Kolobova, A.B. Antonova, O.M. Khitrova, M.Yu. Antipin and Yu.T. Struchkov, J. Organometal. Chem., (1977).
17 K.N. Anisimov and Z.F. Valueva, in A.N. Nesmeyanov and K.A. Kocheshkov (Eds.) Metody elementoorganicheskoy khimii. Podgruppy medi, scandiya, titana, vanadiya, khroma, margantsa. Lantanoidy i Aktinoidy (Methods of Organoelement Chemistry. Subgroups of copper, scandium, titanium, chromium, manganese. Lanthanoids and Actinoids), Nauka, Moscow, 1974, p. 781.
18 A.N. Nesmeyanov, N.E. Kolobova, A.B. Antonova, N.S. Obezyuk and K.N. Anisomov, Izv. AN SSSR, Ser. Khim., (1976) 948.