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Chemistry of Vinylidene Complexes. V*. The Ligand Substitution Reactions at the Platinum Atom in Complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$

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Abstract

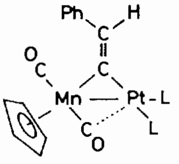
The dimetal μ-vinylidene complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (L = PPh_3 or $P(OPr^i)_3$) react with nucleophylic molecules (phosphines, phosphites or CO), without cleavage of a dimetallacycle, to afford the products of substitution of platinum-bound terminal ligands with geometry depending on the nature of an entering ligand. The reaction of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ and $P(OPr^i)_3$ gives $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3]_2$ and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](PPh_3)$ with the $P(OPr^i)_3$ group *cis* to the μ-C atom. The latter is also formed by treating $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3]_2$ with PPh_3, and as a result of the ligand exchange reaction between bis-phosphine and bis-phosphite compounds. The last ligand redistribution process is reversible, and an equilibrium between all three of the above complexes exists in solution.

Treatment of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ with $Co_2(CO)_8$ yields the tricarbonyl complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(L)(CO)$ with the platinum-bound CO group *trans* to μ-C. All studied reactions are stereoselective, and no mixed-ligand complexes isomeric to the above species have been detected. The IR and ^1H, ^{13}C and ^{31}P NMR spectra of the new complexes are discussed.

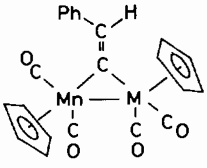
Introduction

Previously [2, 3] we have reported that an addition of the $[PtL_2]$ units to the metal–carbon double bond of the mononuclear vinylidene complex $Cp(CO)_2Mn{=}C{=}CHPh$ results in the dimetal compounds with a bridging phenylvinylidene ligand of the type $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (**A**), where L = PPh_3, $P(OEt)_3$ or $P(OPh)_3$.

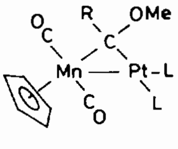
It is of interest to compare properties of the (**A**) type compounds with those of other known cymantrene derivatives containing a $\overline{MnM(\mu\text{-}C)}$ ring system, namely: the μ-phenylvinylidene complexes with the Mn–Mn (**B**) and Mn–Re (**C**) bonds [4–6] and the μ-aryl(methoxy)carbene compounds with the Mn–Pt bond (**D**) [7, 8].



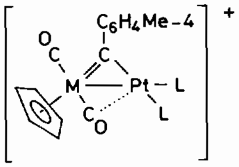
A



B M = Mn
C M = Re



D
R = Ph, C_6H_4Me-4



E
M = Mn, Re

This comparison makes it possible to ascertain on the one hand, what a fresh note is introduced into the $\overline{MnM(\mu\text{-}C{=}C)}$ cycle when the Pt atom being included as M instead of Mn or Re, and on the other hand, what sort of changes in properties of a $\overline{MnPt(\mu\text{-}C)}L_2$ system result from the replacement of Fischer-type carbene bridging ligand by a vinylidene bridge. In this context it is also useful to consider the μ-carbyne complex with the Mn–Pt bond (**E**) [8, 9] as well as the related to (**D**) and (**E**) compounds containing the Cr–Pt and W–Pt bonds [10–12].

In part III of this series [3] we discussed the IR and ^{13}C NMR spectral data for the complexes (**A**), (**B**) and (**D**) and established the appreciable differ-

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*Part IV is ref. 1.

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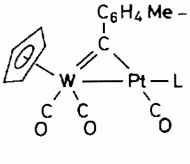
ences in properties of the complexes (**A**) and (**B**), due to the greater donor capacity of the PtL_2 group than $Cp(CO)_2Mn$, and (**A**) and (**D**), caused by more strong electron-withdrawing nature of the μ-C=CHPh ligand compared with the μ-C(OMe)R (R = Ph, C_6H_4-Me-4) group.

The dimetallacyclopropane ring system in the considered compounds is quite stable under usual conditions, except $Cp_2(CO)_4MnRe(\mu\text{-C=CHPh})$ (**C**), which splits gradually both in solutions and in the crystalline state to give $Cp(CO)_2Re=C=CHPh$ [6].

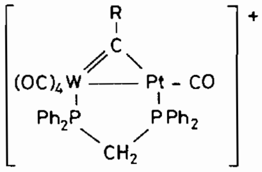
Information necessary for comparison of the reactivity of the compounds (**A**)–(**D**) is as yet rather limited. Nevertheless, it is evident that reactions of the complexes containing a $\overline{\text{MnM}(\mu\text{-C})}$ cycle with electron donor molecules (*e.g.*, phopshines, isonitryles, CO) may proceed by following ways: (a) cleavage of a dimetallacycle to form mononuclear manganese complexes and mono- or polynuclear homometallic carbene derivatives of M; (b) substitution of terminal ligands at one or both metal atoms without cycle opening. Furthermore, a possibility for addition of a phosphine to an unsaturated μ-C atom has been shown by the μ-carbyne cations (**E**) (L = PMe_3 or PMe_2Ph) [9].

The complex $Cp_2(CO)_4Mn_2(\mu\text{-C=CHPh})$ (**B**) does not react with PPh_3 at 20–80 °C, but under UV-irradiation it splits into two halves to form $Cp(CO)(PPh_3)Mn=C=CHPh$ and $CpMn(CO)_2(PPh_3)$ [5]. It was reported [7] that cleavage of a dimetallacycle in $Cp(CO)_2MnPt[\mu\text{-C(OMe)Ph}](PMe_3)_2$ occurs smoothly by treating with CO to give $CpMn(CO)_3$ and $Pt_3[\mu\text{-C(OMe)Ph}]_2(\mu\text{-CO})(PMe_3)_3$, but its reaction with $CNBu^t$ yields the substitution of one PMe_3 *trans* to the μ-carbene group by $CNBu^t$. The complex $(CO)_5WPt[\mu\text{-C(OMe)C}_6H_4\text{Me-4}](\eta^4\text{-}C_8H_{12})$ reacts with CO or $CNBu^t$ (**L**) to yield $W(CO)_6$ and $Pt_3[\mu\text{-C(OMe)C}_6H_4\text{Me-4}]_3L_3$, whereas treating with PMe_3, $Ph_2PCH_2CH_2PPh_2$ or $Me_2AsC_6H_4AsMe_2$ provides a displacement of η^4-cyclooctadiene by these ligands [10]. The reaction of $(CO)_5CrPt[\mu\text{-C(OMe)Ph}](PMe_3)_2$ with $CNBu^t$ results in the substitution of two CO groups at the Cr atom and one platinum-bound phosphine *trans* to μ-C by $CNBu^t$ [11]. The μ-carbyne complexes $Cp(CO)_2WPt(\mu\text{-CC}_6H_4\text{Me-4})L_2$ (L = PMe_3, PMe_2Ph or PPh_3) react with both carbon monoxide and $Co_2(CO)_8$ to produce the tricarbonyl complexes of the type (**F**), in which the platinum-bound CO is *trans* to the μ-C atom [12].

The above data show that cleavage of dimetallacycle by action of CO is characteristic for Fischer-type μ-carbene complexes rather than for μ-carbyne compounds. Indeed, the recent consideration of X-ray data for complexes with the W–Pt bonds bridged by the $C(OMe)C_6H_4Me$-4, CC_6H_4Me-4 or $C=CH_2$ ligands has demonstrated that the bonding in a $\overline{\text{WPt}(\mu\text{-C})}$ ring system in the μ-carbyne complex is close to that in the μ-vinylidene one, but is stronger than that in μ-carbene species [13]. The analogous conclusion follows from the structural comparison of the closely related compounds $Cp_2(CO)_4Mn_2(\mu\text{-X})$, where X = CH_2, $C=CH_2$ and C=CHPh [14].

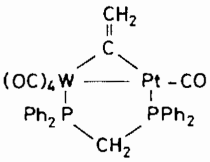


F



G

R = Me, C_6H_4Me-4



H

In all reported ligand substitution reactions at the Pt atom in $\overline{\text{MPt}(\mu\text{-C})}L_2$ systems, proceeding without cleavage of a cycle, the preferable site for the entering ligand was *transoid* to the μ-C atom. It has been concluded [7, 11–13] that the principal factor controlling the choice of the direction in substitution processes is the strong *trans*-influence of the bridging carbene or carbyne ligand.

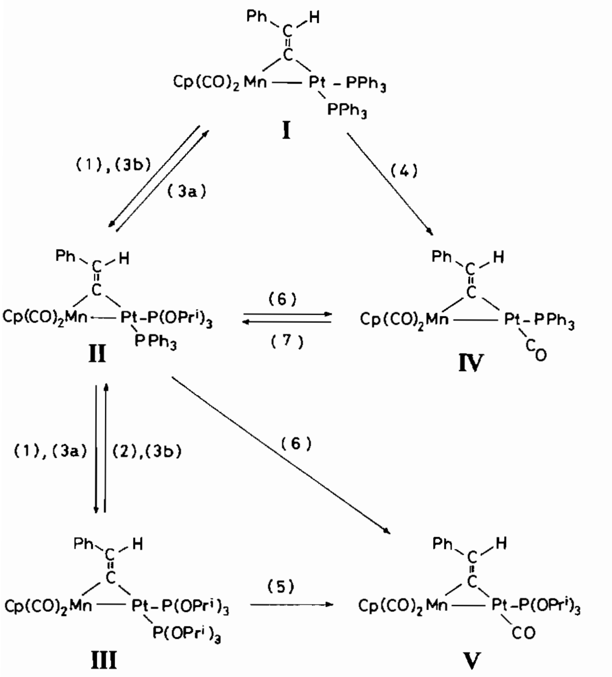
There are, however, some examples of complexes containing platinum-bound carbonyl *cis* to the μ-C atom, *e.g.*, (**G**), (**H**), but in these cases the W–Pt bond is bridged, in addition to μ-carbyne or μ-vinylidene group, by $Ph_2PCH_2PPh_2$ [13, 15].

We have pointed out earlier that the complexes of the type $Cp(CO)_2MnPt(\mu\text{-C=CHPh})L_2$ (**A**) show more tendency to ligand exchange at the Pt atom than to cleavage of the Mn–Pt bond [3]. Herein we describe the results of an investigation of the ligand substitution reactions of these compounds and discuss the IR and ^1H, ^{13}C and ^{31}P NMR spectral data for the new complexes $Cp(CO)_2MnPt(\mu\text{-C=CHPh})LL'$ with different ligands at the Pt atom.

Results and Discussion

We have studied in detail the reactions of $Cp(CO)_2MnPt(\mu\text{-C=CHPh})(PPh_3)_2$ (**I**) and its derivatives with PPh_3, $P(OPr^i)_3$, CO and $Co_2(CO)_8$, summarized in Scheme 1. All reactions were carried out in benzene solutions at room temperature unless otherwise stated. The new complexes **II**–**V** produced in these reactions were characterized by analysis, IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy.

The reaction (1) between $Cp(CO)_2MnPt(\mu\text{-C=CHPh})(PPh_3)_2$ (**I**) and $P(OPr^i)_3$ gave two products: the mixed-ligand complex $Cp(CO)_2MnPt(\mu\text{-C=}$



(1) P(OPr^i)$_3$; (2) PPh$_3$; (3a) disproportionation of II in solutions; (3b) ligands redistribution: I + III → 2II; (4) CO or Co$_2$(CO)$_8$; (5) Co$_2$(CO)$_8$; (6) Co$_2$(CO)$_8$; (7) P(OPr^i)$_3$.

Scheme 1.

CHPh)[P(OPr^i)$_3$](PPh$_3$) (II) and the bis-phosphite compound Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (III) in yields depending on the ratio of reactants. When the I:P(OPr^i)$_3$ molar ratio was equal to *ca.* 1:3, the complexes II and III were isolated in 37% and 62% yields, respectively; in the case of 1:5 ratio, the yield of II reduced to 15%, whereas that of III grew to 75%.

The both complexes II and III were isolated as air-stable yellow-orange crystals decomposing at 178 °C and 146 °C, respectively. According to the ^{1}H, ^{13}C and ^{31}P NMR spectra (*vide infra*) the phosphite ligand in II is *cis* to the bridging carbon atom of a vinylidene group.

The order of formation of II and III in reaction (1) was investigated by means of ^{1}H NMR spectroscopy. Triisopropylphosphite was added dropwise in a NMR tube containing a CDCl$_3$ solution of I, and the course of the reaction was followed by changing the ^{1}H NMR pattern in the region of the η-C$_5$H$_5$ proton signals (Fig. 1). Addition of a first drop of P(OPr^i)$_3$ resulted immediately in the appearance of the signal of the complex II at δ 4.20 ppm and some decrease in the intensity of the signal of I at δ 4.15 ppm; then a growth of intensity of the signal of II was observed as the phosphite was added (Fig. 1a–c). The signal at δ 4.68 ppm due to the complex III appeared only when the content of II in a reaction mixture reached *ca.* 80% (Fig. 1d). After addition of *ca.* 5 mol of P(OPr^i)$_3$ per mol of I, the signal of I disappeared, and the spectrum revealed only the signals of II and III with relative integrated intensities close to 1:6 (Fig. 1f). By chromatography of this mixture on an alumina column II and III were isolated in 15% and 75% yields, respectively. The complex III can be obtained in a quantitative yield by direct action of a great excess of P(OPr^i)$_3$ on II.

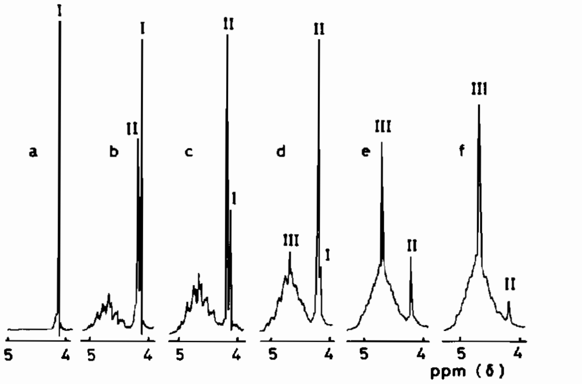
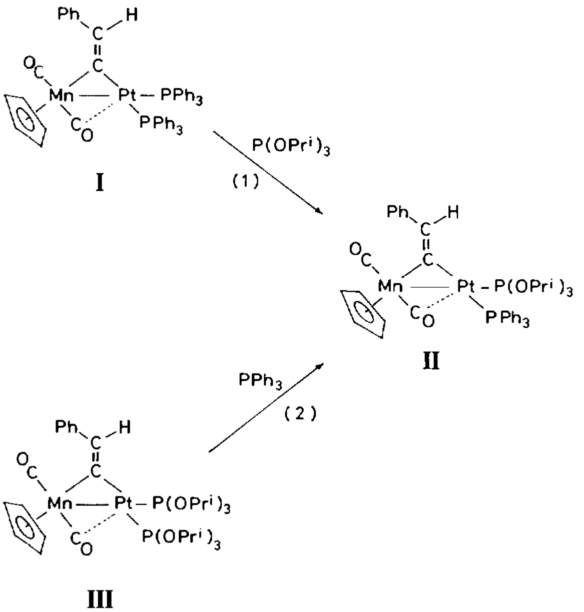


Fig. 1. Changes in the η-C$_5$H$_5$ region of the ^{1}H NMR spectra in the course of the reaction of Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (I) with P(OPr^i)$_3$ in CDCl$_3$ solution, showing sequential formation of Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$](PPh$_3$) (II) and Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (III): (a) peak due to complex I; (b)–(e) changes observed as P(OPr^i)$_3$ was added to I; (f) spectrum measured when *ca.* 5 mol of P(OPr^i)$_3$ per mol of I was added.

The phosphite ligands in the complexes Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OR)$_3$]$_2$ can be smoothly substituted by phosphine. The reaction (2) between Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (III) and PPh$_3$ (molar ratio 1:5) gave the mixed-ligand complex Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$](PPh$_3$) in 69% yield, which, according to the ^{1}H and ^{31}P NMR spectra and TLC, was identical to the complex II described above.

We were unable to detect any signs of formation of the isomer of II with the P(OPr^i)$_3$ group *trans* to the μ-C atom. Thus, both reactions (1) and (2) are stereoselective and yield the same complex II with a phosphite ligand in *cis*-position to the bridging vinylidene α-carbon atom (see later).

The complex II disproportionates slowly in solutions to produce the bis-phosphine and bis-phosphite compounds (reaction 3a). As a result of this transformation, the ^{1}H and ^{31}P NMR spectra of solutions of II, measured after standing for a short while, show the signals of I and III together with those of II. After having a CDCl$_3$ solution of II at 20 °C to stand for 24 h, the molar ratio of the compounds I:II:III, as determined from the integrated intensities of the η-C$_5$H$_5$ proton signals, was 1:8:1.



Interestingly, the reverse reaction (3b) of the ligand redistribution between **I** and **III** also occurs very smoothly. An ^{1}H NMR study of the equimolar mixture of **I** and **III** in CDCl$_3$ solution showed the appearance of the complex **II** within 2 h of dissolving. Concentration of **II** increased gradually within hours, whereas those of **I** and **III** decreased (Fig. 2). Chromatography of the reaction mixture obtained over a period of 20 h led to isolation of the complexes **I**, **II**, and **III** in 8, 76 and 8% yields, respectively. It should be emphasized that almost the same proportion of these complexes has been found as a result of the disproportionation of **II** (reaction (3a)).

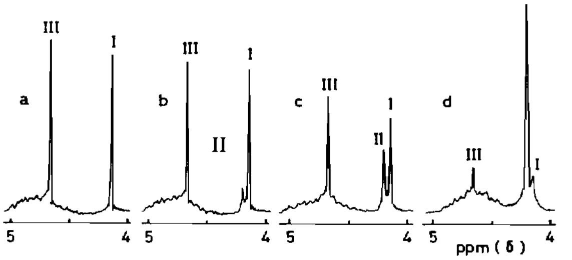


Fig. 2. The time-dependant ^{1}H NMR spectra in the η-C$_5$H$_5$ region demonstrating the gradual formation of Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$](PPh$_3$) (**II**) from the equimolar mixture of Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (**I**) and Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (**III**) in CDCl$_3$ solution at 20 °C. The spectra were measured after: (a) 30 min, (b) 2 h, (c) 6 h, (d) 20 h after dissolving of **I** and **III**.

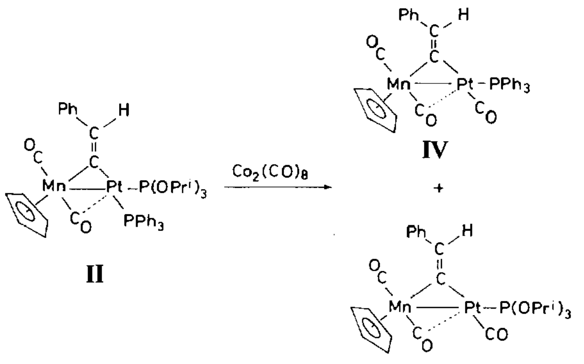
Consequently, the equilibrium in the reversible reaction (3) is substantially shifted to the left:

$$2\mathrm{II} \underset{(b)}{\overset{(a)}{\rightleftarrows}} \mathrm{I} + \mathrm{III} \qquad (3)$$

Unlike the μ-aryl(methoxy)carbene complexes with the M–Pt bonds (M = Mn, W) [7, 10], no appreciable cleavage of the $\overline{\mathrm{MnPt}(\mu\text{-C}{=}\mathrm{C})}$ cycle was observed in reactions of carbon monoxide with complexes **I**–**III**. After bubbling of a stream of CO gas into a benzene solution of **I** at 20 °C for 7 h, 92% of the unreacted **I** was returned, and the tricarbonyl complex Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)(CO) (**IV**) was produced in 5% yield. The bubbling of CO through a benzene solution of **II** for 13 h followed by chromatography afforded 77% of the starting complex, accompanied with small quantities (*ca.* 7% yield for each) of **I** and **III**, which were obviously formed in the disproportionation reaction (3a). The complex **III** proved to be also inert to the action of CO gas.

However, the use of dicobalt octacarbonyl as a source of CO allowed us to obtain the tricarbonyl complexes Cp(CO)$_2$MnPt(μ-C=CHPh)(L)(CO) (L = PPh$_3$ (**IV**), P(OPr^i)$_3$ (**V**)) in good yields. In reaction (4) of **I** with Co$_2$(CO)$_8$ (molar ratio 1:1, 20 °C, 1 h) the yield of **IV** was 95%, and in addition Co$_2$(CO)$_7$(PPh$_3$) was formed. The reaction (5) between **III** and Co$_2$(CO)$_8$ proceeds analogously to give **V** and cobalt carbonyl phosphite species, Co$_2$(CO)$_7$[P(OPr^i)$_3$] and Co$_2$(CO)$_6$[P(OPr^i)$_3$]$_2$. The spectral characteristics of both **IV** and **V** (*vide infra*) indicate that the CO group attached to the Pt atom is *trans* to the bridging carbon atom, as well as in μ-carbyne compounds (**F**) with the W–Pt bonds [12].

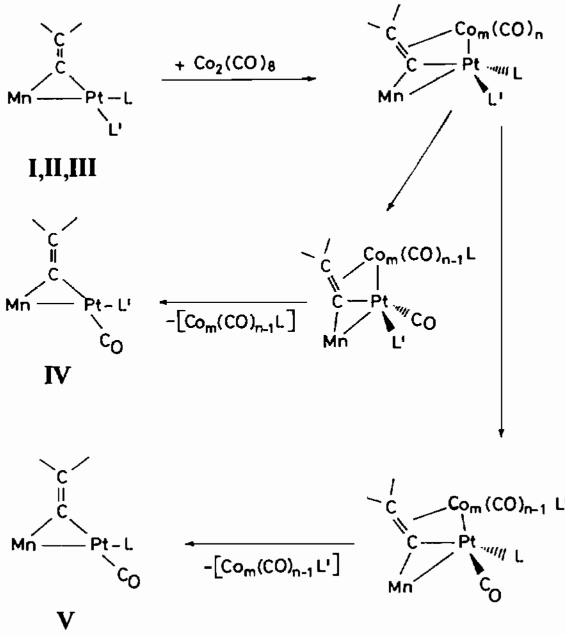
The mixed-ligand complex **II** reacts with Co$_2$(CO)$_8$ to give a mixture of both the tricarbonyl complexes **IV** and **V** in approximate ratio of 1:2 (reaction (6)). Remarkably, the formation of **IV** from **II** involves the changing of a PPh$_3$ ligand position from *trans* to *cis* relative to the μ-C atom:



(6)

The ease of formation of **IV** and **V** in reactions of Co$_2$(CO)$_8$ with **I**, **II** and **III**, in contrast with that by direct action of the gaseous CO on the same complexes, allows us to suppose the pathway of reactions (4), (5) and (6) shown in Scheme 2. Possibly, the first stage consists of a coordination of a Co$_m$(CO)$_n$

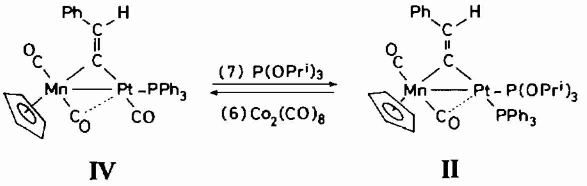
moiety (m = 1 or 2) onto the $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ molecule resulting in three- or four-metal cluster intermediates, whose structure probably resembles those described in [16, 17]. The further intramolecular exchange of CO and L between cobalt- and platinum-bonded positions, followed by the cleavage of a cluster, should generate the tricarbonyl complexes **IV** or **V** together with $Co_2(CO)_{8-n}L_n$ (n = 1 or 2) species. A conformation of the Pt atom in proposed clusters should be very different from the square-planar one, and it makes possible a transfer of both phosphine and phosphite ligand from platinum to cobalt, affording the parallel formation of **IV** and **V** from **II** in the case of reaction (6).



L = L′ = PPh_3 (I); L = $P(OPr^i)_3$, L′ = PPh_3 (II); L = L′ = $P(OPr^i)_3$ (III); L′ = PPh_3 (IV); L = $P(OPr^i)_3$ (V).

Scheme 2.

We made an attempt to prepare the isomer of **II**, containing the *cisoid*-μ-C-Pt-PPh_3 fragment by treating **IV** with $P(OPr^i)_3$ (molar ratio 1:2, 20 °C, 1 h; reaction (7)). However, the only products of this reaction were the complexes **II** and **III** isolated in 38% and 46% yields, respectively. The latter was obviously formed by the action of an excess of $P(OPr^i)_3$ on the complex **II** produced in the first stage (*cf.* reaction (1)). Thus, the equation (7) represents the reverse process to one of the directions of reaction (6) and includes the *cis*-to-*trans* site change of the platinum-bound PPh_3 group relative to the μ-C atom:



It can be seen from Scheme I that the complex **II** has been prepared by four different routes (reactions (1), (2), (3b) and (7)), and that there were no cases of formation of its isomer. The reasons for the preference of the resulting configuration of **II** with $P(OPr^i)_3$ *cis* and PPh_3 *trans* to the bridging carbon atom are not yet clear, as well as a mechanism of a twisting of PPh_3 at the Pt atom in the reactions (6) and (7). This mechanism is possibly similar to that proposed in [18] for a monomolecular *cis-trans* photo-isomerization of the square-planar platinum(II) complexes, including a tetrahedral transitional state.

Decomposition of the μ-vinylidene complexes **I**–**V** under various conditions was studied, since we expected in this way to synthesize, homometallic di- or triplatinum μ-vinylidene species, by analogy with preparation of the μ-carbene polynuclear platinum complexes from compounds with the M–Pt (M = Mn, Cr, W) bonds bridged by Fischer-type carbene [7, 10, 11]. It should be noted that the stable μ-vinylidene diplatinum complex, $[(PhC{\equiv}C)(PEt_3)_4Pt_2(\mu\text{-}C{=}CHPh)][BF_4]$, has been recently reported [19]. Earlier, using $Cp(CO)_2Mn{=}C{=}CHPh$ as a precursor, we have realized a transfer of the $C{=}CHPh$ ligand from manganese to rhenium [6], as well as onto a triosmium metallacycle [1, 20], and showed that these processes occurred via heterometallic intermediate compounds.

However, our attempts to prepare μ-vinylidene platinum complexes from **I**–**V** were unsuccessful. The dicarbonyl compounds **I**–**III** turned out to be quite stable in solution both to the action of CO gas and thermally; thus, **I** did not decompose under reflux in toluene for 10 h. The tricarbonyl complexes **IV** and especially **V**, which is light-sensitive too, are much less stable than are **I**–**III**, but no appreciable decomposition of a benzene solution of **IV** was observed under action of CO gas or $Co_2(CO)_8$ at room temperature for 24 h. UV-irradiation of solutions of **I** or **IV** at 5 °C for 4 h, as well as boiling of **IV** in benzene for 4 h, led to the complete degradation of these compounds to afford, according to TLC data, a great number (about 20) of small fractions, each of them apparently not a desirable product.

The spectroscopic characteristics of the complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ are summarized in Tables I–IV, in which, besides data for new compounds **II**–**V**, more precise data for complexes with

TABLE I. IR Spectra of the Complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ (I–VII) in the CO Stretching Region (in CH_2Cl_2 Solutions).

Compound		ν(CO) (cm^{-1})	$\Delta\nu$ (cm^{-1})
I	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$	1924s, 1838m	86
II	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](PPh_3)$	1926s, 1842m	84
III	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3]_2$	1929s, 1863m	66
IV	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$	2032s, 1938s, 1871m	67
V	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](CO)$	2045s, 1928s, 1867m	61
VI	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OEt)_3]_2$	1930s, 1858m	72
VII	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPh)_3]_2$	1944s, 1876m	68

$L = L' = PPh_3$ (**I**), $P(OEt)_3$ (**VI**) and $P(OPh)_3$ (**VII**) than those reported in [3] are also given.

As was to be expected, the IR spectra of **II** and **III** in the ν(CO) region are very similar to those of **I**, **VI** and **VII** (Table I). The spectra of the tricarbonyl complexes **IV** and **V** each show an additional high-frequency band due to the stretching vibrations of the platinum-bound carbonyl, which frequency, in accordance with a donor capacity of ligands, decreases by 13 cm^{-1} when $P(OPr^i)_3$ is replaced by PPh_3.

On the basis of IR and ^{13}C NMR data, we have previously assumed [3] that in the complexes of this type one of two CO ligands linked to manganese is semi-bridging to platinum. Therefore, it would seem reasonable to expect that a difference in donation of an electron density from platinum onto a semi-bridging CO group, which perhaps takes place within the series studied, must be reflected in separations, $\Delta\nu$, between two manganese-bound carbonyl bands observed in the IR spectra.

The consideration of data given in Table I led to the following observations: (a) the replacement of both PPh_3 ligands in **I** by phosphites (complexes **III**, **VI** and **VII**) results in a decreasing of $\Delta\nu$ values by 14–25 cm^{-1}; (b) when only one ligand *trans* to μ-C is replaced by another, *e.g.*, in going from **I** to **IV** and from **II** to **III**, the changes in $\Delta\nu$ values are also significant (18–19 cm^{-1}); (c) on the contrary, when a ligand *cis* to μ-C undergoes replacement, *i.e.*, in going from **I** to **II** and from **IV** to **V**, the differences in $\Delta\nu$ values are barely noticeable (2–6 cm^{-1}). Hence, it follows that the presence of the strong electron-donor PPh_3 ligand at the Pt atom *trans* to the μ-C=CHPh group is favourable for an increase in a degree of the platinum–semi-bridging carbonyl interaction. On the other hand, the nature of a ligand at the Pt atom in *cis*-position to μ-C only slightly influences this interaction.

The ^{13}C-$\{^1H\}$ NMR spectra of all studied complexes (Table II) each show a characteristic low-field resonance of the α-carbon of bridging phenylvinylidene ligand in a narrow diapason of δ 259–265 ppm, with the ^1J(CPt) coupling constants in the range of 817–917 Hz typical for platinum compounds with the Pt–C σ-bond [21]. The vinylidene proton signals were found in the ^1H NMR spectra (Table III) at δ 7.7–8.9 ppm with ^3J(HPt) values in the range of 17–41 Hz and long-ranged spin–spin coupling constants, ^4J(HP), varying from 11.9 to 22.3 Hz.

The very valuable information concerning the structure of products of the ligand substitution reactions has been obtained from the ^{31}P-$\{^1H\}$ NMR spectra (Table IV). In the spectra of **I**, **III** and **VI** the signals of two non-equivalent phosphorus ligands are observed, and, as it has been accepted in the preceeding paper [3], the signal with the greater value of ^1J(PPt) is assigned to the ligand *trans* to the Mn atom.

The ligand arrangement in $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](PPh_3)$ (**II**) is established by comparison of its ^{31}P and ^{13}C NMR spectra with those of **I** and **III**. In the ^{31}P NMR spectrum of **II** the great value of the ^1J(PPt) constant of 7048 Hz for the phosphite signal at δ 133.9 ppm is in accord with being of the $P(OPr^i)_3$ group in *trans*-position to manganese. On the other hand, the minor value of ^1J(PPt) of 2356 Hz for the PPh_3 signal at δ 29.4 ppm is consistent with *trans*-position of this ligand to the μ-C=CHPh group. An analogous conclusion follows from consideration of the ^2J(CP) values for the bridging carbon resonances in the ^{13}C NMR spectra of **I**–**III** and **VI**. The splitting of this signal in a doublet is due to the coupling with the ^{31}P nucleus of a ligand *trans* to the μ-C atom, and a value of ^2J(CP) depends on the nature of a phosphorus ligand. From Table II it is seen that the ^2J(CP) values for the bis-phosphite complexes **III** and **VI** are greater by *ca.* 30 Hz than that for the bis-phosphine compound **I**, whereas those for **I** and **II** are very close (61.4 and 61.0 Hz, respectively). All these facts indicate unequivocally that only the PPh_3 ligand in **II** is *trans* to the μ-C=CHPh group.

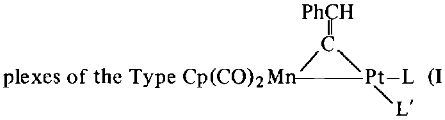
TABLE II. ^{13}C-{^{1}H} NMR Data (δ, ppm relative to TMS [J (Hz)]) for the Complexes Cp(CO)$_2$MnPt(μ-C=CHPh)LL′ (L = L′ = PPh$_3$ (I); L = P(OPr^i)$_3$, L′ = PPh$_3$ (II); L = L′ = P(OPr^i)$_3$ (III); L = PPh$_3$, L′ = CO (IV); L = L′ = P(OEt)$_3$ (VI)) in CDCl$_3$ Solutions at 30 °C.

Compound	μ-C^1=C^{2}H–C$_6$H$_5$					CO	C$_5$H$_5$	Other groups	
	C^1	C^2	C$_6$H$_5$						
			C$_{ipso}$	C$_o$, C$_m$	C$_p$				
I	264.30d [J(CP) 61.4 and ≤2.5, J(CPt) 857.3]	141.25s,br [J(CP) ≤ 6.7, J(CPt) 114.5]	144.00t [J(CP) 12.7, J(CPt) 24.7]	127.35s 125.81s	123.05s	233.75br 229.84br	84.19s	PC$_6$H$_5$	134.74d (C$_o$ [J(CP) 11.1]) 129.45s (C$_p$ [J(CP) ≤ 4]) 127.52d (C$_m$ [J(CP) 5.6]) 127.46d (C$_{ipso}$ [J(CP) 12.1, J(CPt) ≤ 35.0]
II	259.97d [J(CP) 61.0 and ≤2, J(CPt) 858.6]	140.27d [J(CP) 6.0, J(CPt) 122.0]	143.62dd [J(CP) 14.2 and 10.2]	127.65s 125.95s	123.48s	231.30br 229.70br	83.82s	PC$_6$H$_5$	135.15d (C$_{ipso}$ [J(CP) 50.8, J(CPt) 16.3]) 134.64d (C$_o$ [J(CP) 12.2, J(CPt) 12.3]) 129.47s (C$_p$ [J(CP) ≤ 3]) 127.85d (C$_m$ [J(CP) 4.1])
								OCH	69.51s [J(CPt) 16.3]
								CH$_3$	23.78d [J(CP) 4.1]
III	259.48d [J(CP) 91.5 and ≤6, J(CPt) 817.5]	141.36d [J(CP) 6.5, J(CPt) 117.8]	143.44dd [J(CP) 20.7 and 9.8, J(CPt) 26.2]	127.81s 126.12s	123.56s	231.76br 229.21br	84.40s	OCH	68.70s [J(CPt) ≤ 8.7] 69.96s [J(CPt) 19.6]
								CH$_3$	24.37s [J(CP) ≤ 6.5] 24.06s [J(CP) 4.4]
IV	260.48s [J(CP) ≤ 2.5, J(CPt) 916.9]	146.34d [J(CP) 4.5, J(CPt) 123.4]	142.51d [J(CP) 8.1, J(CPt) 9.5]	127.77s 126.37s	124.45s	232.41br 228.14br 195.77d [J(CP) 2.7, J(CPt) 1270.9]	85.05s	PC$_6$H$_5$	134.28d (C$_o$ [J(CP) 12.2, J(CPt) 23.1]) 131.70d (C$_{ipso}$ [J(CP) 50.2, J(CPt) 37.0]) 130.73s (C$_p$ [J(CP) ≤ 4.5]) 128.34d (C$_m$ [J(CP) 9.5])
VI	259.80d [J(CP) 91.6 and ≤3.7, J(CPt) 825.4]	141.08d [J(CP) 6.8 and ≤1.9, J(CPt) 123.3]	143.40dd [J(CP) 19.4 and 10.4, J(CPt) 19.4]	127.80s 126.03s	123.61s	231.19br 229.30br	84.19s	OCH$_2$	60.95s [J(CP) ≤ 0.9, J(CPt) 19.4] 60.48s [J(CP) ≤ 0.5, J(CPt) 13.9]
								CH$_3$	16.25d [J(CP) 7] 16.03d [J(CP) 7]

TABLE III. ^{1}H NMR Spectra (δ, ppm [J(Hz)]) at 20 °C of the Complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ (L = L' = PPh_3 (I); L = $P(OPr^i)_3$, L' = PPh_3 (II); L = L' = $P(OPr^i)_3$ (III); L = PPh_3, L' = CO (IV); L = $P(OPr^i)_3$, L' = CO (V); L = L' = $P(OEt)_3$ (VI); L = L' = $P(OPh)_3$ (VII)).

Complex	Solvent	=CH	C_5H_5	Other groups
I	$CDCl_3$		4.15s	7.50–7.01m (36H, =CH, PC_6H_5 and CC_6H_5)
	C_6D_6	7.92t [J(HP) 12.5, J(HPt) 25.6]	4.12s	7.45m, 7.05m, 6.80m (35H, PC_6H_5 and CC_6H_5)
II	$CDCl_3$	8.72dd [J(HP) 15.2 and 13.3, J(HPt) 16.8]	4.20s	7.73–7.36m (20 H, PC_6H_5 and CC_6H_5) 4.68m (3H, OCH) 1.01d (18H, CH_3)
III	$CDCl_3$	8.64dd [J(HP) 14.9 and 20.2, J(HPt) 23.7]	4.68s	7.73dd and 7.26m (5H, C_6H_5) 4.74m (6H, OCH) 1.35d and 1.33d (36H, CH_3)
IV	$CDCl_3$	7.74d [J(HP) 11.9, J(HPt) 40.5]	4.72s	7.50–7.15m (20 H, PC_6H_5 and CC_6H_5)
	C_6D_6	8.05d [J(HP) 11.9, J(HPt) 40.5]	4.43s	7.68–6.78m (20 H, PC_6H_5 and CC_6H_5)
V	$CDCl_3$	8.85d [J(HP) 15.2, J(HPt) 31.3]	4.69s	7.73dd and 7.28m (5H, C_6H_5) 4.73m (3H, OCH) 1.34d (18H, CH_3)
VI	$CDCl_3$	8.76dd [J(HP) 15.9 and 20.8, J(HPt) 24.7]	4.71s	7.76dd and 7.26m (5H, C_6H_5) 4.12m (12H, OCH_2) 1.36t and 1.32t (18H, CH_3)
VII	$CDCl_3$	8.62dd [J(HP) 16.2 and 22.3, J(HPt) 30.9]	4.24s	7.18–7.10m (35H, OC_6H_5 and CC_6H_5)

TABLE IV. ^{31}P-{^{1}H} NMR Data (in $CDCl_3$) for the Complexes of the Type



$Cp(CO)_2Mn(\mu\text{-}C{=}CHPh)Pt(L)L'$ (I–IV, VI).

Complex	Ligand	δ (ppm)	^2J(PP) (Hz)	^1J(PPt) (Hz)
I[a]	L = PPh_3	43.5d	17.1	4414
	L' = PPh_3	27.4d	17.1	2607
II[b]	L = $P(OPr^i)_3$	133.9d	≤11	7048
	L' = PPh_3	29.4d	≤11	2356
III[b]	L = $P(OPr^i)_3$	142.1d	≤11	6640
	L' = $P(OPr^i)_3$	145.3d	≤11	4020
IV[b]	L = PPh_3	36.5s		3966
	L' = CO			
VI[a]	L = $P(OEt)_3$	138.9d	17.4	6586
	L' = $P(OEt)_3$	148.8d	17.4	3898

[a] At −50 °C, downfield from external 85% H_3PO_4. [b] At 30 °C, downfield from external 1% H_3PO_4.

The ^{13}C NMR spectra of all studied complexes I–IV, VI (Table II) each show two resonances in the range of δ 228–234 ppm, due to the non-equivalent CO groups linked to the Mn atom. The platinum-bound carbonyl in $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (IV) is seen as a narrow doublet signal at δ 195.77 ppm [^2J(CP) 2.7 Hz, ^1J(CPt) 1270.9 Hz] (Fig. 3). The absence of a splitting of the vinylidene α-carbon signal at δ 260.48 ppm in the spectrum of IV indicates the *transoid-μ-*C–Pt–CO relationship. The comparison of the ^1J(PPt) values for IV and I (Table IV) supports this inference.

The substitution of the PPh_3 ligand in I by a more electron-withdrawing CO group leads to the increase in values of ^1J(CPt) by *ca.* 60 Hz and ^3J(HPt) by *ca.* 15 Hz, as well as to the downfield shift of the vinylidene proton resonance by 0.13 ppm in the spectra of IV as compared with those of I (see Tables II and III). The analogous regularities, found from a consideration of the spectral data for II, III and V, confirm the similarity in structures of the tricarbonyl compounds IV and V.

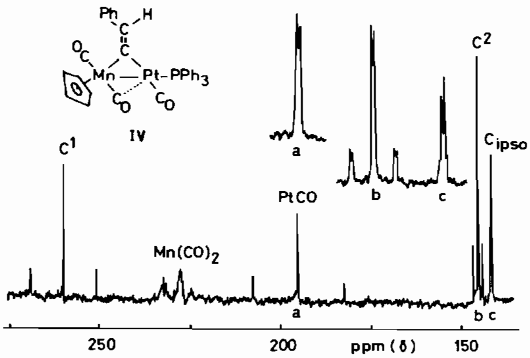


Fig. 3. The low-field part of the $^{13}C\text{-}\{^1H\}$ NMR spectrum of Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)(CO) (**IV**) in CDCl$_3$ solution.

It is of interest that the complexes **I–VII** can be subdivided into two sets depending on the chemical shift of the η-C$_5$H$_5$ protons in the ^{1}H NMR spectra (Table **III**). The complexes **III–VI** get into the first set, where the η-C$_5$H$_5$ signals lie in a narrow interval of δ 4.68–4.72 ppm (in CDCl$_3$ solutions). Characteristically, the nature of alkyl substituents (R) in a P(OR)$_3$ ligand, as well as the replacement of the P(OPr^i)$_3$ ligand being in *cis*-position to the Mn atom by CO, have no influence on the η-C$_5$H$_5$ chemical shift. In the second set, the complexes **I**, **II** and **VII**, each containing PPh$_3$ or P(OPh)$_3$ ligand in *cis*-position to manganese, have the η-C$_5$H$_5$ resonances at δ 4.15–4.24 ppm, which is shifted upfield by *ca.* 0.50 ppm from those of the complexes of the first set. Obviously, this effect is due to an influence of magnetic anisotropy of phenyl groups on the chemical shifts of the cyclopentadienyl protons. It seems to be that in the Cp(CO)$_2$MnPt(μ-C=CHPh)LL′ molecules the distance between the cyclopentadienyl group coordinated the manganese and phenyl substituent of the platinum-bound phosphorus ligand, which is *cis* to the Mn atom, is rather small.

Further conclusions can be drawn from the above results. A chemical behaviour of the μ-phenylvinylidene manganese–platinum complexes (**A**) differs substantially from that of compounds (**B**), (**C**) and (**D**) (see Introduction), and a difference in stability of a dimetallacyclopropane ring system of these compounds plays an important part. The MnM(μ-C) cycle of complexes (**A**), including an electron-rich Pt atom, is more stable than that of (**B**) and especially (**C**), which contain only the VII Group metals. Additional strengthening of the MPt(μ-C) system of (**A**), as compared with those of (**D**) where M = Mn and of related μ-carbene compounds where M = Cr, W is obviously due to the presence of the vinylidene C=C double bond in (**A**), conjugated probably with dimetallacycle.

The phenylvinylidene complexes (**A**) show more resemblance to the μ-arylcarbyne complexes with the μ-C=M double bond (M = W, Mn) than to the μ-aryl(methoxy)carbene species (**D**). The facile ligand substitution reactions at the Pt atom in Cp(CO)$_2$MnPt(μ-C=CHPh)LL′ by PPh$_3$, P(OR)$_3$ or CO, all proceeding without the cycle opening, support this similarity. Nevertheless, it is necessary to emphasize that the direction of substitution reactions for μ-vinylidene compounds (**A**), in contrast to those reported for the μ-carbyne and μ-carbene complexes, is not determined only by *trans*-influence of a bridging carbon atom, but depends on the nature of an entering ligand.

Experimental

All operations were carried out in dry solvents under argon atmosphere. The course of all reactions was followed by means of TLC on Silufol plates. Chromatographic separation of products was performed on columns with neutral alumina (Brockman Activity II). The synthesis of Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (**I**) has been described in [3].

The IR spectra were registered on a Specord IR-75 spectrometer. ^{1}H NMR spectra were recorded on Tesla BS-467 (60 MHz), and $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra on a Bruker WP-200 SY (50.31 and 81.01 MHz, respectively) instruments.

Reaction of Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (I) with P(OPr^i)$_3$

To a solution of 0.300 g (0.30 mmol) of **I** in 25 ml of benzene was added 0.200 g (0.96 mmol) of P(OPr^i)$_3$, and the mixture was stirred at 20 °C for 2 h. After removal of the solvent *in vacuo*, the oily residue was dissolved in a hexane–benzene mixture (2:1) and chromatographed on a column. The first bright-yellow zone eluted with a hexane–benzene mixture (7:1) gave, after evaporation *in vacuo*, 0.166 g (62%) of bright-yellow crystals of Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (**III**), m.p. 146 °C (dec.), from pentane. Found: C 44.70, H 5.99%. $C_{33}H_{53}O_8P_2MnPt$. Calcd.: C 44.54, H 5.96%.

The second bright-yellow zone eluted with a hexane–benzene mixture (5:1) gave 0.105 g (37%) of orange crystals of Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$](PPh$_3$) (**II**), m.p. 178 °C (dec.) after recrystallization from diethyl ether and drying *in vacuo* at 40 °C. Found: C 53.30, H 4.96%. $C_{42}H_{47}O_5P_2MnPt$. Calcd.: C 53.42, H 4.98%.

Reaction of Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPr^i)$_3$]$_2$ (III) with PPh$_3$

A solution of 0.450 g (0.50 mmol) of **III** and 0.655 g (2.50 mmol) of PPh$_3$ in 25 ml of benzene was stirred at 20 °C for 3 h. The solvent was then removed *in vacuo*, the oily residue was dissolved in 3 ml of a hexane–benzene mixture (1:1) and chromatographed. Two yellow bands were successively eluted with hexane–benzene mixtures, (7:1) and then (5:1). The first fraction contained 0.090 g (20%) of unreacted **III**. The second fraction gave 0.330 g (69%) of orange crystalline product identical, according to TLC, m.p. 178 °C (dec.), IR, ^{1}H, and ^{31}P NMR spectra, with the compound **II** prepared in the above experiment.

The Interaction between $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (I) and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3]_2$ (III)

A solution of the mixture of 0.100 g (0.10 mmol) of **I** and 0.090 g (0.10 mmol) of **III** in 0.5 ml of $CDCl_3$ was maintained in a NMR sample tube at 20 °C, and a course of the reaction was followed by means of ^{1}H NMR spectroscopy. The spectrum of an initial solution showed two signals of the η-C_5H_5 protons at δ 4.15 and 4.68 ppm for **I** and **III**, respectively. After 2 h a signal at δ 4.20 ppm of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](PPh_3)$ (**II**) appeared. The reaction continued for 20 h, and the solvent was then removed *in vacuo*. The residue obtained was dissolved in *ca.* 3 ml of a hexane–benzene mixture (1:1) and chromatographed on a column to yield 0.016 g (8%) of **I**, 0.015 g (8%) of **III**, and 0.144 g (76%) of **II**.

Reaction of I with $Co_2(CO)_8$

A solution of 0.400 g (0.40 mmol) of **I** and 0.140 g (0.41 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was stirred at 20 °C for 1 h, until **I** disappeared (in accord with TLC). The reaction mixture was filtered, and the residue obtained after evaporation of the fitrate *in vacuo* was extracted with a benzene–hexane mixture (1:1). The solvent was again removed *in vacuo*, and the resulting oil was dissolved in 3 ml of the same mixture of solvents and placed into an alumina column. The red-brown band eluted with a hexane–benzene mixture (3:1) gave after evaporation the brown precipitate (0.037 g) containing $Co_2(CO)_7(PPh_3)$ (IR identified) and traces of $CpMn(CO)_3$. Further elution with a hexane–benzene mixture (1:1) afforded a bright-yellow zone, which gave 0.290 g (95%) of red-orange crystals of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (**IV**), m.p. 97 °C, from diethyl ether. Found: C 53.77; H, 4.21%. $C_{34}H_{26}O_3PMnPt$. Calcd.: C 53.47, H 3.41%.

Reaction of I with Carbon Monoxide

A stream of CO gas was bubbled in a solution of 0.300 g (0.30 mmol) of **I** in 10 ml of benzene at 20 °C for 7 h. The reaction mixture was concentrated *in vacuo* and separated on a column. Two yellow zones were eluted with hexane–benzene mixtures, (2:1) and then (1:1). From the first fraction after removal of a solvent *in vacuo* and treatment of the resulting oil with a hexane–diethyl ether mixture, 0.011 g (5%) of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (**IV**) was isolated. The second fraction contained 0.276 g (92%) of the starting material.

Reaction of III with $Co_2(CO)_8$

A solution of 0.285 g (0.32 mmol) of **III** and 0.121 g (0.35 mmol) of $Co_2(CO)_8$ in 20 ml of hexane was stirred at 20 °C for 2 h. The reaction mixture was then filtered, the filtrate concentrated to *ca.* 3 ml and chromatographed. Elution with hexane afforded a narrow brown zone, which after removal of the solvent *in vacuo* gave 0.049 g of a red-brown precipitate, identified by IR as $Co_2(CO)_7[P(OPr^i)_3]$. The second brown zone, eluted with a hexane–diethyl ether mixture (15:1), gave 0.016 g of a brick-red precipitate containing $CpMn(CO)_3$ and $Co_2(CO)_6[P(OPr^i)_3]_2$. Further elution with a hexane–diethyl ether mixture (10:1) afforded a broad yellow zone, from which an oily product was obtained. The treatment of this oil with pentane followed by re-crystallization gave 0.116 g (51%) of orange crystals of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](CO)$ (**V**), m.p. 70 °C (dec.). Found: C 41.29, H 4.80%. $C_{25}H_{32}O_6PMnPt$. Calcd.: C 42.31, H 4.50%.

Reaction of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](PPh_3)$ (II) with $Co_2(CO)_8$

A solution of 0.300 g (0.32 mmol) of **II** and 0.110 g (0.32 mmol) of $Co_2(CO)_8$ in 15 ml of benzene was stirred at 20 °C for 2 h. After removal of a solvent *in vacuo*, the residue was extracted with a hexane–benzene mixture (10:1), the extract was filtered, concentrated to *ca.* 3 ml and chromatographed. The elution was followed with first hexane and then with hexane–diethyl ether (25:1), (10:1) and (1:1) mixtures. From the yellow band eluted with (10:1) mixture, 0.120 g (53%) of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3](CO)$ (**V**) was isolated, and the next yellow band eluted with a (1:1) mixture gave 0.074 g (31%) of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (**IV**), both identical with those obtained in above experiments.

Reaction of II with Carbon Monoxide

A stream of CO gas was bubbled at 20 °C in a solution of 0.300 g (0.32 mmol) of **II** in 15 ml of benzene for 13 h. By chromatography of the reaction mixture on a column with successive elution with hexane–diethyl ether (10:1) and (5:1) mixtures and then with diethyl ether, three yellow fractions were obtained, containing 0.020 g (7%) of **III**, 0.230 g (77%) of **II** and 0.024 g (7%) of **I**, respectively.

Reaction of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (IV) with $P(OPr^i)_3$

A solution of 0.223 g (0.30 mmol) of **IV** and 0.125 g (0.60 mmol) of $P(OPr^i)_3$ in 12 ml of benzene was stirred at 20 °C for 1 h, concentrated *in vacuo* and chromatographed. Elution with hexane–benzene mixtures, (7:1) and then (5:1), gave 0.122 g (46%) of **III** and 0.106 g (38%) of **II**, both identical with the corresponding species prepared above.

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