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Chemistry of Vinylidene Complexes.
III*. Binuclear Manganese–Platinum Complexes with Bridging Phenylvinylidene Ligand

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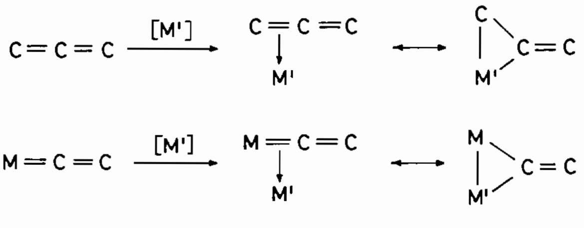
Abstract

The vinylidene manganese complex $Cp(CO)_2Mn{=}C{=}CHPh$ reacts with (η^2-*trans*-PhCH=CHPh)$Pt(PPh_3)_2$ and PtL_4 (L = PPh_3, $P(OEt)_3$ or $P(OPh)_3$) to afford the heteronuclear dimetal compounds of the type $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$, the first platinum-containing complexes with phenylvinylidene ligand. The structures of the novel compounds are suggested on the basis of the IR, ^1H, ^{13}C and ^{31}P NMR spectral data.

Introduction

Previously [2] we have supposed that the metal–carbon double bond of metallallenic M=C=C system (A) in the mononuclear transition metal vinylidene complexes, similar to the C=C bonds of organic allenes or olefins, is able to π-coordinate with metal atom M′ of coordinatively and electronically unsaturated metal-complex fragments. The resulting η^2-system (B) may be regarded as being one of the resonance forms of a dimetallacyclopropanylidene ring system (C).



(A) (B) (C)

This suggestion has been confirmed by syntheses of a number of binuclear compounds containing the Mn–M′ bonds bridged by vinylidene ligands from mononuclear manganese vinylidene complexes. Thus, the complexes $Cp_2(CO)_4MnM'(\mu\text{-}C{=}CHPh)$ (M′ = Mn or Re) have been prepared by reactions of $Cp(CO)_2Mn{=}C{=}CHPh$ with the $[CpM'(CO)_2]$ units [2, 3]. Recently the compounds containing Mn–Fe [4] and Mn–W [5] bonds bridged by the C=CHCOOMe group have been obtained by analogous ways.

Such a method of prediction and realization of the novel reactions of metal complexes by analogy with those of organic compounds may be considered as an application of Hoffmann's *isolobality* principle [6]. An analogous approach to the syntheses of the heteronuclear dimetal compounds from mononuclear carbene or carbyne metal complexes has been widely used by Stone and co-workers [7–11].

To our knowledge, no reactions of the vinylidene metal complexes with platinum compounds have been described. In a preliminary communication [12] we reported the formation of the platinum-containing complexes with vinylidene ligand, $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$, where L = $P(OEt)_3$, $P(OPh)_3$, or PPh_3, resulting from the reactions of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with PtL_4. In the present paper we describe the reactions of I with platinum compounds in more detail and discuss the spectral data for the novel binuclear μ-vinylidene complexes.

Two isomeric μ-vinylidene complexes $WPt(\mu\text{-}C{=}CH_2)(dppm)(CO)_5$ have been very recently prepared from the carbene-bridged heteronuclear complex $WPt[\mu\text{-}C(OMe)Me](dppm)(CO)_5$ [13].

Results and Discussion

It is well known [14] that the platinum(0) compounds of the types PtL_4 and (η^2-olefin)PtL_2 dissociate in solution to form the coordinatively unsaturated $[PtL_2]$ units. In order to ascertain the ability of a metallallenic M=C=C system to add $[PtL_2]$, we have studied the reactions of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with PtL_4 (L = PPh_3, $P(OEt)_3$, or $P(OPh)_3$) and (η^2-*trans*-PhCH=CHPh)$Pt(PPh_3)_2$.

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*Part II is reference [1].

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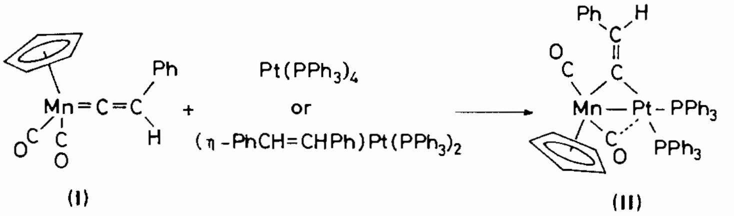
TABLE I. Analytical and Physico-Chemical Data for the Complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (II–IV, VII).

Compound	Color	Yield	M.p.^{a}	IR spectra $\nu(CO)$, cm^{-1} (in CH_2Cl_2)	Analysis: Found (Calcd.)	
		%	°C		C	H
II $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$	yellow	80	182	1923s, 1838m	61.38(61.38)	4.58(4.11)
III $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OEt)_3]_2$	orange	74	121	1930s, 1858m	40.38(40.27)	5.18(5.09)
IV $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPh)_3]_2$	orange	76	141	1942s, 1875m	56.12(56.01)	3.73(3.75)
VII $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(CO)(PPh_3)$	orange		97	2034s, 1940s, 1872m	53.77(53.47)	4.21(3.41)

^{a}With decomposition.

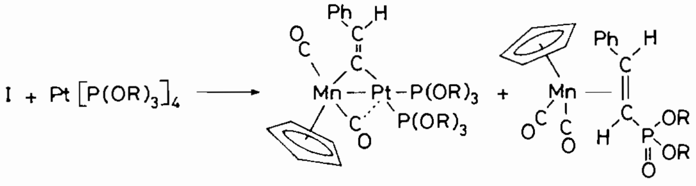
Complex **I** reacts smoothly with both $Pt(PPh_3)_4$ and $(PhCH{=}CHPh)Pt(PPh_3)_2$ (benzene, 20 °C, 4–7 h) to give the binuclear complex $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**II**) in good yields:



(I) (II)

(1)

Unlike reaction (1), the treatment of **I** with platinum–phosphite derivatives yields products of two different types: the μ-vinylidene heteronuclear compounds **III**, **IV** and the mononuclear manganese complexes **V**, **VI** containing *trans*-β-phenylvinylphosphonate η^2-ligands:



(III, IV) (V, VI)

(2)

where R = Et (**III**, **V**) or Ph (**IV**, **VI**).

Obviously, the complexes **V** and **VI** arise from the interaction between **I** and the $P(OR)_3$ molecules produced by dissociation of $Pt[P(OR)_3]_4$ in the reaction mixtures. Previously [15, 16] we have obtained **V** and **VI** in quantitative yields by direct reactions of **I** with the corresponding phosphites in the absence of platinum compounds.

For preparation of the binuclear complexes **III** and **IV** in good yields a 3–4-fold excess of complex **I** is required, because two mol of **I** are spent in reaction (2) for formation of the vinylphosphonate compounds **V** or **VI**. Since the dissociation of PtL_4 is slowed down in the order of L = $PPh_3 > P(OEt)_3 > P(OPh)_3$, either significant lengthening of the procedure or some increase of the temperature is needed for completing reaction (2) compared with (1).

The complexes **II**–**IV** are yellow-orange crystalline solids, well soluble in polar organic solvents and slightly soluble in aliphatic hydrocarbons. In contrast to $Cp_2(CO)_4MnRe(\mu\text{-}C{=}CHPh)$, which rapidly decomposes even in the cold with rupture of the Mn–Re bond to afford $Cp(CO)_2Re{=}C{=}CHPh$ [3], the complexes **II**–**IV** are thermally stable both in the solid state and in solutions, and their stability increases in the order: **III** < **IV** < **II**. We have found that these compounds have more tendency to the ligand exchange at the Pt atom than to cleavage of the Mn–Pt bond. Thus, the exchange of $P(OEt)_3$ for PPh_3 occurs on stirring a solution of **III** and PPh_3 in benzene at 20 °C. The bubbling of a stream of CO gas in benzene solution of **II** leads to formation of the tricarbonyl complex $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(CO)(PPh)_3$ (**VII**), unlike the reaction of CO with μ-carbene compound $Cp(CO)_2$-

TABLE II. The ^{31}P NMR Parameters of the Complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (L = PPh_3 (**II**) and $P(OEt)_3$ (**III**)) (in $CDCl_3$ solutions at −50 °C; the signals downfield from external 85% H_3PO_4).

Complex	δ (ppm)	^2J(PP), (Hz)	^1J(PPt), (Hz)
II	43.5 d	17.1	4414
	27.4 d	17.1	2607
III	148.8 d	17.4	3898
	138.9 d	17.4	6586

$MnPt[\mu\text{-}C(OMe)Ph](PMe_3)_2$ resulting in the cleavage of the Mn–Pt bond [9]. The complex **VII** may be also prepared in good yields by reaction of **II** with $Co_2(CO)_8$ or $Fe_2(CO)_9$.

The analytical and physico-chemical data for the binuclear compounds **II–IV** and **VII** are given in Table I.

The IR spectrum of each of the compounds $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (**II–IV**) showed two carbonyl stretching bands with different intensities: a strong band at 1942–1923 cm^{-1} due to the terminal CO group linked to the Mn atom, and a broad-medium band in region 1875–1838 cm^{-1}. The ν(CO) frequencies of both bands decrease in the order L = $P(OPh)_3 > P(OEt)_3 > PPh_3$. It is notable that the former band lies in a narrow interval of ν(CO) and is shifted to low frequency by only 19 cm^{-1} for complex **II** as compared with **IV**, whereas the frequency of the latter band is decreased in the same order by 37 cm^{-1}. Both the low frequency and the shape of the latter band, as well as the greater sensitivity of the position in the spectra of **II–IV** to the nature of L at the Pt atom, indicate that this band may well be assigned to the carbonyl ligand attached to the Mn and semi-bridged to the Pt atom.

It was recently shown [9, 11, 13, 17, 18] that the presence of semi-bridging CO ligands is typical for many heteronuclear metal carbonyl complexes containing the Pt atom. Thus, the semi-bridging CO groups have been found by X-ray studies of a series of dimetal μ-carbene, -carbyne and -vinylidene compounds, *e.g.*, $(CO)_5WPt(\mu\text{-}C{=}CH_2)(Ph_2PCH_2PPh_2)$ [13] and $[Cp(CO)_2MnPt(\mu\text{-}CC_6H_4Me\text{-}p)(PMe_3)_2]BF_4$ [17]. Probably this type of coordination of CO ligands reflects a tendency of the electron-rich Pt atom to reduce its electron density by means of back-donation into π^* orbitals of CO linked to a neighbouring metal atom [17].

The IR spectrum of complex **VII** shows three ν(CO) bands. The strong band at 2034 cm^{-1} is apparently due to the vibration of a CO group attached to the Pt atom; the bands at 1940 and 1872 cm^{-1} are both close to those found in the spectra of **II–IV**.

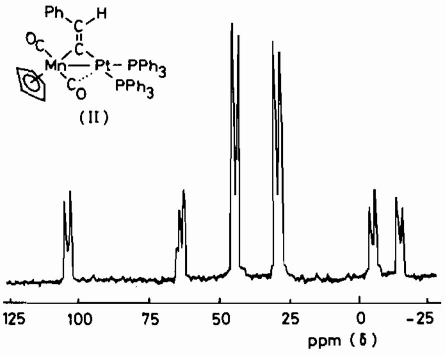


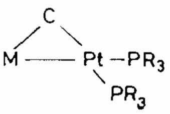
Fig. 1. The $^{31}P\text{–}\{^1H\}$ NMR spectrum of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**II**) in $CDCl_3$ solution.

The appreciable shift of the low-frequency ν(CO) band in the series **IV** ~ **VII** > **III** > **II** is perhaps due to an increasing of interaction between the Pt atom and a semi-bridging CO group affected by a growth of the electron-donating capacity of the L ligands at the Pt atom.

The significant increase in the ν(CO) frequencies, observed in going from the known related μ-carbene compounds, *e.g.*, $Cp(CO)_2MnPt[\mu\text{-}C(OMe)Ph]\cdot(PMe_3)_2$ (1871 and 1814 cm^{-1} in hexane) [9], to the μ-vinylidene complexes (Table I) (the difference in solvents and in phosphorus ligands is taken into account), indicates a stronger electron-withdrawing ability of the μ-vinylidene ligand.

The intense band at 1545 cm^{-1} in the IR spectrum of **III** may be assigned to ν(C=C) of the vinylidene group. An analogous band at 1550 cm^{-1} has been found for $Cp_2(CO)_4Mn_2(\mu\text{-}C{=}CHPh)$ (**VIII**) [2]. The identification of ν(C=C) bands in the spectra of **II**, **IV** and **VII** is difficult, due to the intense absorption of phenyl rings in this region.

The ^{31}P NMR spectra (^1H decoupled) of compounds **II** and **III** (Table II, Fig. 1) each revealed two resonances of ^{31}P nuclei of the non-equivalent ligands attached to the Pt atom. The values of ^1J(PPt) and ^2J(PP) coupling constants are in accord with the square-planar coordination of the Pt atom with *cis*-configuration of the PtL_2 fragment. By analogy with known [8–10, 17] binuclear complexes containing



fragments (M = Mn, W), the signal with the greatest J(PPt) value is assigned to the ligand *trans* to the Mn–Pt bond. The other signal belongs to the phosphorus *trans* to μ-vinylidene group.

The ^{13}C NMR spectra (^1H decoupled) of complexes **II** and **III** (Table III, Fig. 2) each show the signals of the carbon atoms of two non-equivalent CO groups. The difference of their chemical shifts

TABLE III. ^{13}C NMR Data[a] for Compounds $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (L = PPh_3 (**II**) and $P(OEt)_3$ (**III**))[b] and $Cp_2(CO)_4Mn_2(\mu\text{-}C{=}CHPh)$ (**VIII**).[c]

Compound	$C^1{=}C^2\begin{array}{l}\diagup C_6H_5\\ \diagdown H\end{array}$					CO	C_5H_5	Other groups
	C^1	C^2	C_6H_5					
			C_{ipso}	C_{orto}, C_{meta}	C_{para}			
II	264.30 d $[{}^2J(CP) = 61.4$ and $\leqslant 2.5$; ${}^1J(CPt) = 857.3]$	141.25 s,br $[{}^3J(CP) \leqslant 6.7$; ${}^2J(CPt) = 114.5]$	144.00 t $[{}^4J(CP) = 12.7$; ${}^3J(CPt) = 24.7]$	127.35 s 125.81 s	123.05 s	233.75 br[d] $[{}^2J(CP) = 18$; ${}^2J(CP) = 29]$ 229.84 br	84.19 s	134.74 d (PC_6H_5, C_o $[J(CP) = 11.1]$) 129.45 s (PC_6H_5, C_p $[J(CP) \leqslant 4]$) 127.52 d (PC_6H_5, C_m $[J = 5.6]$) 127.46 d (PC_6H_5, C_i $[J = 108.7]$)
III	259.80 d $[{}^2J(CP) = 91.6$ and $\leqslant 3.7$; ${}^1J(CPt) = 825.4]$	141.08 d $[{}^3J(CP) = 6.8$ and $\leqslant 1.9$; ${}^2J(CPt) = 123.3]$	143.40 dd $[{}^4J(CP) = 19.4$ and 10.4; ${}^3J(CPt) = 19.4]$	127.80 s 126.03 s	123.61 s	231.19 br 229.3 br	84.19 s	60.95 s (OCH_2 $[J(CP) \leqslant 0.9$; ${}^3J(CPt) = 19.4]$) 60.48 s (OCH_2 $[J(CP) \leqslant 0.5$; ${}^3J(CPt) = 13.9]$) 16.25 d (CH_3 $[{}^3J(CP) = 7]$) 16.03 d (CH_3 $[{}^3J(CP) = 7]$)
VIII	284.16	146.4 $[J(CH) = 150]$	139.3	128.2 125.3 $[J(CH) \sim 160]$	124.6 $[J(CH) \sim 160)]$	235.53 234.07 232.41 229.16	88.65 88.36 $[J(CH) = 180]$	

[a] δ in ppm relative to TMS, the values of coupling constants, J in Hz, are given in parentheses. [b] In $CDCl_3$ solution at 30 °C. [c] In CH_2Cl_2 solution at −20 °C. [d] The signal/noise ratio is 2:1.

TABLE IV. ^{1}H NMR Spectra (δ, ppm [J, Hz]) of the Compounds $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (L = PPh_3 (II), $P(OEt)_3$ (III), $P(OPh)_3$ (IV)), $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(CO)(PPh_3)$ (VII) and $Cp_2(CO)_4Mn_2(\mu\text{-}C{=}CHPh)$ (VIII).[a]

Complex	=CH	C_5H_5	Other groups
II	7.92 t [^{4}J(HP) = 12.5; ^{3}J(HPt) = 25.6]	4.12 s	7.45 m, 7.05 m, 6.80 m (35H, PC_6H_5 and C_6H_5)
III	8.76 dd [^{4}J(HP) = 15.9 and 20.8; ^{3}J(HPt) = 24.7]	4.71 s	7.76 dd, 7.26 m (5H, C_6H_5) 4.12 m (12H, OCH_2) 1.36 t, 1.32 t (18H, CH_3)
IV	8.62 dd [^{4}J(HP) = 16.2 and 22.3; ^{3}J(HPt) = 30.9]	4.24 s	7.18–7.10 m (35H, OC_6H_5 and C_6H_5)
VII	8.05 d [^{4}J(HP) = 11.9; ^{3}J(HPt) = 40.5]	4.43 s	7.68–6.78 m (20H, PC_6H_5 and C_6H_5)
VIII	8.34 s	4.70 s 4.60 s	7.55–7.02 m (5H, C_6H_5)

[a] At 20 °C; II and VII in C_6D_6, III, IV and VIII in $CDCl_3$ solutions.

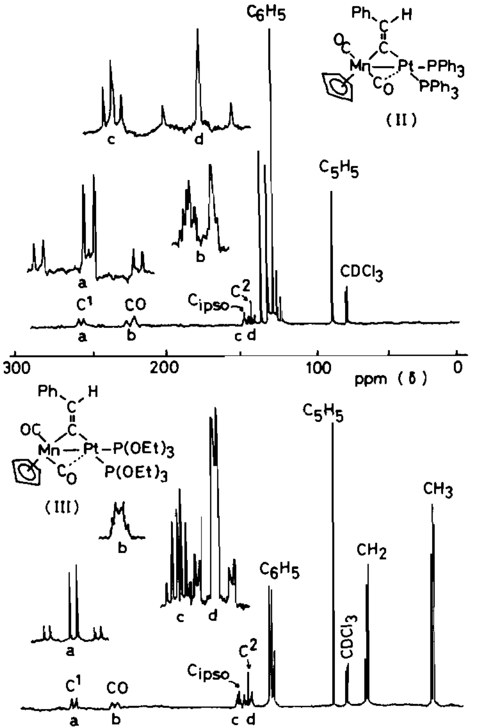


Fig. 2. The ^{13}C–{^{1}H} NMR spectra of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (II) and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OEt)_3]_2$ (III) in $CDCl_3$ solutions.

for complex II is increased by 2.1 ppm compared with that for III, and this increase apparently reflects the influence of the nature of L linked to the Pt atom on the chemical shift of a low-field signal. Moreover, in the spectrum of II the signal of CO at δ 233.75 ppm is broader than that at δ 229.84 ppm (Δν are 72 and 25 Hz, respectively) and is split, probably in a doublet of doublets, due to the coupling with two ^{31}P nuclei. Both these observations may be regarded as being confirmation of the semi-bridging nature of one of CO ligands, assumed from the above IR spectral data.

The appearance in the ^{13}C NMR spectra of II and III of the signals at δ 264.30 and 259.80 ppm, respectively, is a direct evidence of the existence of the bridging phenylvinylidene ligands in these molecules [2, 13, 19, 20]. The ^{1}J(CPt) values of 857.3 and 825.4 Hz are typical for platinum compounds with σ C–Pt bond [21].

The signals of α-carbon atoms of vinylidene ligands in the spectra of II and III are shifted upfield by 115–120 ppm from the value of 379.54 ppm of the parent compound $Cp(CO)_2Mn{=}C{=}CHPh$ (I) [2]. An analogous effect has been found for complex $Cp(CO)_2MnPt[\mu\text{-}C(OMe)C_6H_4Me\text{-}p](PMe_3)_2$, in which the signal of the bridging carbon atom is shifted upfield by *ca.* 140 ppm from that of the parent carbene complex $Cp(CO)_2Mn[C(OMe)C_6H_4Me\text{-}p]$ [17]. However, the resonance of a bridging carbon atom in the spectrum of homometallic μ-vinylidene compound $Cp_2(CO)_4Mn_2(\mu\text{-}C{=}CHPh)$ (VIII) is shifted upfield by *ca.* 95 ppm from that of I. The increase in shielding of the carbene–carbon atoms observed for the bridged systems, involving Pt atoms, may be explained by the greater electron-donating capacity of the PtL_2 groups (L = phosphine or phosphite) compared with that of the $Cp(CO)_2Mn$ fragment.

The signals of the bridging α-carbon atoms in the spectra of II and III are split into doublets due to the spin–spin coupling with ^{31}P nuclei in the *transoid*-C–Pt–P fragments. The resonance of the vinylidene β-carbon atom of III is also a doublet. The key carbon nucleus of a phenyl ring, C_{ipso}, in spectra of II and III is coupled with both phos-

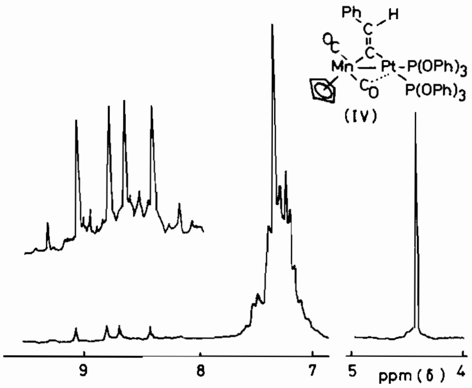


Fig. 3. The ^{1}H NMR spectrum of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPh)_3]_2$ (IV) in $CDCl_3$ solution.

phorus nuclei. The values of $^4J(CP)$ constants for **III** are different, and the resonance of C_{ipso} is a doublet of doublets with ^{195}Pt satellite peaks; for **II** the values of $^4J(CP)$ are equal, and the signal of C_{ipso} is a triplet.

The resonance of the vinylidene proton in the ^{1}H NMR spectra of the complexes **II–IV** and **VII** (Table IV, Fig. 3) lies in the low field, and its chemical shift is close to that of **VIII**. For complex **II** the signal is a triplet, and those in the spectra of **III** and **IV** are doublets of doublets with close values of the $^4J(HP)$ constants: 15.9 and 20.8 Hz for **III**, and 16.2 and 22.3 Hz for **IV**. In the spectrum of the mono-phosphine complex **VII** this signal is a doublet with ^{195}Pt satellites. Previously, high values of the $^4J(HP)$ constants have been observed in the ^{1}H NMR spectra of the η^2-allene complexes of the type $(\eta^2\text{-}RCH{=}C{=}CHR)Pt(PR_3)_2$ [22, 23] and of the σ-vinyl compounds such as *cis*-$(Et_3P)_2Pt[C(CF_3){=}CH_2]Cl$ [24, 25], but in these cases the coupling occurs with one of two ^{31}P nuclei. The constants of the vicinal coupling $^3J(HPt)$ for these compounds are approximately twice the $^3J(HPt)$ values measured from the spectra of the μ-vinylidene complexes **II–IV**. Therefore, it is possible that the structures of the $PhCH{=}CPtP_2$ fragments in compounds **II–IV** are close to η^1-allenic type, *i.e.*, the substituents H and C_{ipso} at the vinylidene β-carbon atom lie in the plane perpendicular (or close to perpendicular) to the plane of *cis*-PtP_2 fragment. Such geometry should result in the appearance of the long-ranged $^4J(HP)$ and $^4J(CP)$ coupling constants with both phosphorus nuclei and the same multiplicity of the signals of vinylidene proton in the ^{1}H NMR spectra and of C_{ipso} atom in the ^{13}C NMR spectra. The resonance patterns for these signals observed in both ^{1}H and ^{13}C NMR spectra of the complexes **II** and **III** are thus the same: triplets for **II** and doublets of doublets for **III**.

In conclusion it is useful to emphasize some differences in the properties of the manganese–platinum vinylidene-bridged compounds and the closely related μ-carbene complexes [9, 17]. We have previously pointed out [2] that the terminal vinylidene C=CHPh group, in contrast to the carbene groups, is among the ligands having the greatest electron-withdrawing capacity. Evidently, an acceptor character of the vinylidene ligand is retained when it transforms from a terminal form into a bridging one, and the influence of a bridging ligand is extended onto both metal atoms of the dimetallacyclopropane ring. As a result, the frequencies of the stretching vibrations of the CO groups linked to the Mn atom are higher, the ligand exchange at the Pt atom goes more smoothly, and the Mn–Pt bond is stronger for the vinylidene-bridged complexes in comparison to the analogous properties of the related μ-carbene compounds.

Experimental

All operations were carried out in dry solvents under argon atmosphere. Chromatography was performed on a column packed with neutral alumina; Silufol plates were used for TLC.

IR spectra were registered on a Specord IR-75 spectrometer. The ^{1}H, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on Tesla BS-467 (60 MHz), Bruker HX-90 (36.43 MHz) and Bruker WP-200 SY (50.31 MHz) instruments, respectively.

Reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ *(I) with (trans-*$PhCH{=}CHPh)Pt(PPh_3)_2$

A solution of 0.061 g (0.22 mmol) of **I** and 0.180 g (0.20 mmol) of $(PhCH{=}CHPh)Pt(PPh_3)_2$ in 20 ml of benzene was stirred at 20 °C for 7 h. The solvent was then removed *in vacuo*, the residue was dissolved in $CHCl_3$ and the solution was filtered through a 1 cm alumina pad and evaporated. The dark-red oil was dissolved in ether, and after cooling at –20 °C, 0.160 g (80%) of bright-yellow crystals of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**II**) was obtained.

Reaction of **I** *with* $Pt(PPh_3)_4$

A solution of 0.061 g (0.22 mmol) of **I** and 0.249 g (0.20 mmol) of $Pt(PPh_3)_4$ in 20 ml of benzene was stirred at 20 °C for 4 h and then evaporated. The residue was dissolved in a hexane–benzene mixture (2:1) and chromatographed on an alumina column. A narrow dark-red zone, eluted with hexane–benzene (2:1) contained unreacted **I**, $CpMn(CO)_3$ and $Cp_2(CO)_4Mn_2(\mu\text{-}C{=}CHPh)$ (**VIII**), all identified by IR spectra and TLC. A broad orange band was eluted with hexane–benzene (1:1). The residue after removal of the solvent was treated as described in above. 0.130 g (65%) of **II** was obtained.

Reaction of **I** *with* $Pt[P(OEt)_3]_4$

A solution of 0.180 g (0.65 mmol) of **I** and 0.172 g (0.20 mmol) of $Pt[P(OEt)_3]_4$ in 15 ml of benzene was stirred at 20 °C for 24 h. Then a solution was concentrated *in vacuo* and chromatographed on a column. With a hexane–benzene mixture (10:1) a dark-red band containing unreacted **I**, Cp-$Mn(CO)_3$ and **VIII** (identified by IR spectra and TLC) was eluted. Elution with hexane–ether (5:1) gave a bright-yellow fraction, which after removal of solvent and recrystallization of the residue from ether–hexane mixture, yielded 0.120 g (74%) of orange crystals of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OEt)_3]_2$ (**III**). The following yellow band eluted with ether gave 0.126 g (76%) of dark-yellow crystals of $Cp(CO)_2Mn[\eta^2\text{-}PhCH{=}CHP(O)(OEt)_2]$ (**V**), identical to that described in [16]. Found: C 55.12, H, 5.45%. $C_{19}H_{22}O_5PMn$. Calcd.: C 54.81, H 5.29%.

Reaction of I with $Pt[P(OPh)_3]_4$

A solution of 0.111 g (0.40 mmol) of **I** and 0.144 g (0.10 mmol) of $Pt[P(OPh)_3]_4$ in 15 ml of benzene was stirred at 50 °C for 8 h. The reaction mixture was chromatographed on a column. From the yellow fraction eluted with a hexane–ether mixture (3:1), after evaporation and recrystallization of the residue from CH_2Cl_2–hexane mixture, 0.083 g (76%) of orange crystals of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPh)_3]_2$ (**IV**) were obtained. The next yellow band eluted with ether yielded 0.058 g (56%) of Cp-$(CO)_2Mn[\eta^2\text{-}PhCH{=}CHP(O)(OPh)_2]$ (**VI**), identical to that described in [16]. Found: C 63.76, H 4.66%. $C_{27}H_{22}O_5PMn$. Calcd.: C 63.31, H 4.30%.

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