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Review

Use of the $Mn=C=C$ system in organometallic and organic synthesis

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This article is dedicated to the memory of my colleagues, joint authors and good friends Professor Alfred A. Johansson (Ioganson) (1939–1996), Mrs. Nina A. Deykhina (1955–2002) and Dr. Dmitry A. Pogrebnyakov (1972–2003).

Contents

Abbreviations: Acac, acetylacetonate, OCMeCHCMeO; AVR, acetylene-vinylidene rearrangement; Cp, η^5-cyclopentadienyl, C_5H_5; Cp′, η^5-methylcyclopentadienyl, C_5H_4Me; Cp*, η^5-pentamethylcyclopentadienyl, C_5Me_5; CV, cyclic voltammetry; depe, 1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$; dippe, 1,2-bis(diisopropylphosphino)ethane, $(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$; dmpe, 1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$; DmSP, dimetallaspiropentane; dppe, 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; dppm, bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$; dppp, 1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$; Fp, $Fe(CO)_2Cp$; Fp*, $Fe(CO)_2(\eta^5\text{-}C_5Me_5)$; Hfac, hexafluoroacetylacetonate, $OC(CF_3)CHC(CF_3)O$; HMTA, hexamethylenetetramine, $C_6H_{12}N_4$; MCP, methylenecyclopropane; py, pyridine, C_5H_5N; SP, spiropentane; THF, thf, tetrahydrofuran, C_4H_8O; TMM, trimethylenemethane; Tol, *p*-Tolyl, $C_6H_4Me\text{-}4$; XRD, X-ray diffraction

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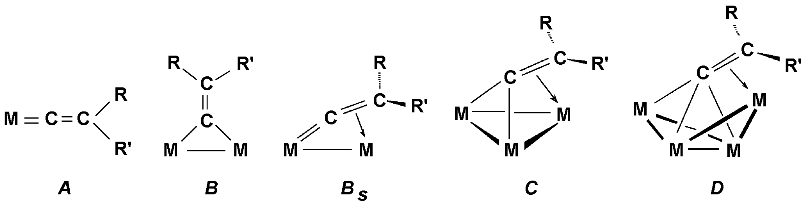
Abstract

The present review summarizes the syntheses, structures, physicochemical properties and reactivity of complexes containing η^1-, μ-, μ_3- and μ_4-vinylidene ligands. Consideration of mononuclear vinylidene complexes is limited to cymantrene derivatives, one of which, viz. $Cp(CO)_2Mn$=C=CHPh (**1**), has served as the precursor for syntheses of many organometallic and some organic compounds. The reactions between phosphites $P(OR)_3$ and complex **1** afford styrylphosphonates PhCH=CHP(O)$(OR)_2$. All the transformations of complex **1** occur under very mild conditions. Special attention is paid to heterometallic complexes**,** containing Mn, Fe and the platinum Group metals with bridging vinylidene ligands. The Mn=C=CHR system is used as a "building block" for a series of dimetal μ-vinylidene complexes including Mn—M bonds (M = Mo, W, Mn, Re, Fe, Rh, Pd, Pt, Cu) and trimetallic MnFePt μ_3-vinylidene clusters. Transmetalation reactions of the MnPd and MnPt complexes have given a series of μ_4-vinylidene $PdFe_3$ and $PtFe_3$ clusters. Transfer of vinylidene from the Mn atom to another metal atom (Re), to the dinuclear (FePt) and cluster (Os_3, $PdFe_3$, $PtFe_3$) systems has been shown. A systematic study of a dependence of structural and spectroscopic parameters of mono-, di-, tri- and tetra-nuclear complexes on the vinylidene coordination mode has been carried out.

Keywords: Vinylidene complexes; Clusters; Manganese; Transition metals; Synthesis; Structures

1. Introduction

Today vinylidene complexes are known for virtually all transition metals [1–5]. Many vinylidene complexes, belonging to five structural types, in which vinylidene is coordinated with one metal atom (***A***), two (***B***, ***B***$_s$), three (***C***) and four (***D***) identical or different metal atoms, have been synthesized. Complexes ***B***, ***C*** and ***D*** can be obtained from the Mn=C=C system.



Various organic compounds and groups, including such monocarbons as CO, CH_2, CH, may serve as a source of vinylidene ligands C=CRR′ (R, R′ = H, alkyl, aryl, halogen, COOR, OR, etc.).

However, when we obtained our first vinylidene complexes $Cp(CO)_2Mn$=C=CHPh (**1**) and $[Cp(CO)_2Mn]_2(\mu$-C=CHPh) (**2**) and determined their structures [6–9], only four crystallographically characterized complexes with $C=CR_2$ ligands were known [10–13], and all had been prepared from organic compounds including C=C bonds, namely ketene and olefins. Thus, starting from Ph_2C=C=O, Pauson and Bagga synthesized the first vinylidene complex $Fe_2(\mu_2$-C=$CPh_2)(CO)_8$, the structure of which (***B*** type) was determined by Mills and Redhouse [10]. King obtained the first vinylidene complex containing a linear metalla-allene system, viz. $Cp[P(OMe)_3]_2(Cl)Mo$=C=$C(CN)_2$ (***A*** type) [11] from Cl_2C=$C(CN)_2$. The same olefin was a precursor for $Cp_2(CO)_2Fe_2[\mu$-C=$C(CN)_2](\mu$-CO) (***B*** type) [11c,12]. Ethylene was a source of vinylidene in the first vinylidene cluster $Os_3(\mu_3$-C=$CH_2)(\mu$-H$)_2(CO)_9$ (***C*** type), obtained by Deeming and Underhill [13].

When we discovered that complexes with C=CHPh ligands could be obtained from PhC≡CH and $CpMn(CO)_2$(thf) at room temperature [7], it seemed incredible. It was known [14] that for the formation of free phenylvinylidene [:C=CHPh] from phenylacetylene, a temperature higher than 550 °C was necessary.

The late Academician A.N. Nesmeyanov, my chief Professor K.N. Anisimov and Professor Yu.T. Struchkov showed great interest in the vinylidene complexes and stimulated research in this new class of organometallic compounds. Professor M.E. Vol'pin, who possessed a wonderful insight, advised us to test our unusual reaction straight away, using different transition metals. Indeed, immediately after $Cp(CO)_2Mn$=C=CHPh (**1**) and $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) [7,15], their rhenium analogues $Cp(CO)_2Re{=}C{=}CHPh$ and $[Cp(CO)_2Re]_2(\mu\text{-}C{=}CHPh)$ were obtained from $Cp(CO)_2Re(thf)$ and $PhC{\equiv}CH$ under the same mild conditions [16].

At the same time, Bellerby and Mays obtained a stable complex of iron $(Cl)(depe)_2Fe{=}C{=}CHPh$, starting from phenylacetylene [17]. Bruce synthesized a series of ruthenium and osmium vinylidene complexes $[Cp(PR_3')_2M{=}C{=}CHR]^+$ (M = Ru, Os; R = H, Me, Ph, C_6F_5, CO_2Me, etc.) from alkynes $RC{\equiv}CH$ and opened a simple way to vinylidene complexes $[L_nM{=}C{=}CRR']$ by means of protonation or alkylation of σ-acetylides $[L_nM{-}C{\equiv}CR]$ [18]. Davison et al. found that similar transformations of $Cp(L)_2Fe{-}C{\equiv}CR$ gave the vinylidene cations $[Cp(L)_2Fe{=}C{=}CRR']^+$ [19]. Shortly after that, it became obvious that vinylidene complexes of any transition metal could be obtained from acetylenes [1–4]. The most common methods of synthesis, viz. the acetylene-vinylidene rearrangement (AVR) on a metal center and protonation or alkylation of σ-acetylide complexes, discovered in 1976–1979, made vinylidene complexes accessible and promoted further development of their chemistry.

After the structure of $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) had been determined [7], the question emerged whether the formation of this dinuclear complex was a result of addition of the $[Cp(CO)_2Mn]$ unit to $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**). The reaction of **1** with $Cp(CO)_2Mn(thf)$, which led to μ-vinylidene complex **2**, confirmed this conjecture [15].

The first heterometallic μ-vinylidene complex $Cp_2(CO)_4MnRe(\mu\text{-}C{=}CHPh)$ was synthesized analogously, by the addition of the $[Cp(CO)_2Re]$ unit to $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) [20]. Addition of the coordinatively unsaturated $[M'L_n]$ fragments to the $M{=}C{=}CHR$ system (***A***) became a common method of synthesis of the dinuclear heterometallic μ-vinylidene complexes with the central $MM'(\mu\text{-}C{=}CHR)$ fragment (***B***) [2]. Dozens of μ-vinylidene complexes with Mn–M, Rh–M, Os–M bonds (M = Mo, W, Mn, Fe, Rh, Pd, Pt, Cu) were obtained by this method by the groups of Kolobova in Moscow, of Werner in Würzburg and in our group in Krasnoyarsk [21–30].

Application of Hoffmann's isolobal relationship [31] resulted in the discovery of a new approach to the synthesis of heterometallic vinylidene clusters [2,32], namely consecutive assembling of the MM′M″ framework with the use of the metalla-allene $M{=}C{=}C$ and methylenedimetallacyclopropane $MM'(\mu\text{-}C{=}C)$ systems as "building blocks". As a result, trimetal μ_3-vinylidene complexes with triangular MnFePt frameworks and MnFePt chain [32,33] and a series of μ_4-vinylidene $PtFe_3$ [33–35] and $PdFe_3$ [29,36–38] clusters were synthesized. The possibility of transfer of the vinylidene from one metal (Mn) to another metal (Re), to the dinuclear (FePt) system and to cluster (Os_3, $PdFe_3$, $PtFe_3$) systems was shown for the first time.

Many aspects of chemistry of vinylidene complexes and their applications to organic synthesis and catalysis have been reviewed [1–5,39–42]. The formation of the mononuclear complexes (***A***), including the $M{=}C{=}C$ system, and their further transformations were mostly considered. However, the formation and specific properties of the systems $M_2(\mu\text{-}C{=}C)$ (***B***), $M_3(\mu_3\text{-}C{=}C)$ (***C***) and $M_4(\mu_4\text{-}C{=}C)$ (***D***) were paid considerably less attention.

Our systematic long-term study of vinylidene complexes chemistry is based mainly on the transformations of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), which is one of the most inexpensive and available of vinylidene complexes. Special attention in the present review is paid to its structure, physicochemical properties and reactivity. The most interesting related complexes including the $Mn{=}C{=}C$ system as well as complexes of other transition metals are separately and compared with **1**. While studying the reactivity of **1**, it has been shown that vinylidene, coordinated to a metal center, can be subjected to hydrogenation, dehydrogenation, C–C bond formation, carbonylation and phosphonylation processes, all under mild conditions. The synthesis of styrylphosphonates $PhCH{=}CHP(O)(OR)_2$ from **1** and phosphites $P(OR)_3$ will be considered in detail.

One of the tasks of the present review is to show the possibility of using the $Mn{=}C{=}C$ system (***A***) in organometallic synthesis by consecutive transitions from ***A*** to ***B*** and further to ***C*** and ***D***, and to discuss the influence of the vinylidene coordination mode (η^1, μ_2, μ_3, μ_4) on the structural and spectroscopic characteristics of vinylidene complexes.

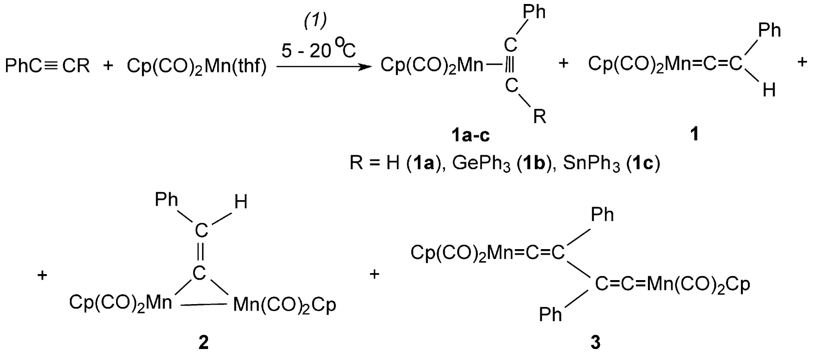
2. Formation and properties of the Mn=C=CRR′ system

2.1. Formation of manganese and rhenium vinylidene complexes from acetylenes

First, we would provide a brief retrospective and describe the history of the discovery of acetylene-vinylidene rearrangement on a metal center.

The unusual manganese complexes obtained by us in 1974 [6] by the interaction of $Cp(CO)_2Mn(thf)$ with alkynes $PhC{\equiv}CGePh_3$, $PhC{\equiv}CSnPh_3$ and $PhC{\equiv}CH$ (reaction *(1)*), were at first formulated as compounds of new types with the C_8H_6 and $C_{16}H_{10}$ ligands, one of which, $Cp(CO)_2Mn(C_8H_6)$ (**1**), was an isomer of π-complex $Cp(CO)_2Mn(PhC{\equiv}CH)$ (**1a**). These compounds differed greatly from all the cymantrene derivatives known at that time by their bright coloring, stability and spectroscopic characteristics. Crystals of **1** were a beautiful wine-red color with a metallic sheen in contrast to the usual color of complexes $Cp(CO)_2Mn(L)$, which are normally yellow or orange. Unlike its unstable oily isomer **1a** [43], complex **1** is quite stable both as solid (dec. >74 °C) and in solution. The ν(CO) bands in the IR spectrum of **1** are 30–70 cm^{-1} higher than those of $Cp(CO)_2Mn(L)$, where L = η^2-alkyne, η^2-olefin, PPh_3. Violet $[Cp(CO)_2Mn]_2(C_8H_6)$ (**2**) and rose $[Cp(CO)_2Mn]_2(C_{16}H_{10})$ (**3**) decompose at 144 and 204 °C, respectively.

Further studies showed three compounds containing phenylvinylidene ligands, viz. $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) and $Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**), were the products of reaction *(1)* along with η^2-alkyne complexes $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CR)$ (**1a–c**) [7,15,44,45].



The proportion of the products of reaction *(1)* depended appreciably on the nature of alkynes $PhC{\equiv}CR$ ($R = H$, $GePh_3$, $SnPh_3$ or $SiPh_3$) [15]. The interaction of $PhC{\equiv}CH$ with $Cp(CO)_2Mn(thf)$ led to a mixture of $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CH)$ (**1a**) (∼20%), vinylidene complexes **1** (2%), **2** (2%) and **3** (3%), and also to $CpMn(CO)_3$ (65%). Complexes $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CGePh_3)$ (**1b**, 15%) and **1** (1%) were obtained from $PhC{\equiv}CGePh_3$. Unstable $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CSnPh_3)$ (**1c**) was converted rapidly into **1**, which was isolated in 15% yield. In contrast, the reaction of $PhC{\equiv}CSiPh_3$ with $Cp(CO)_2Mn(thf)$ gave the stable (dec. >140 °C) orange crystalline $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CSiPh_3)$ (**1d**, 30%), and no sign of vinylidene complex **1** was seen in this reaction.

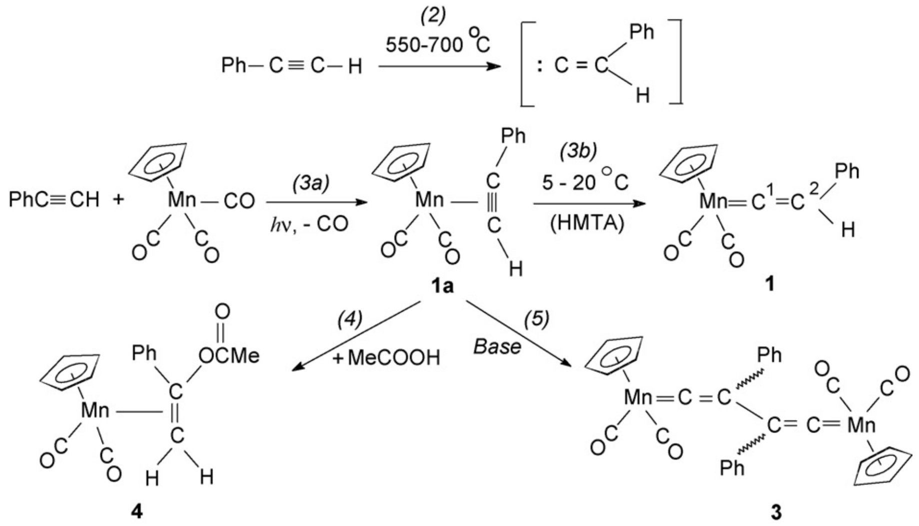
It was evident that the η^2-alkyne complexes $Cp(CO)_2Mn(\eta^2\text{-}PhC^2{\equiv}C^1R)$ (**1a–c**) were formed in the first stage of reaction *(1)*, after which they rearranged into the η^1-coordinated form, i.e. $Cp(CO)_2Mn{=}C^1{=}C^2HPh$ (**1**). The rearrangement of **1b**, **c** was accompanied by the exchange of the $GePh_3$ and $SnPh_3$ groups for the H atom. The fact that these transformations occurred at 5–20 °C seemed most surprising. It was reported [14] that the hypothetical intermediate phenylvinylidene could be formed from phenylacetylene under very harsh conditions (reaction *(2)* in Scheme 1).

The acetylene-vinylidene rearrangement, which occurred in the coordination sphere of the transition metal atom under mild conditions and resulted in the formation of the stable vinylidene complexes, was without precedent at that time. We supposed that the Mn atom played a role of internal catalyst in this process. It was reflected in the scheme of the probable mechanism of rearrangement of alkyne into vinylidene on the manganese center (Scheme 2) [15].

Strohmeier and Hellmann who were the first to get $Cp(CO)_2Mn(PhC{\equiv}CH)$ (**1a**) by reaction *(3a)* [43], noted an extreme instability of this π-complex. Complex **1a** is not isomerized in neutral medium, and chromatography on basic (pH 9–10) alumina provided complex **1** only in a low yield due to decomposition of both **1a** and **1** [15]. The action of amines, pyridine or $KOH/H_2O/ROH$ on **1a** resulted in the bis-vinylidene dimer **3** (reaction *(5)* in Scheme 1).

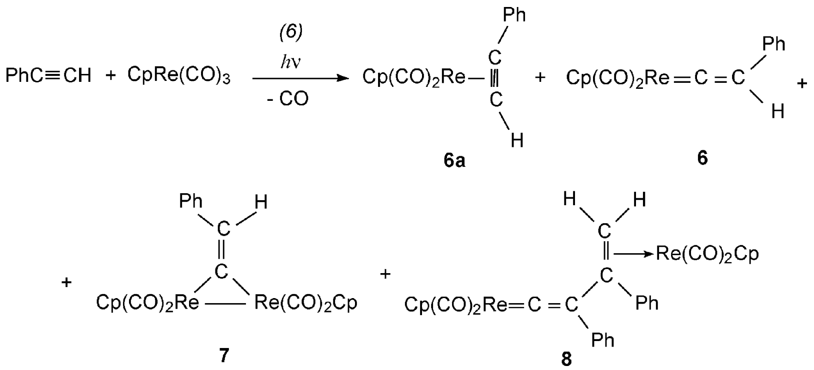
The rearrangement **1a** → **1** (reaction *(3b)* in Scheme 1) is best catalyzed by HMTA, when added to the UV irradiated mixture of $CpMn(CO)_3$ and $PhC{\equiv}CH$ [46].

The action of acetic acid on **1**a (reaction *(4)*) led to the η^2-olefinic complex $Cp(CO)_2Mn[\eta^2\text{-}CH_2{=}C(Ph)OC(O)Me]$ (**4**) [15]. Addition of MeCOOH to the η^2-$PhC{\equiv}CH$ ligand followed Markovnikov's rule [47]. The C=C bond length in **4** is 1.385(2) Å, the average Mn–C (olefin) distances for two independent molecules are 2.20 Å. Free $Ph(MeCOO)C{=}CH_2$, an unstable liquid, was obtained from $PhC{\equiv}CH$ and MeCOOH in the presence of $(MeCOO)_2Hg/BF_3{\cdot}OEt_2$ as catalyst [48].



Scheme 1. *(2)* Isomerization of a free phenylacetylene into phenylvinylidene at 550–700 °C. *(3)* Transformations of the η^2-$PhC{\equiv}CH$ ligand into η^1-$C{=}CHPh$; *(4)* into η^2-$CH_2{=}C(Ph)OC(O)Me$; *(5)* into η^1,η^1-$C{=}CPhCPh{=}C$ on the Mn center at 5–20 °C.

The first rhenium vinylidene complex $Cp(CO)_2Re{=}C{=}CHPh$ (**6**) was also formed as a result of AVR [16]. Reactions of $Cp(CO)_2Re(thf)$ with $PhC{\equiv}CR$ (R = H, $GePh_3$, $SnPh_3$) in the dark gave η^2-alkyne $Cp(CO)_2Re(\eta^2\text{-}PhC{\equiv}CR)$ (**6a–c**) and vinylidene complexes **6** and **7** [16b]. The dinuclear complex $Cp(CO)_2Re[\eta^2\text{-}H_2C{=}C(Ph)C(Ph){=}C{=}Re(CO)_2Cp]$ (**8**) was an unexpected product of a photochemical reaction *(6)*. According to X-ray data, it contained a terminal vinyl-substituted vinylidene η^2-coordinated to the second rhenium atom [16a].

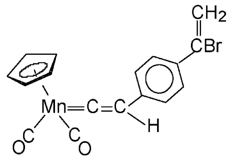


In contrast to the reaction **1a** → **1** *(3b)*, isomerization of **6a** to **6** occurred without the catalyst, due to the higher basicity of the metal center in **6a**. Likewise, $(L)_2(Cl)Rh(\eta^2\text{-}HC{\equiv}CR)$ (L = P(*i*-Pr)$_3$; R = H, Me, Ph, etc.) rearranged into $(L)_2(Cl)Rh{=}C{=}CHR$ in the presence of pyridine (Scheme 3), but analogous $(L)_2(Cl)Ir{=}C{=}CHR$ were formed without pyridine [3a,49a,b].

Unlike **1a**, isomerization of $(\eta^5\text{-}C_5H_4Et)(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CH)$ to $(\eta^5\text{-}C_5H_4Et)(CO)_2Mn{=}C{=}CHPh$ [15] and $Cp^*(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CH)$ (**5a**) into $Cp^*(CO)_2Mn{=}C{=}CHPh$ (**5**) [45b] can occur spontaneously, although HMTA accelerates the AVR and raises the yield of **5**.

Complexes $Cp(CO)_2Mn{=}C{=}CH_2$ (**9**) and $Cp'(CO)_2Mn{=}C{=}CH_2$, formed from $HC{\equiv}CH$, were not isolated under the usual conditions. They were stabilized *in statu nascendi* converting into $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$ (**10**) [50] and $[Cp'(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$ [51], respectively. Complex **9** can be observed in solution at −50 °C [52]. The only mononuclear manganese complex with the parent vinylidene stable at RT is $(Me_3SiC{\equiv}C)Mn{=}C{=}CH_2(dmpe)_2$ (**11**), synthesized by Berke and co-workers [53].

Complexes $(\eta^5\text{-}C_5H_4R)(CO)_2Mn{=}C{=}CHR'$ (R = H, Me), where the R′ substituents include carbon chains, functional groups, heteroatoms or organometallic groups, such as $CH(OMe)_2$ (**12**), $CH(OEt)_2$, $CH[O(CH_2)_3O]$ [54], COOMe (**13**) [55a], $PPh_2[Mn(CO)_2Cp]$ [55b], $Fe(CO)_2Cp^*$ (**14**) [56], were obtained with the help of AVR. The interaction of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CC_6H_4C{\equiv}CH)$ with PhLi and then with H^+ led to $Cp(CO)_2Mn{=}C{=}CHC_6H_4{-}C{\equiv}CH$ [55c]. Addition of HBr to the C≡C bond of the latter gave $Cp(CO)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ (**15**). The reaction of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CC_6H_4C{\equiv}CH)$ with $Cp(CO)_2Mn(thf)$ gave the dinuclear dialkyne $[Cp(CO)_2Mn]_2(\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CC_6H_4C{\equiv}CH)$, where both the C≡C bonds were coordinated to the Mn atoms. After treating this π-complex with an excess of PhLi and then with HCl/Et_2O, the dinuclear bis-vinylidene complex **16** was isolated [55c].



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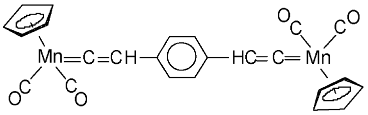

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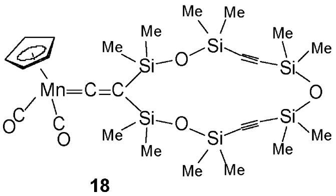

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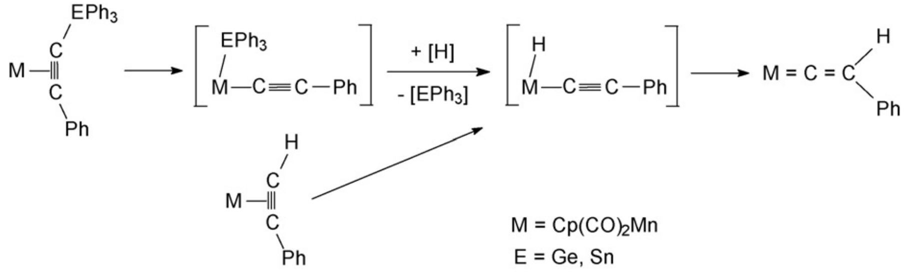
Unusual instances of AVR with migration of iodine or silicon atoms are known. Complexes $Cp(CO)_2Mn[\eta^2\text{-}IC{\equiv}CCH(OR)_2]$, where $(OR)_2 = (OMe)_2$, $(OEt)_2$, $[{-}O(CH_2)_3O{-}]$ rearranged by 1,2-migration of the I atom to form vinylidenes $Cp(CO)_2Mn{=}C{=}C(I)CH(OR)_2$, one of which, $Cp(CO)_2Mn{=}C{=}C(I)CH(OMe)_2$ (**17**), was structurally characterized [57]. The analogous π-complexes with chloro- or bromopropyne-acetals were not subjected to AVR.

Complex $Cp(CO)_2Mn{=}C{=}C(SiMe_2OSiMe_2C{\equiv}CSiMe_2)_2O$ (**18**) was obtained as a result of a cyclic siloxytriyne rearrangement [58]. The 1,2-shift of the Si atom initiated the ring contraction, giving an exocyclic C=C bond, which coordinated to the Mn atom as the terminal vinylidene.

2.2. *Mechanism of acetylene-vinylidene rearrangement*

The probable mechanism of AVR (Scheme 2) was proposed by us for the first time in ref. [15].

By analogy with the known oxidative addition of PhC≡CH or $PhC{\equiv}CSnPh_3$ to complexes of the platinum Group metals, we



Scheme 2. AVR on the Mn center [15].

suggested [15] that rearrangement of π-acetylene complexes $Cp(CO)_2M(RC^1{\equiv}C^2Ph)$ (M = Mn (**1a**–**c**), Re (**6a**–**c**); R = H, $GePh_3$, $SnPh_3$) into vinylidene $Cp(CO)_2M{=}C^1{=}C^2HPh$ (**1**, **6**) occurred through the intermediate formation of σ-phenylethynyl complexes $[(R)M–C^1{\equiv}C^2Ph]$. Subsequent addition of a hydrogen atom to the acetylide C^2 atom led to **1** and **6**. Consequently, Scheme 2 explained the role of the metal atom M = Mn, Re in the then unprecedented formation of **1** [6,7,15] and **6** [16] from $RC{\equiv}CPh$ and $Cp(CO)_2M(thf)$ under very mild conditions.

At present acetylene-vinylidene rearrangements are known for many mono- and polynuclear systems including the Group 3–10 metals [1–5,41,42,49,57–63]. Vahrenkamp et al. have discovered rearrangements of μ_3-acetylene clusters with the M_2M' and $MM'M''$ (M, M′, M″ = Mo, W, Fe, Ru, Co, Ni) frameworks into their μ_3-vinylidene isomers [61]. Werner et al. have synthesized numerous Rh, Ir, Ru vinylidene complexes from various alkynes and have made important contributions to the investigation of the AVR [3,49,62].

In general, AVR is favorable due to thermodynamic and steric factors. Being a part of the linear M=C=C system, vinylidene requires less space than the η^2-coordinated alkyne. As a rule, vinylidene complexes $L_nM{=}C{=}CHR$ are 10–30 kcal/mol more stable than their alkyne precursors $L_nM(\eta^2\text{-}HC{\equiv}CR)$. The tendency towards loss of electron density from electron-rich metal centres is realized here by rearrangement of the η^2-coordinated alkyne into much stronger acceptor η^1-vinylidene, particularly for d^6 and d^8 metal complexes.

AVR becomes more favorable with increase in electron density on a metal center down the Group from Mn to Re, from Fe to Ru and to Os, from Rh to Ir, and also with stronger donor ligands in the metal coordination sphere. For instance, numerous stable non-carbonyl complexes $[Cp^*(PR_3)_2M{=}C{=}CHR]^+$ (M = Ru, Os) have been obtained as a result of AVR [1–5,59,63]. On the contrary, the electron-poor dicarbonyl systems $[Cp(CO)_2Fe{=}C{=}CRR']^+$ (R, R′ = Me, Ph), formed from acyls, transform into π-alkyne complexes [64a]. AVR is unfavorable for some d^2 metal complexes. According to calculations, $F_4W(HC{\equiv}CH)$ is 10.4 kcal/mol more stable than its vinylidene isomer [64b]. The energies of the isomers $[Cp_2(PH_3)Nb{=}C{=}CHMe)]^+$ and $[Cp_2(PH_3)Nb(HC{\equiv}CMe)]^+$ are close to each other, i.e. 0.0 and 2.9 kcal/mol, respectively [64c].

Hoffmann and Silvestre initiated theoretical studies of AVR in 1985 [65]. Three alternative pathways for the transformation of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CH)$ into $Cp(CO)_2Mn{=}C{=}CH_2$ were considered, and intramolecular rearrangement with 1,2-hydrogen shift was calculated to be the energetically preferable process. A barrier for 1,3-hydrogen shift accompanying the oxidative addition of alkyne was considerably higher.

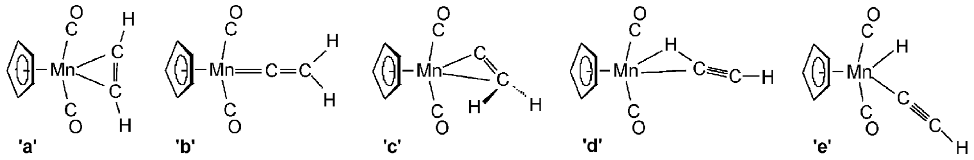
Modern theoretical investigations of the AVR mechanism are mainly based on the calculations with gradient-corrected DFT and on post-Hartree-Fock MP2 calculations. Wakatsuki has recently reviewed the mechanistic and theoretical aspects of AVR [5c].

Based on these calculations, two most probable pathways for the rearrangement of alkyne $\eta^2\text{-}HC^1{\equiv}C^2R$ into vinylidene $\eta^1\text{-}C^1{=}C^2HR$ on a metal center were determined:

(i) intermediate formation of an $\eta^2\text{-}C^1–H$ agostic alkyne followed by 1,2-H shift;
(ii) oxidative addition of an alkyne followed by 1,3-H shift to the C^2 atom.

Pathway (i) is characteristic of d^6 metal complexes.

The rearrangement of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CH)$ to $Cp(CO)_2Mn{=}C{=}CH_2$ was studied with DFT [66a]. Relative energies of five stationary structures in which the $[C_2H_2]$ unit is bound to the $[Cp(CO)_2Mn]$ fragment, namely η^2-acetylene ‘**a**’ ($\Delta E = 9.0$ kcal/mol), η^1-vinylidene ‘**b**’ ($\Delta E = 0.0$ kcal/mol), η^2-vinylidene ‘**c**’ ($\Delta E = 38.4$ kcal/mol), η^2-C–H-coordinated acetylene ‘**d**’ ($\Delta E = 22.6$ kcal/mol) and alkynylhydride ‘**e**’ ($\Delta E = 28.7$ kcal/mol) were calculated.



The energetically preferable route for transformation of ‘**a**’ into ‘**b**’ via the η^2-C–H agostic intermediate ‘**d**’ corresponds to a direct 1,2-H shift with an activation barrier of 27.3 kcal/mol. Another pathway involves transformation of ‘**a**’ into η^2-vinylidene ‘**c**’ via direct 1,2-H shift. The aggregate activation barrier in this case is 45.3 kcal/mol. An alternative mechanism, which includes the oxidative addition with formation of alkynylhydride complex '**e**' also goes via the η^2-C–H agostic alkyne '**d**'. The barrier for transformation of '**a**' into '**e**' is 35.0 kcal/mol, and the barrier for rearrangement of '**e**' into η^1-vinylidene '**b**' by 1,3-H shift is 25.8 kcal/mol.

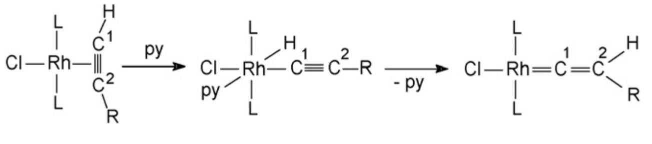
According to the MP2 calculations of $[Cl_2(PH_3)_2Ru(HC{\equiv}CH)]^+$ [67], the minimum activation energy measured with respect to energies of acetylene and $(Cl_2)(PH_3)_2Ru$ of 10 kcal/mol corresponds to a 1,2-H shift. For AVR via alkynylhydride, the barrier is 67.5 kcal/mol.

Rearrangements of $[Cp(PMe_3)_2Ru(HC{\equiv}CH)]^+$ and $[Cp(PMe_3)_2Ru(HC{\equiv}CMe)]^+$ were analyzed by the DFT approach [66b]. The relative energies of the stationary structures considered were found to be in qualitative agreement with those for $Cp(CO)_2Mn(C_2H_2)$ [66a]. Corresponding to the global energy minimum, the η^1-vinylidene Ru derivatives are 13.1 and 10.4 kcal/mol more stable than η^2-ethyne and η^2-propyne complexes, respectively. The 1,2-H shift, proceeding via the η^2-C–H agostic alkyne, is energetically most favorable for both ethyne and propyne. However, the barriers for 1,2-H shift and for the oxidative addition are almost comparable in the case of ethyne rearrangement (26.8 kcal/mol versus 31.7 kcal/mol). This implies that the process (ii) might become competitive. In the cases of the similar Ru complexes with the more electron-releasing ligands, $[Cp^*(PR_3)_2Ru(\eta^2\text{–}HC{\equiv}CR')]^+$, the AVR via alkynylhydride can become preferable [5a,63] (see below).

Pathway (ii) is preferable for d^8 metal complexes. Bianchini et al. provided the experimental proof of the stepwise character of the transformation η^2-$HC{\equiv}CR \rightarrow (H)(C{\equiv}CR) \rightarrow C{=}C(H)R$ on the cationic system $[(PP_3)Co]^+$, where $PP_3 = P(CH_2CH_2PPh_2)_3$ [68a]. MP2 calculations of rearrangements of complexes $[(PP_3)M(HC{\equiv}CH)]^+$ (M = Co, Rh) [68b] showed that the concerted 1,3-H migration from M to C^2 in alkynylhydride $(H)M\text{–}C^1{\equiv}C^2H$ appears a feasible process for these systems.

Square-planar Rh and Ir complexes with the ligands η^2-$HC{\equiv}CR$ (R = H, alkyl, Ph, COOMe, etc.) are transformed into alkynylhydride derivatives, which are further converted into the stable vinylidene complexes (Scheme 3) [3a,49a,b]. Some of complexes $(i\text{-}Pr_3P)_2(Cl)(H)(py)Rh\text{-}C{\equiv}CR$ and $(i\text{-}Pr_3P)_2(Cl)(H)Ir\text{–}C{\equiv}CR$ were isolated and spectroscopically characterized.

The model complex $(PH_3)_2(Cl)Rh{=}C{=}CH_2$ is 7.8 kcal/mol more stable than $(PH_3)_2(Cl)Rh(\eta^2\text{-}HC{\equiv}CH)$ [69]. The AVR cannot be realized in this case via a 1,2-H shift, and the reaction proceeds via initial oxidative addition to form $(PH_3)_2(Cl)(H)RhC^1{\equiv}C^2H$. The activation barrier of this transformation is 26.9 kcal/mol. In the final stage, a bimolecular hydrogen shift takes place, with a proton moving from the metal atom of one molecule to the terminal C^2 atom of a second molecule. The activation energy of such process is <4 kcal/mol, while the barrier for the alternative intramolecular 1,3-H shift is 42.9 kcal/mol. For a more realistic system $(i\text{-}Pr_3P)_2(Cl)Rh(HC{\equiv}CR)$, the estimated energy of the bimolecular process is 15 kcal/mol less than that for intramolecular 1,3-H shift.



Scheme 3. AVR on the Rh center: R = H, alkyl, Ph, etc.; L = PR_3' [3a,49a].

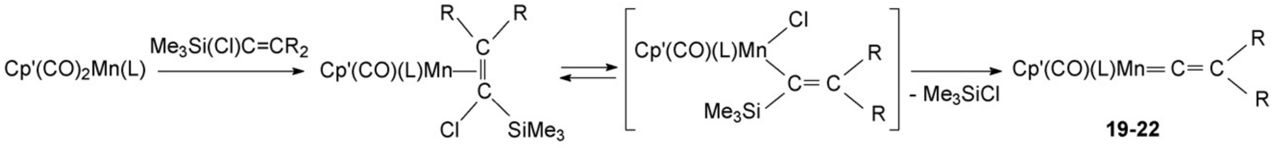
Puerta, Valerga et al. showed that the isomerization of alkynylhydrides $[Cp^*(dippe)(H)Ru\text{-}C{\equiv}CR]^+$ formed in the reactions of $Cp^*(dippe)Ru(Cl)$ with $HC{\equiv}CR$ (R = COOMe, Ph, $SiMe_3$), into $[Cp^*(dippe)Ru{=}C{=}CHR]^+$ can proceed both in solution and in the solid state. The structures of both cations, where R = COOMe, were confirmed with the X-ray data [5a,63a]. Three isomers resulting from the consecutive stages of the reaction of $Cp^*(PEt_3)_2Ru(Cl)$ with $HC{\equiv}CH$ gas (MeOH, $NaBPh_4$): π-alkyne $[Cp^*(PEt_3)_2Ru(\eta^2\text{-}HC{\equiv}CH)][BPh_4]$ ('**f**'), alkynylhydride $[Cp^*(PEt_3)_2(H)Ru\text{-}C{\equiv}CH][BPh_4]$ ('**h**') and vinylidene $[Cp^*(PEt_3)_2Ru{=}C{=}CH_2][BPh_4]$ ('**v**'), were first isolated and structurally characterized [63b]. The transformations '**f**' → '**h**' → '**v**' are spontaneous and irreversible, with the isomers '**f**' and '**h**' being isolated at −20 °C.

Despite the results of theoretical studies of the transformation of $HC{\equiv}CH$ into $C{=}CH_2$ on the $[Cp(CO)_2Mn]$ fragment [65,66a], many experimental observations still need explanation. Indeed, in practice, isomerization of $HC{\equiv}CH$ into $C{=}CH_2$ on the $[Cp(CO)_2Mn]$ [50] or $[Cp'(CO)_2Mn]$ [51] fragments proceeds in the presence of KOH/H_2O or Et_3N. Complex $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) is formed from $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CPh)$ (**1a**) in satisfactory yield only with the addition of an aqueous solution of HMTA as a catalyst. However, dry HMTA in absolute benzene or THF does not initiate the rearrangement **1a** → **1** [46]. In some cases, the water can serve as a catalyst of AVR (see ref. [4] and references therein). The MeOH solvent or H_2O attached to alumina can provide a proton for $L_nM{=}C{=}CH_2$ (M = Fe, Ru, Rh, Ir) formed from $HC{\equiv}CSiMe_3$ [2,49b,63,70]. Probably, THF solvent serves as a source of the H atom for the formation of **1** from $PhC{\equiv}CGePh_3$ or $PhC{\equiv}CSnPh_3$ [15]. Thus, the real pathway, the mechanism of action of catalytic additives, the effect of solvent and other long-standing questions concerning many AVR reactions still have to be elucidated.

2.3. *Other methods of formation of the Mn=C=CRR′ system*

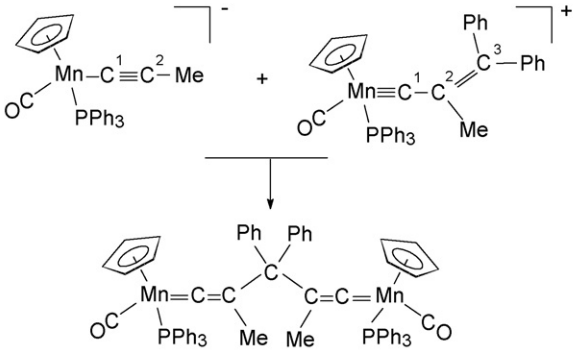
A series of complexes $Cp'(CO)(L)Mn{=}C{=}CR_2$ (**19**–**22**) was obtained from photochemical reactions between $Cp'(CO)_2Mn(L)$ and olefins $Me_3Si(Cl)C{=}CR_2$ by Schubert and Grönen [71] (Scheme 4). Vinylidene ligands were formed via oxidative addition of chloro(vinyl)silane to the $[Cp'(CO)(L)Mn]$ fragment and subsequent elimination of Me_3SiCl.

Complexes $Cp(CO)_2Mn{=}C{=}C(R)COOMe$ (R = H (**13**) or Me) were prepared by protonation or methylation of the C^2 atom of the alkynyl anion $[Cp(CO)_2MnC{\equiv}C^2COOMe]^-$ [72]. Complex $Cp(CO)_2Mn{=}C{=}CMe_2$ (**23**) was obtained by the action of an excess of MeLi on $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CCOOMe)$ and subsequent treatment of the intermediate



L = CO, R = Me (**19**), Ph (**20**); L = PMePh$_2$, R = Me (**21a**), Ph (**21b**); L = P(OPh)$_3$, R = Me (**22a**), Ph (**22b**)

Scheme 4. Synthesis of manganese vinylidene complexes from chloro(vinyl)silanes [71].



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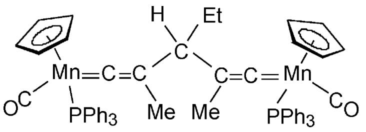
Scheme 5. Formation of the bis-vinylidene complex **24** by coupling of acetylide and carbyne complexes [74a].

σ-acetylide with MeOSO$_2$F [73a,b]. The allenylidene complex Cp′(CO)$_2$Mn=C=C=CPh$_2$ reacts with *t*-BuLi to give alkynyl anion [Cp′(CO)$_2$Mn-C≡C-C(*t*-Bu)Ph$_2$]$^-$, protonation or methylation of which led to the vinylidene complexes Cp′(CO)$_2$Mn=C=CRC(*t*-Bu)Ph$_2$ (R = H, Me) [73b].

Bis-vinylidene complex **24** was obtained as two diastereoisomers by coupling of an acetylide anion with a carbyne cation (Scheme 5) [74a]. Complex [Cp(CO)(PPh$_3$)MnC^1≡C^{2}Me]$^-$ acts as a nucleophile, by adding its C^2 atom to C^3 of vinylcarbyne [Cp(CO)(PPh$_3$)Mn≡C^{1}C^{2}Me=C^{3}Ph$_2$]$^+$.

Treatment of [Cp(CO)(PPh$_3$)Mn-C≡CMe]$^-$ with MeOH or Me$_3$SiCl gave bis-vinylidene complex **25**. Vinylcarbyne complexes [Cp(CO)(PPh$_3$)Mn≡CCMe=CRCHR$_2$′]$^+$ (R = H, *t*-Bu, Tol; R′ = H, Me) were deprotonated by Et$_2$NH or Et$_3$N to form a series of vinylvinylidene complexes similar to **26** [74a].



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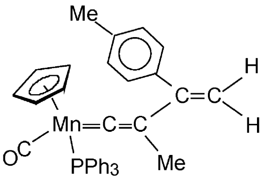

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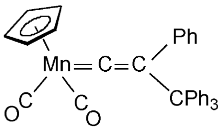

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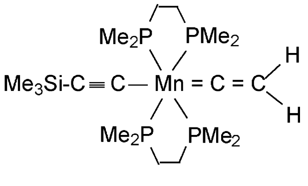

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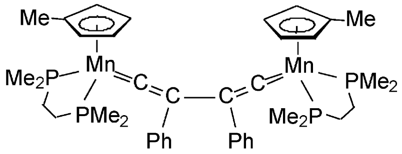

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The reaction between Cp(CO)$_2$Mn=C=C^{2}HPh (**1**) and [Ph$_3$C]PF$_6$ gave the stable complex Cp(CO)$_2$Mn=C=C(CPh$_3$)Ph (**27**) [45a]. The authors believed that the process involved the electrophilic attack of trityl cation on the C^2 atom of **1** and subsequent proton elimination.

The unique *trans*-alkynyl-vinylidene complex Me$_3$SiC≡CMn=C=CH$_2$(dmpe)$_2$ (**11**) was obtained by disproportionation of bis-alkynyl complex (Me$_3$SiC≡C)$_2$Mn(dmpe)$_2$ with NaBF$_4$ in MeOH [53]. The paramagnetic d^5 complexes Cp′(dmpe)MnC≡CPh and Cp′(dmpe)MnC≡CSiMe$_3$ were converted into Cp′(dmpe)Mn=C=CHPh (**28**) and Cp′(dmpe)Mn=C=CHSiMe$_3$, respectively, in the presence of Bu$_3$SnH or CpMo(CO)$_3$H [75]. Without an H$^\bullet$ radical donor, Cp′(dmpe)MnC^1≡C^{2}Ph dimerized slowly via C^2–C^2 coupling to form the red bis-vinylidene Cp′(dmpe)Mn=C=CPhCPh=C=Mn(dmpe)Cp′ (**29**).

2.4. *Properties, structural and spectroscopic parameters of Cp(CO)$_2$Mn=C=CRR′ and related complexes*

Most known complexes (η^5-C$_5$H$_{5-n}$Me$_n$)(L)(L′)Mn=C=CRR′ (*n* = 0, 1, 5; L, L′ = CO, PR$_3$) are relatively stable as solids and in solution. The structural and spectroscopic characteristics of manganese complexes of type ***A*** are considered in this section (Tables 1–3).

2.4.1. *Structures of Cp(L)(L′)Mn=C=CRR′*

Complex Cp(CO)$_2$Mn=C=CHPh (**1**) (Fig. 1) has the familiar “piano stool” structure [7,9]. Angles between the C=CHPh and CO ligands are 89–94°. The Mn=C^1=C^2 fragment is close to linear with an angle at C^1 of 174(2)°. The Mn=C^1=C^2 system is almost coplanar with the phenyl ring, as the torsion angle around the C^2–C^3 bond is 10°.

The Mn=C^1 bond lengths in the majority of η^1-vinylidene complexes are in the range 1.73–1.79 Å (Table 1). Com-

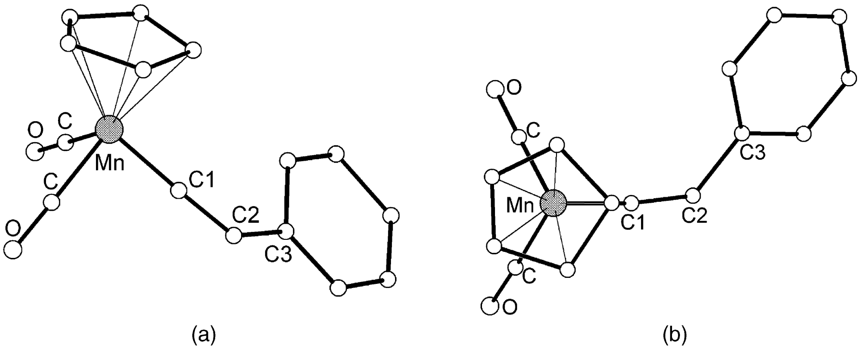


Fig. 1. Molecular structure of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**): (a) overall view of the molecule and (b) projection onto the Cp ring plane. The H atom at C2 was not located [7,9].

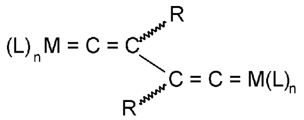
Table 1
X-ray parameters [bond distances (*d*, Å) and bond angles (*ω*, °)] of manganese η^1-vinylidene complexes

Complex	*d* (Å)		*ω* (°)	Ref.
	$M{=}C^1$	$C^1{=}C^2$	$\angle MC^1C^2$	
$Cp(CO)_2Mn{=}C{=}CRR'$ and $Cp'(CO)_2Mn{=}C{=}CRR'$				
$Cp(CO)_2Mn{=}C{=}CHPh$ (**1**)	1.68(2)	1.34(3)	174(2)	[7,9]
$Cp'(CO)_2Mn{=}C{=}CH[Fe(CO)_2Cp^*]$ (**14**)	1.837(6)	1.269(8)	178.7(5)	[56]
$Cp(CO)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ (**15**)	1.75(2)	1.32(2)	177(2)	[55c]
$Cp(CO)_2Mn{=}C{=}C(I)CH(OMe)_2$ (**17**)	1.777(6)	–	175.5(6)	[57]
$Cp(CO)_2Mn{=}C{=}CMe_2$ (**23**)	1.79(2)	1.33(2)	176(2)	[73b]
$Cp(CO)_2Mn{=}C{=}C(CPh_3)Ph$ (**27**)	1.778(2)	1.326(3)	176.3(2)	[45a]
$Cp(CO)(L)Mn{=}C{=}CRR'$				
$Cp(CO)(PPh_3)Mn{=}C{=}C(Me)$*t*-Bu	1.764(9)	1.339(11)	177.1(6)	[74b]
$Cp(CO)(PPh_3)Mn{=}C{=}CMeCHEtCMe{=}C{=}Mn(PPh_3)(CO)Cp$ (**25**)	1.793(7), 1.772(7)	1.317(10), 1.311(11)	175.9(6), 177.2(6)	[74a]
$Cp(CO)(PPh_3)Mn{=}C{=}CMeC(Tol){=}CH_2$ (**26**)	1.761(6)	1.336(9)	176.5(5)	[74a]
$(L)(dmpe)_nMn{=}C{=}CRR'$ ($n = 1, 2$)				
$(Me_3SiC{\equiv}C)Mn{=}C{=}CH_2(dmpe)_2$ (**11**)	1.782(4)	1.317(6)	179.2(4)	[53]
$Cp'(dmpe)Mn{=}C{=}CHPh$ (**28**)	1.731(5)	1.344(6)	178.2(5)	[75]
$(L)(L')Mn{=}C{=}CPhCPh{=}C{=}Mn(L')(L)$				
$Cp'(dmpe)Mn{=}C{=}CPhCPh{=}C{=}Mn(dmpe)Cp'$ (**29**)	1.742(5), 1.737(4)	1.351(6), 1.353(6)	177.4(4), 177.4(4)	[75]
$Cp^*(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp^*$ (**30**)	1.762(5), 1.760(5)	1.332(6), 1.342(6)	176.3(4), 176.7(4)	[45c]

plex **1** having the shortest $Mn{=}C^1$ bond (1.68(3) Å) [7,9] and $Cp'(CO)_2Mn{=}C{=}C(H)Fe(CO)_2Cp^*$ (**14**) having the longest $Mn{=}C^1$ bond (1.837(6) Å) and the unusually short $C^1{=}C^2$ bond (1.269(8) Å) [56] are exceptional. The $Mn{=}C^1$ bonds in η^1-vinylidene complexes are much shorter than the Mn–C bonds (1.94–2.25 Å) in σ-alkyl, σ-vinyl, σ-alkynyl complexes and shorter than the Mn=C bonds in carbenes $Cp(CO)_2Mn{=}CRR'$ (1.82–1.89 Å) and allenylidenes $Cp(CO)_2Mn{=}C{=}C{=}CRR'$ (1.80–1.81 Å) and come nearer to the Mn≡C bonds (1.67–1.69 Å) in carbynes $[Cp(CO)_2Mn{\equiv}CR]^+$ [76]. Strengthening of the M=C bonds during the transition from carbene M=C to allenylidene M=C=C=C and vinylidene M=C=C systems is also observed for M = Re, Rh, Ir (see Section 2.4.2). The $C^1{=}C^2$ bond lengths in η^1-vinylidene complexes are 1.31–1.34 Å, close to C=C in olefins (1.34 Å) and allenes $R_2C{=}C{=}CR_2$ (1.31 Å) [77]. The MnC^1C^2 bond angles are near 180° for all compounds including the $Mn{=}C^1{=}C^2$ system.

The metalla-allene system in $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) (Fig. 1) is weakly shielded by other ligands and can easily be attacked even by bulky reagents. This is one of the reasons for the high reactivity of **1**. The presence of the phenyl group at C^2 provides stability of **1** under usual conditions. Complex $Cp(CO)_2Mn{=}C{=}CH_2$ (**9**), where metalla-allene system lacks any protection, is not capable of existing under usual conditions [50]. On the contrary, $Me_3SiC{\equiv}C{-}Mn{=}C{=}CH_2(dmpe)_2$ (**11**) is stable due to the shielding of the $Mn{=}C{=}CH_2$ system by two bulky chelating dmpe ligands [53].

A special kind of η^1-vinylidene complex is the dinuclear bis-vinylidene complexes $(L)_nM{=}C{=}CRCR{=}C{=}M(L)_n$ (M = Nb, Mo, Mn, Re, Fe, Ru; R = H, alkyl, Ph, etc.) containing unsaturated of four-carbon bridging ligands (see refs. [4,42e,45,75] and references therein).



$$(L)_nM{=}C{=}C(R){-}C(R){=}C{=}M(L)_n$$

Two manganese complexes from this series, $Cp'(dmpe)Mn{=}C{=}CPhCPh{=}C{=}Mn(dmpe)Cp'$ (**29**) [75] and $Cp^*(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp^*$ (**30**) [45c], were characterized crystallographically. Complex $Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**) was in fact the first representative of this type, but because of the absence of the X-ray data, it was published as $Cp_2Mn_2(CO)_4(C_{16}H_{10})$ [6,7,15] or $[Cp(CO)_2Mn]_2(C_{16}H_{10})$ [44]. The spectroscopic data (Section 2.4.2) provided unambiguous interpretation of **3** as the bis-vinylidene complex. The unit cell parameters for complex **3** were determined by X-ray powder diffraction [78a]. Complexes $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) [78a], η^4-$\{C[Mn(CO)_2Cp](CO)CHPh\}Fe(CO)_3$ (**51**), $Cp(CO)MnPt(\mu\text{-}C{=}CHPh)(\mu\text{-}CO)(dppm)$ (**58**) and $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ (**67**) [78b] were also studied by this method.

The presence of a linear system of cumulated double bonds Mn=C=C in $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and related η^1-vinylidene complexes of type ***A*** allows them to be considered as metalla-allenes, i.e. organometallic analogs of organic allenes $R_2C{=}C{=}CR_2$.

2.4.2. Spectroscopic characteristics of Cp(L)(L′)M=C=CRR′ (M = Mn, Re)

2.4.2.1. Mass spectra. Electron impact on $Cp(CO)_2M{=}C{=}CHPh$ (M = Mn (**1**), Re (**6**)) causes consecutive elimination of the CO groups from the molecular ion $[P]^+$ and then a splitting of the M=C and M–Cp bonds [44]. A very strong increase in the intensity of the $[P\text{–}2CO]^+$ ion in the mass spectrum of **6**, compared to **1**, is due to the greater Re=C bond strength. The mass spectrum of **1** contains the $[MnC_8H_5]^+$ ion, which probably has an acetylide structure $[MnC{\equiv}CPh]^+$.

The fragmentation of $Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**) and $Cp(CO)_2Re[\eta^2\text{-}H_2C{=}CPhCPh{=}C{=}Re(CO)_2Cp]$ (**8**) occurs in two parallel directions. One consists in the removal of four CO groups from the molecular ions $[P]^+$ and results in the $[CpMn(C_{16}H_{10})MnCp]^+$ and $[CpRe(C_{16}H_{12})ReCp]^+$ ions, respectively. The unusual second direction begins with the elimination of the $[CpM(CO)_2]$ fragment from each $[P]^+$ ion to give the $[Cp(CO)_2Mn(C_{16}H_{10})]^+$ and $[Cp(CO)_2Re(C_{16}H_{12})]^+$ peaks. Finally, both directions result in very intense $[CpMn(C_{16}H_{10})]^+$ or $[CpRe(C_{16}H_{12})]^+$ peaks, respectively. The second direction is explained by the absence of metal–metal bonds in **3** and **8**. The mass spectrum of **3** contains the $[PhC{\equiv}CPh]^+$ ion, confirming the presence of the central C=CPhCPh=C fragment [44]. The existence of this four-carbon chain in molecule **8** was shown by XRD [16a].

A very intense dehydrogenation process under electron impact was observed while studying the mass spectra of $Cp(CO)_2Re{=}C{=}CHPh$ (**6**), $[Cp(CO)_2Re]_2(\mu\text{-}C{=}CHPh)$ (**7**) and $Cp(CO)_2Re[\eta^2\text{-}H_2C{=}CPhCPh{=}C{=}Re(CO)_2Cp]$ (**8**) [44]. The elimination of hydrogen is likely to occur from both Cp and vinylidene ligands. The ion $[CpRe]^+$ in the mass spectrum of **6** loses two H_2 molecules, whereas the $[CpReC_8H_6]^+$ ion formed from **7** loses four H_2 molecules and the $[CpRe(C_{16}H_{12})ReCp]^+$ ion from **8** loses successively 5 (!) H_2 molecules. “Internal catalysis” by the central rhenium atom is probably the driving force for such large dehydrogenation processes.

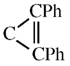
2.4.2.2. IR and Raman spectra. The ν(C=C) frequencies appear in the IR and Raman spectra of Cp(L)(L′)Mn=C=CRR′ between 1660 and 1590 cm^{-1} as strong or medium bands, whose positions depend greatly on the nature of L, L′ and R, R′ (Table 2). The IR and FT-Raman spectra and DFT calculations

Table 2
^{13}C NMR (δ, ppm) and IR (ν, cm^{-1}) data for manganese η^1-vinylidene complexes

Complex	^{13}C NMR, δ (ppm)		IR, ν (cm^{-1})		Ref.
	C^1	C^2	C=C	CO	
$Cp(CO)_2Mn{=}C{=}CRR'$, $Cp'(CO)_2Mn{=}C{=}CRR'$ and $Cp^*(CO)_2Mn{=}C{=}CRR'$					
$Cp(CO)_2Mn{=}C{=}CHPh$ (**1**)	379.5	123.5	1592	2009, 1955[a]; 2003, 1943[b]	[15]
$Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**)	374.9	135.1	–	2015, 1998, 1944[b]	[15,45a]
$Cp^*(CO)_2Mn{=}C{=}CHPh$ (**5**)	377.9	134.5	–	1982, 1922	[45b]
$Cp(CO)_2Mn{=}C{=}CHCH(OMe)_2$ (**12**)	–	–	1657	2009, 1953	[54]
$Cp(CO)_2Mn{=}C{=}CH(COOMe)$ (**13**)	371.5	115.9	1615	2030, 1975[a]	[55a]
$Cp(CO)_2Mn{=}C{=}C(I)CH(OMe)_2$ (**17**)	–	96.2	1657	2014, 1961	[57]
$Cp'(CO)_2Mn{=}C{=}CMe_2$ (**19**)	387.1	122.3	–	1996, 1942	[71c]
$Cp'(CO)_2Mn{=}C{=}CPh_2$ (**20**)	395.7	129.9	–	1981, 1918	[71c]
$Cp(CO)_2Mn{=}C{=}CMe_2$ (**23**)	–	–	–	1999, 1946	[73a]
$Cp(CO)(L)Mn{=}C{=}CRR'$ and $Cp'(CO)(L)Mn{=}C{=}CRR'$					
$Cp'(CO)(PMePh_2)Mn{=}C{=}CMe_2$ (**21a**)	383.0	117.5	–	1963	[71c]
$Cp'(CO)(PMePh_2)Mn{=}C{=}CPh_2$ (**21b**)	381.4	116.9	–	1965	[71c]
$Cp(CO)(PPh_3)Mn{=}C{=}CMeCPh_2CMe{=}C{=}Mn(PPh_3)(CO)Cp$ (**24**)	364.8	147.7	1614	1888	[74a]
$Cp(CO)(PPh_3)Mn{=}C{=}CMeCHEtCMe{=}C{=}Mn(PPh_3)(CO)Cp$ (**25**)	363.6	–	1637	1900	[74a]
$Cp(CO)(PPh_3)Mn{=}C{=}CMeC(Tol){=}CH_2$ (**26**)	369.7	136.4	1592	1890	[74a]
$Cp(CO)(PPh_3)Mn{=}C{=}CHPh$ (**31**)	–	137.5	–	1920	[15,45b]
$Cp(CO)[P(OPh)_3]Mn{=}C{=}CHPh$ (**32**)	–	–	1590[c]	1946	[15]
$(L)(dmpe)_nMn{=}C{=}CRR'$ ($n = 1, 2$)					
$(Me_3SiC{\equiv}C)Mn{=}C{=}CH_2(dmpe)_2$ (**11**)	345.1	90.21	1595	–	[53]
$Cp'(dmpe)Mn{=}C{=}CHPh$ (**28**)	342.5	142.2	1594	–	[75]
$Cp'(dmpe)Mn{=}C{=}CPhCPh{=}C{=}Mn(dmpe)Cp'$ (**29**)	342.6	143.5	1589	–	[75]

[a] Cyclohexane solution.
[b] CH_2Cl_2 solution.
[c] Raman spectrum.

Table 3
IR data (ν(CO), cm^{-1}, and force constants, K_{CO}, mdn/Å) for $\mathrm{Cp(CO)_2Mn(L)}$

L	Solvent	ν(CO) (cm^{-1})[a]	K_{CO} (mdn/Å)
$\mathrm{SO_2}$	Benzene	2028, 1969	16.15
CS	Hexane	2012, 1962	15.96
C=CHPh	Cyclohexane	2009, 1955	15.88
$\mathrm{C{=}CHCH(OMe)_2}$	Hexane	2009, 1953	15.86
$\mathrm{AsF_3}$	Cyclohexane	2006, 1953	15.84
CO	Cyclohexane	2035, 1953	15.84
$\mathrm{C{=}CMe_2}$	Hexane	1999, 1946	15.73
$\mathrm{C{=}C{=}CPh_2}$	Hexane	1995, 1945	15.68
$\mathrm{PF_3}$	Cyclohexane	1996, 1938	15.64
PhC≡CPh	Cyclohexane	1983, 1929	15.41
PhC≡CH	Cyclohexane	1981, 1921	15.38
$\mathrm{CPh_2}$	Hexane	1977, 1919	15.33
$\mathrm{H_2C{=}CH_2}$	Hexane	1976, 1917	15.31
MeC≡CMe	Pentane	1963, 1904	15.11
C(OMe)Ph	Hexane	1969, 1898	15.11
$\mathrm{PPh_3}$	Cyclohexane	1946, 1880	14.80
	Pentane	1935, 1868	14.62

[a] References are given in ref. [15].

for a series $\mathrm{(PR_3{}')_2(X)Rh{=}C{=}CHR}$ (R′ = H, Me, *i*-Pr; X = F, Cl, Br, I; R = H, Me, Ph) showed ν(Rh=C) to be at 575–560 cm^{-1} and ν(C=C) to be between 1660 and 1580 cm^{-1} [79a,b].

Using ν(CO) frequencies and force constants (K_{CO}) of the C≡O bonds calculated on the basis of ν(CO) for cymantrene derivatives, $\mathrm{Cp(CO)_2Mn(L)}$ (L = η^1-vinylidene, η^1-carbene, η^2-alkyne, η^2-olefin, $\mathrm{PR_3}$, etc.) (Table 3), we were able to compare the electronic effects of the C=CRR′ ligands with those of other two-electron ligands [15].

The L ligands are arranged in order of decreasing of their electron withdrawing properties:

$$\mathrm{SO_2} > \mathrm{CS} > \mathrm{C{=}CHPh} \sim \mathrm{AsF_3} \sim \mathrm{CO} > \mathrm{C{=}CMe_2} > \mathrm{C{=}C{=}CPh_2} > \mathrm{PF_3} > \eta^2\text{-}\mathrm{PhC{\equiv}CPh} >$$

$$\eta^2\text{-}\mathrm{PhC{\equiv}CH} > \mathrm{CPh_2} \sim \eta^2\text{-}\mathrm{H_2C{=}CH_2} >> \eta^2\text{-}\mathrm{MeC{\equiv}CMe} \sim \mathrm{C(OMe)Ph} > \mathrm{PPh_3} > \overline{\mathrm{CC(Ph)}{=}\mathrm{C}}\mathrm{Ph}$$

The ν(CO) bands for $\mathrm{Cp(CO)_2Mn{=}C{=}CRR'}$ are 30–40 cm^{-1} higher than those of the corresponding η^2-alkyne isomers $\mathrm{Cp(CO)_2Mn(\eta^2\text{-}RC{\equiv}CR')}$. The ν(CO) for $\mathrm{Cp(CO)_2Re{=}C{=}CHPh}$ (**6**) (2003, 1938 cm^{-1}) are also higher than those for $\mathrm{Cp(CO)_2Re(\eta^2\text{-}PhC{\equiv}CH)}$ (**6a**) (1980, 1911 cm^{-1}) [16]. At the same time, ν(CO) for $\mathrm{Cp(CO)_2Re(L)}$, where L = η^1-vinylidene, η^1-carbene, η^2-alkyne, CO, etc., are 5–20 cm^{-1} lower as compared with their manganese analogues $\mathrm{Cp(CO)_2Mn(L)}$ [15]. The IR spectrum of $\mathrm{Cp(CO)_2Re[\eta^2\text{-}H_2C{=}CPhCPh{=}C{=}Re(CO)_2Cp]}$ (**8**) contains two pairs of ν(CO) bands of equal intensity: at 2000 and 1930 cm^{-1} belonging to η^1-vinylidene fragment, and at 1982, 1914 cm^{-1} belonging to η^2-olefinic fragment [16a].

According to the IR data for complexes $\mathrm{Cp(CO)_2M(L)}$ (M = Mn, Re), the vinylidenes are members of the ligand set having the highest π-acceptor capacity. Phenylvinylidene, in this regard, is comparable with CS, $\mathrm{AsF_3}$ and CO and considerably exceeds η^2-olefins, η^2-alkynes, carbenes CRR′ and allenylidenes $\mathrm{C{=}C{=}CR_2}$. There is an interdependence between the strengthening of π-acceptor ability of L = carbene, allenylidene, vinylidene and the shortening of the Mn=C bonds in complexes $\mathrm{Cp(CO)_2Mn(L)}$ (see Section 2.4.1 and Table 3).

The same conclusion was drawn from the CV study of complexes *trans*-$\mathrm{(\textit{i}\text{-}Pr_3P)_2(Cl)Rh(L)}$ (L = $\mathrm{{:}C({=}C)_\mathit{n}Ph_2}$, $\mathrm{C_2H_4}$, CO; *n* = 0, 1, 2, 4) [79c]. The ligands L are arranged in order of increasing π-acceptor ability:

$$\mathrm{CPh_2} < \mathrm{C{=}C{=}CPh_2} \sim \mathrm{C{=}C{=}C{=}C{=}CPh_2} < \eta^2\text{-}\mathrm{H_2}$$

$$\mathrm{C{=}CH_2} < \mathrm{C{=}CPh_2} < \mathrm{CO}.$$

The increase in π-acceptor ability of ligands correlates well with the Rh=C distances shortening in *trans*-$\mathrm{(\textit{i}\text{-}Pr_3P)_2(Cl)Rh(L)}$, from carbene L = $\mathrm{CPh_2}$ to allenylidene C=C=CPh(*o*-Tol), and then to vinylidene C=CHMe. The same tendency was shown for iridium analogs, *trans*-$\mathrm{(\textit{i}\text{-}Pr_3P)_2(Cl)Ir(L)}$ [79c].

According to the electrochemical study of an extensive series of complexes [79d], the organic ligands, in terms of Pickett's $\mathrm{P_L}$ and Lever's $\mathrm{E_L}$ values, can be ordered according to their *net* π-electron acceptance minus σ-donor character as follows:

$$\text{carbynes} > \text{CO} > \text{vinylidenes} > \text{allenylidenes} > \text{carbenes}$$

$$> \text{alkynyls}.$$

2.4.2.3. NMR spectra. The presence of the η^1-$\mathrm{C^1{=}C^2RR'}$ ligand is characterized by the $\mathrm{C^1}$ signal in the ^{13}C NMR spectrum at very low field, δ 340–400 ppm. $\mathrm{C^2}$ resonates from δ 90 to 150 (Table 2). These chemical shifts are due to the reduced electron density on vinylidene carbons, especially on the $\mathrm{C^1}$ atom. The signals of $\mathrm{C^1}$ at 379.54 and $\mathrm{C^2}$ at 123.54 were found for $\mathrm{Cp(CO)_2Mn{=}C^1{=}C^2HPh}$ (**1**) [15].

The presence of the μ-η^1:η^1-bis-vinylidene group in $\mathrm{Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp}$ (**3**) is shown by signals at δ 374.9 and 135.1 in the ^{13}C NMR spectrum [45a]. A shift of the $\mathrm{C^1}$ resonance to δ 340 for $\mathrm{Cp'(dmpe)Mn{=}C{=}CPhCPh{=}C{=}Mn(dmpe)Cp'}$ (**29**) [75] is due to the electron donor influence of the dmpe ligands.

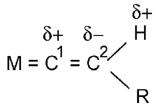
The vinylidene protons in the ^{1}H NMR spectra of $\mathrm{Cp(CO)_2Mn{=}C{=}CHPh}$ (**1**) [15], $\mathrm{Cp^*(CO)_2Mn{=}C{=}CHPh}$ (**5**) and $\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}CHPh}$ (**31**) [45b] resonate at δ 6.91, 6.59 and 6.17 ppm, respectively.

2.5. Reactivity of $\mathrm{Cp(CO)_2Mn{=}C{=}CHR}$

The results of the X-ray, spectroscopic and theoretical studies [5c,65–69,80] allow formulation of the basic factors determining the chemical behavior of η^1-vinylidene complexes $\mathrm{L_\mathit{n}M{=}C{=}CHR}$, and $\mathrm{Cp(CO)_2Mn{=}C{=}CHR}$ in particular:

(1) the presence of the linear $\mathrm{M{=}C^1{=}C^2}$ system including the strong electron-rich $\mathrm{M{=}C^1}$ bond;

(2) a lowered electron density on the C^1 and H atoms of the $C^1{=}C^2HR$ ligand and alternation of charges in the system



(3) a strong electron acceptor influence of vinylidene C=CHR, which is transmitted through a metal atom to other ligands;

(4) a weak steric shielding of the M=C=CHR system by other ligands.

The geometry and electronic structure result in many reactions of the type ***A*** vinylidene complexes being characterized by high regioselectivity. Attack of electrophilic reagents is usually directed to the C^2 atom, and the addition of nucleophiles occurs exclusively to the C^1 atom. Electron deficient metal-containing fragments and carbene moieties add only to the $M{=}C^1$ bond (see Section 3.1), and unsaturated organic molecules, generally, to the $C^1{=}C^2$ bond.

Insertion of alkynes occurs across the C^2–H bond. The splitting of the M=C and C=C bonds is not typical for the M=C=C system. On the contrary, deprotonation of vinylidene is inherent in this type of complex. The dehydrodimerization processes resulting in the C^2–C^2 coupling and formation of bis-vinylidenes are also characteristic of complexes $L_nM{=}C{=}C^2HR$. Competition between the vinylidene and CO ligands for d_π-electrons of the central metal atom facilitates the substitution of the CO groups in $Cp(CO)_2Mn{=}C{=}CHR$ by L = PR_3, $P(OR)_3$.

2.5.1. *Participation of $Cp(CO)_2M{=}C{=}CHPh$ (M = Mn, Re) in C–C bond formation*

The formation of the new C–C bonds in the course of the transformations of metal vinylidene complexes or intermediates is considered in reviews [1–5,39–42]. King described, in 1974, C–C coupling with the participation of a metal vinylidene intermediate [11c,81]. The formation of dicyano(tetraphenyl)fulvene by the thermal reaction between $Cp(CO)_3MoCCl{=}C(CN)_2$ and tolan occurred through the intermediate $[Cp(CO)_2(Cl)Mo{=}C{=}C(CN)_2]$. In other words, fulvene was a product of co-cyclization of vinylidene $[C{=}C(CN)_2]$ with two molecules of PhC≡CPh.

As far as we know, the first vinylidene complexes to be formed as a result of C–C coupling were $Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**) [6,15] and $Cp(CO)_2Re[\eta^2\text{-}H_2C{=}CPhCPh{=}C{=}Re(CO)_2Cp]$ (**8**) [16a]. Complex **3** appears in small amounts in the course of synthesis, isolation and storing of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), and is often present among products of reactions of **1** due to spontaneous dehydrodimerization. Treatment of **1** with KOH/MeOH, NaOMe or BuLi leads to **3** in high yield (reaction *(5)* in Scheme 1) [15].

Ustynyuk et al. studied in detail the oxidatively induced dehydrodimerization of complexes $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), $Cp^*(CO)_2Mn{=}C{=}CHPh$ (**5**), $Cp(CO)(PPh_3)Mn{=}C{=}CHPh$ (**31**), etc., by CV, and also by treatment with some chemical reagents [42c,45]. The initial product of oxidation of **1** is the radical cation $[Cp(CO)_2Mn{=}C^1{=}C^2HPh]^{+\bullet}$. Homolytic cleavage of the C^2–H bond and dimerization of the $[Cp(CO)_2Mn{-}C^1{\equiv}C^2Ph]^+$ cation gives bis-vinylidene complex **3**.

The composition of $Cp(CO)_2Re[\eta^2\text{-}H_2C{=}CPhCPh{=}C{=}Re(CO)_2Cp]$ (**8**) corresponds to a dimer of $Cp(CO)_2Re{=}C{=}CHPh$ (**6**). However, **8** is not formed by dimerization of **6** [16a]. Complex **8** was not found among the products of the dark reaction between $Cp(CO)_2Re(thf)$ and PhC≡CH [16b], and was obtained only by UV irradiation of $CpRe(CO)_3$ with PhC≡CH (reaction *(6)*) [16a]. Complex **8** is supposed to be formed via an insertion of PhC≡CH across the C^2–H bond of $Cp(CO)_2Re{=}C{=}C^2HPh$ (**6**) and subsequent coordination of the $[Re(CO)_2Cp]$ unit to the $C^3{=}C^4$ bond of the intermediate $[Cp(CO)_2Re{=}C^1{=}C^2PhC^3Ph{=}C^4H_2]$.

2.5.2. *Reactions of $Cp(CO)_2Mn{=}C{=}CHR$ with phosphines and phosphites*

Reactions of complexes $Cp(CO)_2Mn{=}C^1{=}C^2HR$ with tertiary phosphines PR'_3 and phosphites $P(OR')_3$ could occur in four directions (Scheme 6):

(a) substitution of CO for the P-containing ligand;

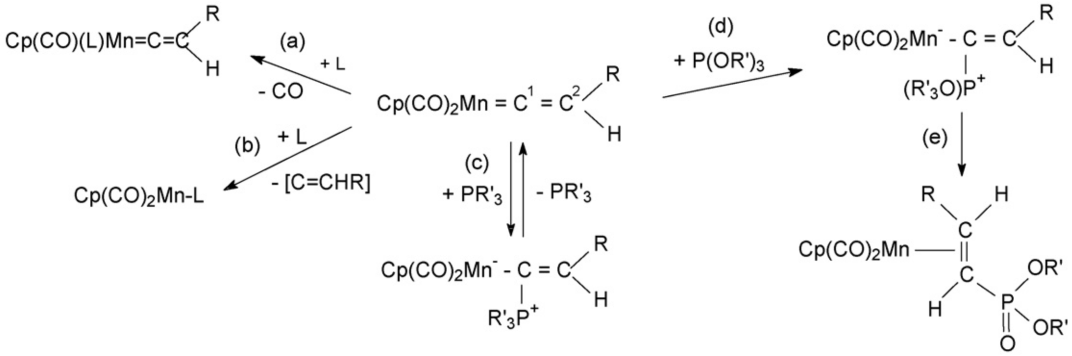
(b) substitution of vinylidene for the P-containing ligand (but not actually found);

(c) addition of PR'_3 to the C^1 atom to form a bipolar adduct;

(d) addition of phosphite $P(OR')_3$ accompanied by spontaneous rearrangement (e) of an adduct to form the η^2-vinylphosphonate complex (see Section 2.5.3).

Complex **1** reacts with PPh_3 and $P(OR)_3$ under UV irradiation or in bright sunlight to afford $Cp(CO)(PPh_3)Mn{=}C{=}CHPh$ (**31**), $Cp(CO)[P(OPh)_3]Mn{=}C{=}CHPh$ (**32**) and $Cp(CO)[P(OEt)_3]Mn{=}C{=}CHPh$ (**33**) (reaction (a) in Scheme 6) [15,45b]. Complexes $Cp(CO)(L)Mn{=}C{=}CPhCPh{=}C{=}Mn(L)(CO)Cp$ (L = PPh_3 (**34**), $P(OEt)_3$ (**35**)) were obtained by UV irradiation of $Cp(CO)_2Mn{=}C{=}CPhCPh{=}C{=}Mn(CO)_2Cp$ (**3**) with PPh_3 or $P(OEt)_3$ [82]. Complex **34** was also formed by an oxidative induced dehydrodimerization of $Cp(CO)(PPh_3)Mn{=}C{=}CHPh$ (**31**) [42c,45b]. Direction (b) was not realized. Only traces of $Cp(CO)_2Mn(L)$ were found among the products of photochemical reactions (a).

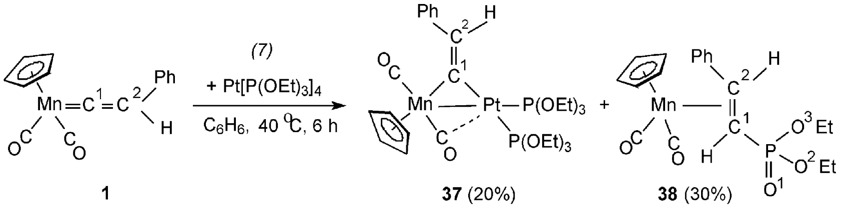
Directions (c–e) were realized in the absence of irradiation. A reversible addition of PR_3' = PPh_3, PPh_2Me, etc., to $Cp(CO)_2Mn{=}C{=}CHR$ (R = Ph (**1**), COOMe (**13**)) led to the vinylphosphonium complexes $Cp(CO)_2Mn^-{-}C(P^+R_3'){=}CHR$ [83]. These compounds can be easily isolated since they precipitate in the course of reaction. The bipolar adducts are stable in solids, but form the initial components in THF and $CHCl_3$ solutions. The ability of $Cp(CO)_2Mn^-{-}C(P^+Ph_3){=}CHPh$ (**36**) to dissociate was used to exchange of PPh_3 for PPh_2Me and dppe [83b]. The ν(CO) in the IR spectra of bipolar adducts are 110–130 cm^{-1} lower than those of **1** and **13**.



Scheme 6. The direction of the reactions of Cp(CO)$_2$Mn=C=CHR with phosphines and phosphites.

2.5.3. *Synthesis of β-phenylvinylphosphonic acid esters (styrylphosphonates)*

Along with the expected dinuclear complex Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OEt)$_3$]$_2$ (**37**) (see Section 3.1.3), reaction *(7)* between Cp(CO)$_2$Mn=C=CHPh (**1**) and Pt[P(OEt)$_3$]$_4$ gave the mononuclear product Cp(CO)$_2$Mn[η^2-PhCH=CHP(O)(OEt)$_2$] (**38**) [22]. According to the X-ray analysis [84], **38** contains the η^2-*trans*-1-diethylphosphonato-2-phenylethylene ligand. The bond lengths are C^1=C^2 1.395(8), Mn–C^1 2.145(5), Mn–C^2 2.168(6) Å; P=O^1 1.462(5), P–O^2 1.581(5) and P–O^3 1.597(5) Å. The C^2–C^1–P bond angle is 120.4(4)°.



The direct reaction *(8)* between P(OEt)$_3$ and complex **1** afforded complex **38** in 96% yield (Scheme 7) [85].

Not only simple phosphites P(OR)$_3$ (R = alkyl, Ph), but phosphonites and cyclic phosphites, such as phospholanes or phosphorinanes, can enter into this reaction (Scheme 7) [86]. The products are stable solids, except for the oily Cp(CO)$_2$Mn[η^2-PhCH=CHP(O)(OBu)$_2$] (**41**), and decompose in solutions to eliminate free styrylphosphonate.

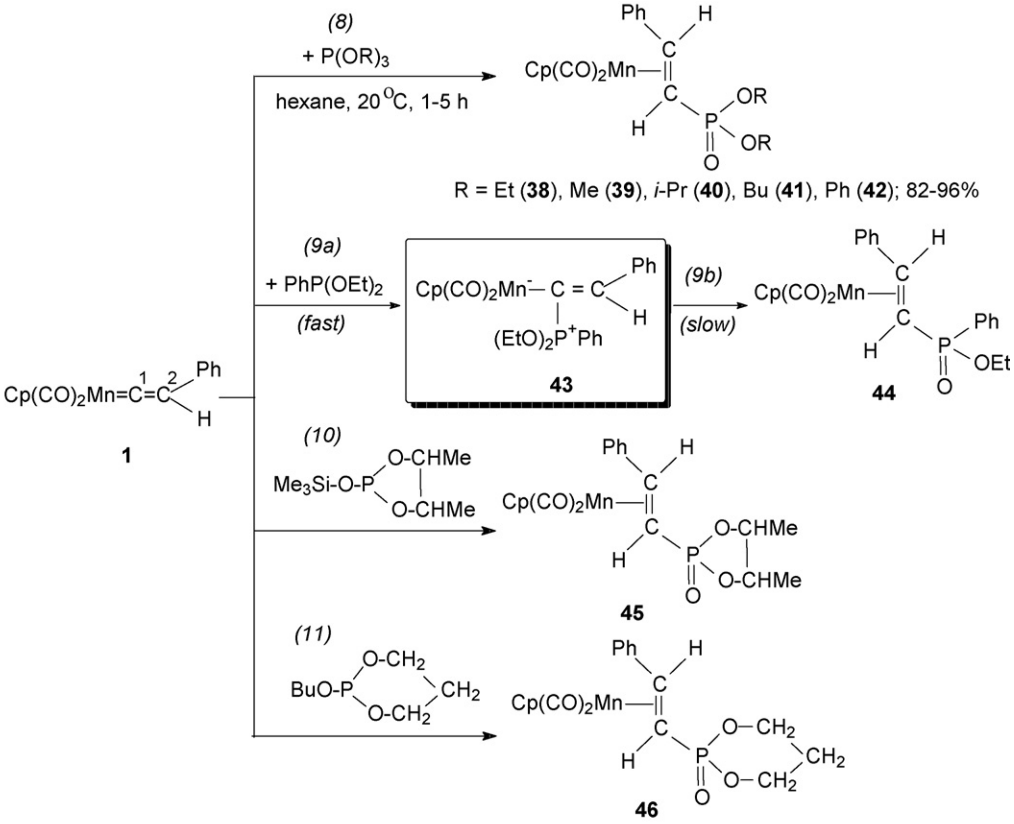
An initial stage of synthesis of η^2-styrylphosphonate complexes was clarified in the course of reaction *(9)* in Scheme 7 between **1** and phosphonite PhP(OEt)$_2$ [86]. Complex **1** disappeared within 15 min and strong bands at 1905 and 1842 cm^{-1} indicated the formation of bipolar adduct Cp(CO)$_2$Mn$^-$C[P$^+$(OEt)$_2$Ph]=CHPh (**43**), similar to Cp(CO)$_2$Mn$^-$C(P$^+$Ph$_3$)=CHPh (**36**) (ν(CO) 1900, 1830 cm^{-1}) [83a]. Slow transformation of intermediate **43** (reaction *(9b)*) resulted in a mixture of two diastereoisomers **44** separated by chromatography [86].

Reactions (*(10)* and *(11)*) (Scheme 7) between **1** and cyclic phosphites gave mixtures of products. Three stereoisomers **45** were isolated in a total 69% yield. Crystalline **46** and several oily complexes, originating from opening of the dioxaphosphorinane ring, were obtained from reaction *(11)*.

According to the NMR and IR spectra [86], the structures of Cp(CO)$_2$Mn[η^2-PhCH=CHP(O)(OR)$_2$] (**39–42**, **44–46**) are close to that of **38** [84], despite the different P(OR)$_2$ groups. The PhCH=CHP(O)(OR)$_2$ ligand in all the complexes has a *trans*-configuration. The ν(CO) frequencies in the IR spectra of complexes **38–42**, **44–46** [86] indicate a noticeable electron withdrawing capacity of the η^2-PhCH=CHP(O)(OR)$_2$ ligands.

The reactions between P(OR)$_3$ and Cp(CO)$_2$Mn=C=CHPh (**1**) represent an unusual variant of the Arbuzov's reaction which occur within the coordination sphere of a transition metal atom. We supposed [84] that like the classical Arbuzov's reaction, the first stage is the addition of phosphite to the electrophilic C^1 atom of the Mn=C^1=C^2 system, resulting in the intermediate bipolar adduct Cp(CO)$_2$Mn$^-$–C[P$^+$(OR)$_3$]=CHPh. Formation of **43** in reaction *(9a)* confirmed this assumption. Subsequent transformations of Cp(CO)$_2$Mn$^-$–C[P$^+$(OR)$_3$]=CHPh occur by a cyclic *cis*-β-elimination mechanism, i.e. by cleavage of one of the O–R bonds, formation of the P=O bond, hydrogenation of η^1-vinyl group and its rearrangement into η^2-olefin [84].

The compounds Cp(CO)$_2$Mn[η^2-PhCH=CHP(O)(OR)$_2$] (**38–42**, **44–46**) are the first transition metal phosphonatoethylene π-complexes [22,84–86], in spite of the fact that free vinylphosphonates RCH=CHP(O)(OR′)$_2$ (R and R′ = alkyl, Ph) were synthesized in the middle of the twentieth century [87,88]. However, the known processes were either extremely non-ecological, since they proceeded in rather aggressive and toxic media (PhCH=CHP(O)Cl$_2$, phenol, pyridine) [87,88a] or required temperatures 150–165 °C, which caused side reactions and lowered the yield of RCH=CHP(O)(OR′)$_2$ to 6–50% [88b,88c]. Earlier it was impossible to obtain diaryl(styryl)phosphonates with the help of the Arbuzov's reaction [88d].

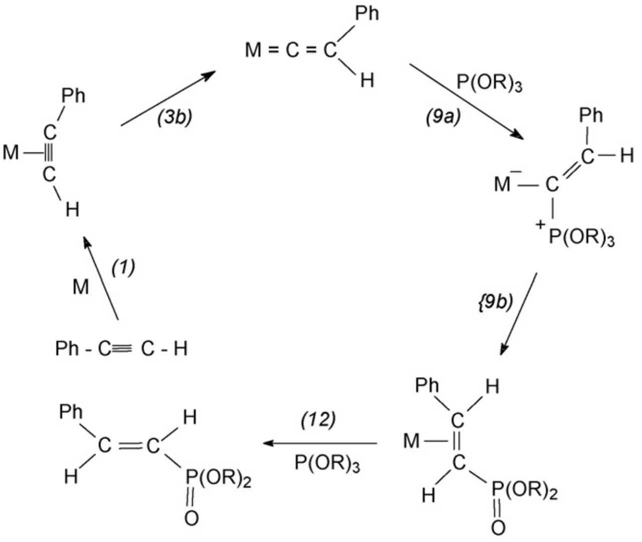


Scheme 7. Formation of the manganese η^2-styrylphosphonate complexes from $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and phosphites.

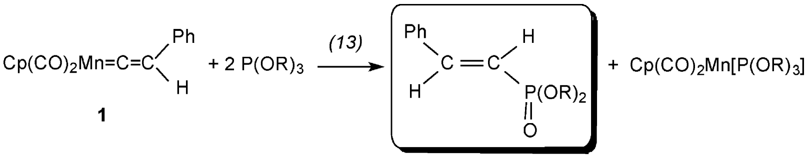
Styrylphosphonates are of significant practical interest, because they can be used as monomers for fire-resistant polymers and impregnations, as plasticizers, additives to oils, as components of surface-active materials.

The extraordinary readiness of formation of η^2-$PhCH{=}CHP(O)(OR)_2$ ligands on a metal center was a stimulus to the search of rational ways of isolation of these olefins from complexes. While the reactions of CO or $PhC{\equiv}CH$ with $Cp(CO)_2Mn[\eta^2\text{-}PhCH{=}CHP(O)(OR)_2]$, where R = Et (**38**), Ph (**42**), were not appropriate, the use of $P(OR)_3$ (reaction *(12)* in Scheme 8) giving $PhCH{=}CHP(O)(OR)_2$ in 98% yield, appeared to be the most successful.

We elaborated the method of preparation of the dialkyl and diaryl esters of styrylphosphonic acid without an intermediate isolation of η^2-olefin complexes [89]. The synthesis of styrylphosphonates $PhCH{=}CHP(O)(OR)_2$ is carried out in a petroleum-ether or in benzene solution at 20 °C, according to reaction *(13)* and is stereoselective resulting in yields of 95–98% of *trans*-styrylphosphonates $PhCH{=}CHP(O)(OR)_2$ (R = alkyl, aryl). The elimination of $PhCH{=}CHP(O)(OPh)_2$ from complex is faster at 50 °C.



Scheme 8. The conversion of phenylacetylene into styrylphosphonates on the metal center $M = Mn(CO)_2Cp$.



1

(R = alkyl, aryl)

The distinctive feature of a basically new method of synthesis of styrylphosphonates with the use of the Mn=C=CHPh system, is the possibility of introduction in reaction *(13)* of trialkylphosphites, cyclic phosphites and phosphonites as well as triphenylphosphite, $P(OPh)_3$, which does not enter into the classical Arbuzov's reaction. An active role of the Mn atom as an intramolecular catalyst undoubtedly explains the fact that these reactions occur under unusually mild conditions.

3. Formation of complexes with Mn–M bonds

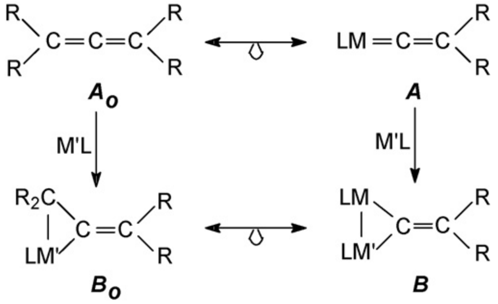
One of the most important properties of vinylidene complexes is the ability to add metal-containing fragments, first discovered during our study of transformations of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) into dinuclear MnMn, MnRe and MnFe derivatives [15,20,90]. In this section, we consider the synthesis of MnM complexes with bridging vinylidenes and give details of their structures (Table 4), spectroscopic characteristics (Table 5) and reactivity.

3.1. Dinuclear Mn–M μ-vinylidene complexes

Our approach to the synthesis of dinuclear heterometallic μ-vinylidene complexes ***B*** was based on the supposition [15] that the $M{=}C^1$ bond of mononuclear vinylidene complexes ***A***, similarly to the C=C bond of olefins and allenes $R_2C{=}C{=}CR_2$ (***A₀***), would be able to coordinate a transition metal atom M′ (Scheme 9).

The addition of [M′L′] units to complexes ***A*** is the most common method of synthesis of vinylidene complexes ***B***. With the help of this reaction, μ-vinylidene complexes (L)MM′(μ-C=CHR)(L′) (M = Mn, Rh, Os; M′ = Cr, Mo, W, Mn, Re, Fe, Pd, Pt, Cu; R = H, alkyl, aryl, COOMe) were prepared from $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**), $Cp(CO)_2Mn{=}C{=}C(H)COOMe$ (**13**), $Cp(PR_3)Rh{=}C{=}CHR$, $(\eta^6\text{-}C_6H_6)(PR_3)Os{=}C{=}CHR$ [2,4,20–30].

Taking into account the isolobal analogy between allene π-complexes ***B₀*** and dinuclear vinylidene complexes ***B*** (Scheme 9), the compounds $LMM'(\mu\text{-}C^1{=}C^2R_2)(L')$ (***B***) can be represented as the π-complexes of M′ with the metalla-allene ligand $LM{=}C^1{=}C^2R_2$ (***A***) [27]. Therefore, the Dewar-Chatt-Duncanson model can be used to describe the bonding in complexes ***B***. There is a donor–acceptor interaction between the $M{=}C^1$ double bond of "heteroallene" $LM{=}C^1{=}C^2R_2$ and atom M′ (σ component) and back-donation $d_\pi(M') \rightarrow \pi^*(M{=}C^1)$ (π component) (Scheme 11).

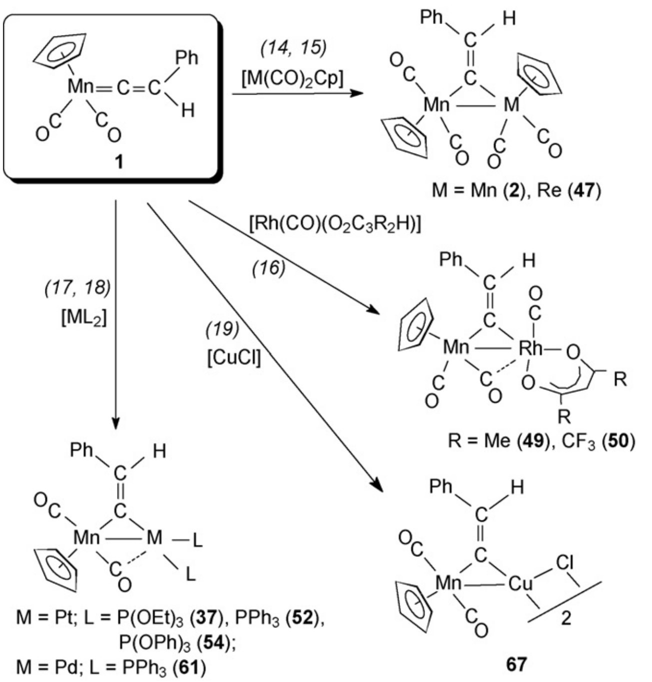


Scheme 9. Isolobal relationship of organic allenes *(**A₀**)* with η^1-vinylidene complexes *(**A**)* and η^2-allene complexes *(**B₀**)* with μ-vinylidene complexes *(**B**)*.

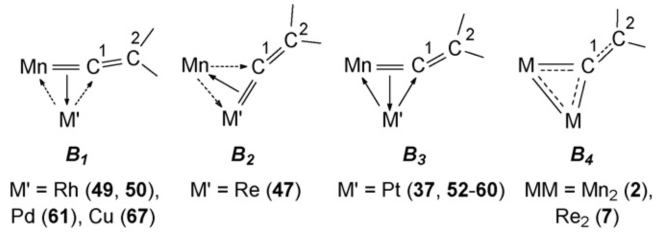
To estimate the σ component in π-olefinic complexes in terms of the Dewar-Chatt-Duncanson model, the rotational barrier around the metal-olefin bond is used, and the π component is estimated from the bending of substituents at the C=C bond from the olefin plane. In the case of the vinylidene complexes ***B***, the π contribution can be estimated from the $M–C^1–C^2$ angle: the nearer this angle to 180° is, the less π contribution there is (structure ***B₁*** in Scheme 11). Barriers to rotation around the bond between the M′ atom and "heteroolefin" $Mn{=}C^1$ have not been determined. The relative σ and π contributions can be determined by the aggregate of such factors as the nature, the oxidation level and dimensions of the M and M′ atoms, the ligand environment, the substituents at the C^2 atom, etc. The ^{13}C NMR and IR data allow the composition and structure of complex $Cp(CO)_2MnM'(\mu\text{-}C{=}CHR)L'$ as well as the donor–acceptor properties of the [M′L′] fragments to be determined.

The *cis–trans* isomerism is possible for dinuclear μ-vinylidene complexes [27] due to different orientations of ligands, such as Cp, CO relative to the $MM'(\mu\text{-}C^1)$ plane or the $M–C^1$ bond. The *E–Z*-isomerism caused by various positions of the R and R′ substituents in the $\mu\text{-}C^1{=}C^2RR'$ ligand relative to the M and M′ atoms is also known [21a].

Among the chemical properties, the further metalation of complexes LMM′(μ-C=CHR′)L′ (Sections 4 and 5) attracts the most attention. The homodinuclear μ-vinylidene complexes ***B*** are, as a rule, more stable than their mononuclear precursors ***A***. At the same time, the splitting of the $\overline{MM'(\mu\text{-}C^1)}$ cycle is charac-



Scheme 10. Synthesis of μ-vinylidene MnM complexes based on the Mn=C=CHPh system: *(14)* M = Mn; THF, 5–20 °C, 2 h, 27%; *(15)* M = Re; THF, 5–20 °C, 4 h, 4%; *(16)* M = Rh; hexane, 20 °C, 0.25 h, 88%; *(17)* M = Pt; C_6H_6, 20 °C, 4–24 h, 80%; *(18)* M = Pd; Et_2O, 20 °C, 1 h, 95%; *(19)* M = Cu; THF, 20 °C, 0.5 h, 98%.



Scheme 11. A donor-acceptor interaction between the M=C^1=C^2 system and the M′ atom and back-donation in μ-vinylidene complexes ***B*** (M = Mn, Re; M′ = Rh, Pd, Cu, Re, Pt).

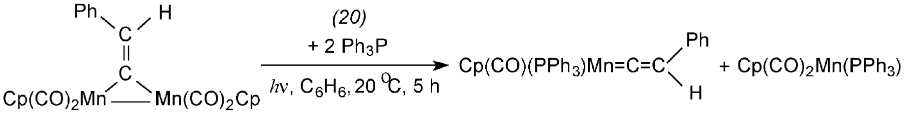
teristic of many heteronuclear complexes ***B***. In this connection, vinylidene transfer from one metal to another, where complexes ***B*** may be intermediates**,** is of special interest.

3.1.1. Mn–Mn and Mn–Re μ-vinylidene complexes

The dinuclear complex [Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**) [6,7] was obtained in moderate yield from the reaction between **1** and Cp(CO)$_2$Mn(thf) [15] (reaction *(14)* in Scheme 10). The central fragment of molecule **2** (Fig. 2) is an almost planar methylenedimetallacyclopropane Mn^1-Mn^2(μ-C^1=C^{2}HPh) system [7,8], inasmuch as the declination angle of the C^1=C^2 bond from the Mn^{1}Mn^{2}C^1 plane is 7°, the torsion angle around the C^2–C^3 bond is 11°. The dihedral angle between the Mn^{1}Mn^{2}C^1 and the Ph planes is 16°. The C^1=C^2 bond length is 1.35(2) Å.

The most important features of structure **2** are short σ-bonds Mn^1–C^1 (1.94(1) Å) and Mn^2–C^1 (1.99(1) Å) and an unusually short Mn–Mn distance (2.734(2) Å) [8], compared with the Mn–Mn bonds (2.90–2.92 Å) in non-vinylidene complexes [76]. This is due to the constricting effect of the vinylidene bridge and it indicates the existence of conjugation in the Mn^1-Mn^2(μ-C^1=C^{2}HPh) system [8] (structure ***B$_4$*** in Scheme 11).

The presence of a symmetric and very strong carbodimetallacycle causes both thermal stability (dec. >144 °C) and chemical inactivity of **2**. Molecule **2** splits into two mononuclear fragments under prolonged UV irradiation with PPh$_3$ in benzene solution (reaction *(20)*) [15].



2 **31**

Complex [Cp(CO)$_2$Re]$_2$(μ-C=CHPh) (**7**) is thermally more stable (dec. >194 °C) than the manganese analogue **2** [16]. The mass spectra of **2** and **7** indicate a greater strength of the Re–Re bond in comparison with the Mn–Mn bond [44].

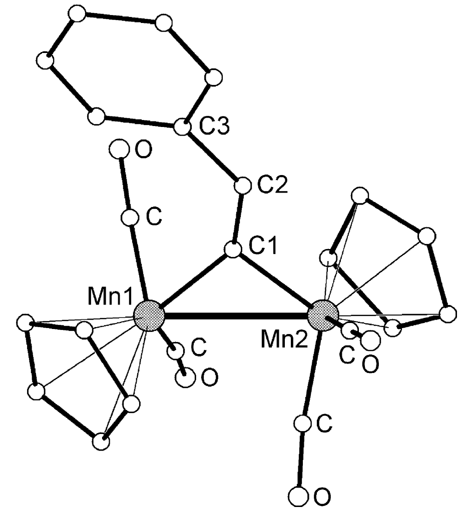
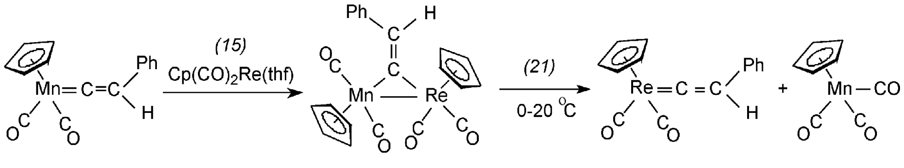


Fig. 2. Molecular structure of [Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**). The H atom at C2 was not located [7,8].

The complexes [Cp(CO)$_2$Mn]$_2$(μ-C=CH$_2$) (**10**) [50], [Cp′(CO)$_2$Mn]$_2$(μ-C=CH$_2$) [51] and [Cp(CO)$_2$Mn]$_2$(μ-C=CHR) (R = CH(OMe)$_2$, CH(OEt)$_2$, CH[O(CH$_2$)$_3$O] [54], COOMe [55a], COPh [91]) were obtained in small yields as a result of spontaneous transformations of the corresponding mononuclear complexes Cp(CO)$_2$Mn=C=CH$_2$, Cp′(CO)$_2$Mn=C=CH$_2$ and Cp(CO)$_2$Mn=C=CHR. The ease of the above transformations is due to the steric accessibility of the Mn=C bond to attack by the [Mn(CO)$_2$Cp] unit (see Section 2.4.1).

The first heterometallic vinylidene complex was orange Cp$_2$(CO)$_4$MnRe(μ-C=CHPh) (**47**) [20]. It was obtained in two ways: by the addition of the [Cp(CO)$_2$Mn] unit to Cp(CO)$_2$Re=C=CHPh (**6**) and with the counter reaction *(15)* — by the addition of [Cp(CO)$_2$Re] to **1**. The small yield of **47** is due to its instability and due to the concurrent formation of [Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**) and [Cp(CO)$_2$Re]$_2$(μ-C=CHPh) (**7**).

The ν(CO) frequencies in the IR spectra of **2** [15], **7** [16] and **47** [20] are almost identical (Table 5). The ν(C=C) bands for **2**, **7** and **47** were found in a narrow interval of 1548–1555 cm^{-1}.



1 **47** **6**

Complex **47** differed amazingly from its homodinuclear “relatives” **2** and **7**. It decomposed spontaneously at 0 °C within

Table 4
X-ray parameters [bond distances (d, Å) and bond angles (ω, °)] of μ-vinylidene complexes with Mn—M bonds (M = Mn, Mo, W, Fe, Rh, Pt, Pd, Cu)

Complex	d (Å)					ω (°)	Ref.
	Mn—M	Mn—C^1	M—C^1	Δd[a]	C^1=C^2	∠MnC^{1}C^2	
[Cp(CO)$_2$Mn]$_2$(μ-C=CHR)							
[Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**)	2.734(2)	1.94(1)	1.99(1)	0.05	1.35(2)	144(1), 128(1)	[7,8]
[Cp(CO)$_2$Mn]$_2$(μ-C=CH$_2$) (**10**)	2.759(2)	1.971(6)	1.979(7)	0.008	1.308(10)	136.0(5), 135.4(5)	[50]
[Cp(CO)$_2$Mn]$_2$(μ-C=CHCHO)	2.753(1)	1.945(4)	1.949(4)	0.004	1.347(5)	137.8(3)	[54]
[Cp(CO)$_2$Mn]$_2$[μ-C=CHCHO(CH$_2$)$_3$O]	2.748(1)	1.954(4)	1.983(3)	0.029	1.329(5)	133.0(3)	[54]
Cp(CO)$_2$MnM(μ-C=CHR)(L)							
Cp(CO)MnRh(μ-C=CH$_2$)(μ-CO)(i-Pr$_3$P)(Cp) (**48**)	2.667(1)	1.901(3)	2.056(3)	0.155	1.294(6)	144.2(3)	[25]
Cp(CO)$_2$MnRh(μ-C=CHPh)(Acac)(CO) (**49**)	2.648(1)	1.882(2)	2.038(3)	0.156	1.326(3)	153.2(2)	[27]
Cp(CO)$_2$MnPt(μ-C=CHPh)(dppm) (**58**)	2.6068(10)	1.924(7)	1.991(6)	0.067	1.363(9)	143.3(5)	[95]
(dppe)PdMn(μ$_3$-C=CHPh)PdMn(μ-C^1=C^{2}HPh)-(CO)$_4$Cp$_2$ (**66**)	2.6023(6), 2.6463(5)	1.893(4)	2.009(3)	0.116	1.345(5)	150.4(3)	[102]
[Cp(CO)$_2$MnCu(μ-C=CHPh)(μ-Cl)]$_2$ (**67**)	2.438(1)	1.874(5)	1.924(5)	0.05	1.322(7)	157.2(4)	[30]
[Cp(CO)$_2$Mn]$_2$Mo(μ-C=CHCOOMe)$_2$(CO)$_2$ (**69**)	2.9638(3)	1.909(2)	2.110(2)	0.201	1.346(3)	145.8(2)	[21b]
Cp(CO)$_2$MnW(μ-C=CHCOOMe)(CO)$_4$ (**70**)	2.9939(8)	1.903(5)	2.130(5)	0.227	1.337(7)	144.7(4)	[21b]
Cp(CO)$_2$MnFe(μ-C=CHCOOMe)(CO)$_4$ (**71**)	2.703(4)	1.95(2)	1.94(2)	−0.01	1.30(2)	133(1)	[21a]
η^4-{C[Mn(CO)$_2$Cp](CO)(CHPh)}Fe(CO)$_3$ (**51**)	2.760(4)	2.03(2)	2.00(1)	−0.03	1.44(2)	124.8(1)	[90]

[a] $\Delta d = d(\text{M–C}^1) - d(\text{Mn–C}^1)$.

Table 5
IR [ν(CO), cm^{-1}], ^{13}C and ^{1}H NMR (δ, ppm) and electrochemical [$E_{1/2}$, V] characteristics of μ-vinylidene complexes Cp(CO)$_2$MnM(μ-C^1=C^{2}HPh)(L) (M = Mn, Re, Rh, Pt, Pd, Cu)

Complex[a]	IR spectrum (cm^{-1})		NMR spectrum, δ (ppm)			$E_{1/2}$ (V)[b,c]	Ref.
	ν(CO)(Mn)	$\Delta\nu$[d]	^{13}C		^{1}H		
			C^1	C^2	=C^{2}H		
(I) [Cp(CO)$_2$M]$_2$(μ-C=CHPh) (M = Mn, Re)							
[Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**)	1983, 1953, 1928	–	284.16	146.40	8.34	−1.81[e], −2.23	[15,137]
Cp$_2$(CO)$_4$MnRe(μ-C=CHPh) (**47**)	1983, 1952, 1920	–	–	–	–	–	[20]
[Cp(CO)$_2$Re]$_2$(μ-C=CHPh) (**7**)	1983, 1953, 1916	–	–	–	–	–	[16]
(II) Cp(CO)$_2$MnM(μ-C=CHPh)(L) (M = Cu, Rh)							
[Cp(CO)$_2$MnCu(μ-C=CHPh)(μ-Cl)]$_2$ (**67**)	2005, 1953	52	317.05	136.26	7.69	−0.78, −2.08	[30,138]
Cp(CO)$_2$MnRh(μ-C=CHPh)(Hfac)(CO) (**50**)[f]	2058, 2033 (RhCO), 1994, 1928	66	–	–	8.71	–	[27]
Cp(CO)$_2$MnRh(μ-C=CHPh)(Acac)(CO) (**49a**)	2020 (RhCO), 1975, 1902	73	290.60	132.40	8.75	–	[27]
Cp(CO)$_2$MnRh(μ-C=CHPh)(Acac)(CO) (**49b**)	2050 (RhCO), 1975, 1902	73	292.62	133.74	–	–	[27]
Cp(CO)MnRh(μ-C=CH$_2$)(μ-CO)(Pi-Pr$_3$)(Cp) (**48**)	1895, 1800	95	278.87	121.51	6.55, 6.45	–	[25]
(III) Cp(CO)$_2$MnPt(μ-C=CHPh)(L)(L′)							
Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OPh)$_3$]$_2$ (**53**)	1944, 1876	68	–	–	8.62	−2.39	[23,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)(CO) (**56**)	2032 (PtCO), 1938, 1871	67	260.48	146.34	7.74	−2.10	[93,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OEt)$_3$]$_2$ (**37**)	1930, 1858	72	259.80	141.08	8.76	-	[23]
Cp(CO)$_2$MnPt(μ-C=CHPh)[P(O-i-Pr)$_3$]$_2$ (**55**)	1929, 1863	66	259.48	141.36	8.64	−2.60	[93,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)[P(O-i-Pr)$_3$](CO) (**57**)	2045 (PtCO), 1928, 1867	61	–	–	8.85	−2.23	[93,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)[P(O-i-Pr)$_3$](PPh$_3$) (**54**)	1926, 1842	84	259.97	140.27	8.72	−2.54	[93,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (**52**)	1924, 1838	86	264.30	141.25	7.92	−2.37	[23,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)(dppp) (**60**)	1913, 1822	91	265.96	140.48	–	−2.54[e]	[94,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)(dppe) (**59**)	1906, 1784	122	269.75	141.63	8.27	−2.54[e]	[94,137]
Cp(CO)$_2$MnPt(μ-C=CHPh)(dppm) (**58**)	1902, 1768	134	271.14	141.20	8.33	−2.37[e]	[94,137]
(IV) Cp(CO)$_2$MnPd(μ-C=CHPh)(L)(L′)							
Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)(η^1-dppm) (**62**)	1930, 1860	70	–	–	–	–	[99]
Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)$_2$ (**61**)	1927, 1846	81	287.22	141.13	6.42	−2.24	[29,140]
Cp(CO)$_2$MnPd(μ-C=CHPh)(dppp) (**65**)	1918, 1836	82	283.92	141.37	7.14	−2.54[e]	[99,140]
Cp(CO)$_2$MnPd(μ-C=CHPh)(dppe) (**64**)	1922, 1819	103	286.38	141.55	7.50	−2.54[e]	[29,140]
Cp(CO)$_2$MnPd(μ-C=CHPh)(dppm) (**63**)	1900, 1795	105	–	–	–	–	[99]

[a] The complexes are ordered in each series (I–IV) according to the lowering of the frequency of the CO$_t$ group at the Mn atom.

[b] Dropping mercury electrode, MeCN, 0.1 M [Et$_4$N]BF$_4$, Ag/0.1 M AgNO$_3$ in MeCN.

[c] Potentials are given vs. Ag/0.1 M AgNO$_3$ in MeCN; adding 0.337 V can convert them to V vs. SCE.

[d] $\Delta\nu = \nu(\text{CO}_t) - \nu(\text{CO}_{sb})$, where CO$_t$ is terminal CO group at the Mn atom, CO$_{sb}$ is semibridging CO group.

[e] Reversible stage.

[f] Two isomers.

several hours to form complex **6** and CpMn(CO)$_3$ (reaction *(21)*). Such behaviour of complex **47** corresponds with the structure ***B$_2$*** in Scheme 11, viz. the manganese complex with π-ligand Cp(CO)$_2$Re=C^1=C^{2}HPh.

The consecutive reactions *(15)* and *(21)* showed for the first time the possibility of a transfer of the vinylidene ligand from one transition metal atom to another metal atom [20].

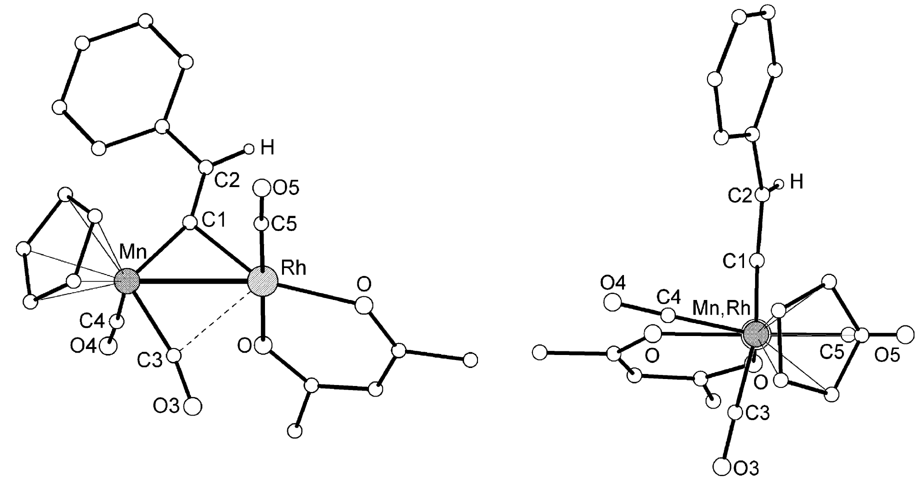
3.1.2. Mn–Rh μ-vinylidene complexes

Contrary to Cp$_2$(CO)$_4$MnRe(μ-C=CHPh) (**47**), μ-vinylidene complexes with the Mn-Rh bond are quite stable. Werner et al. synthesized the first of them, viz. Cp(CO)$_2$MnRh(μ-C=CHR)(*i*-Pr$_3$P)(Cp) (R = H (**48**), Me, Ph), by means of reactions between Cp(*i*-Pr$_3$P)Rh=C=CHR and Cp(CO)$_2$Mn(thf) [25].

By the isolobal analogy (Scheme 9) between allenes R$_2$C=C=CR$_2$ (***A$_o$***) and complexes LM=C=CR$_2$ (***A***), both add the fragments [Rh(CO)(L)] (L = Acac, Hfac) to form the π-complexes (η^2-R$_2$C=C=CR$_2$)Rh(CO)(L) (***B$_o$***) [92] and the μ-vinylidene MnRh complexes (***B***) [26,27], respectively.

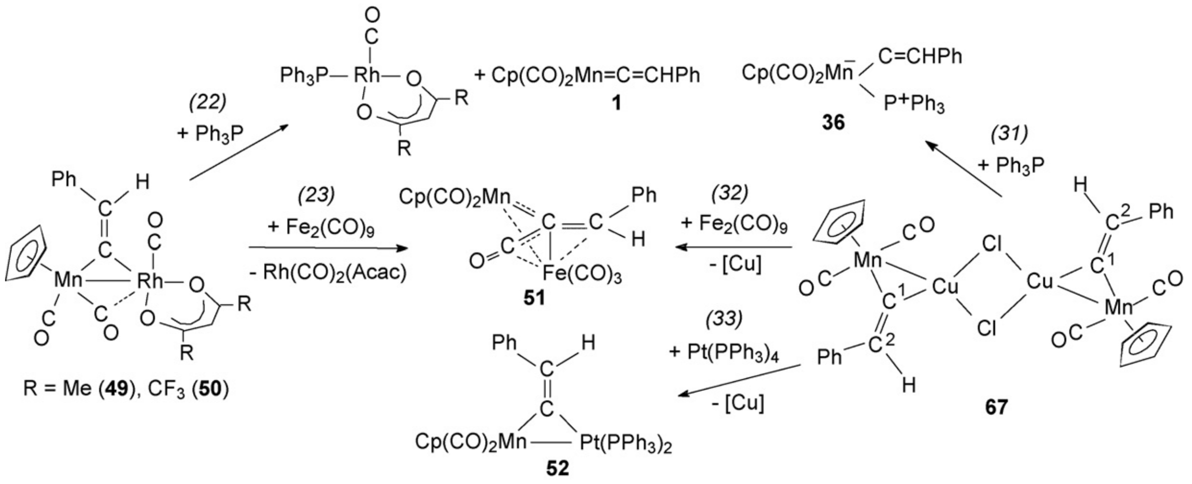
Dark green complexes Cp(CO)$_2$MnRh(μ-C=CHPh)(Acac)(CO) (**49**) and Cp(CO)$_2$MnRh(μ-C=CHPh)(Hfac)(CO) (**50**) are formed from Cp(CO)$_2$Mn=C=CHPh (**1**) and (Acac)Rh(CO)$_2$ or (Hfac)Rh(CO)$_2$, respectively (reaction *(16)* in Scheme 10) [26,27].

Complex **49** (Fig. 3) differs from other μ-vinylidene MnM complexes (M = Mn, Mo, W, Fe, Pt) (Table 4) by the presence of a short Mn–C^1 bond and a large MnC^{1}C^2 angle [27]. This angle (153.2(2)°) is comparable to the C=C=C angles (147–153°) in (η^2-R$_2$C=C=CR$_2$)Rh(Acac)(L) (L = CO or R$_2$C=C=CR$_2$). The Rh-C^1 bond length in **49** (2.038(3) Å) is close to the Rh–C$_{sp}$ distances (2.03–2.06 Å) in π-allene complexes [92b]. Therefore, **49** and **50** can be represented as π-complexes of Rh(I) with the mangana-allene ligand Cp(CO)$_2$Mn=C^1=C^{2}HPh. Bonding occurs for the most part by donation of electron density from π-MO of the Mn=C^1 bond to unoccupied d-orbitals of the Rh



(a) (b)

Fig. 3. Molecular structure of Cp(CO)$_2$MnRh(μ-C=CHPh)(C$_5$H$_7$O$_2$)(CO) (**49**): (a) overall form of the molecule and (b) view along the Mn-Rh bond [27].



Scheme 12. The reactions of the MnRh (**49**, **50**) and MnCu (**67**) μ-vinylidene complexes with Ph$_3$P, Fe$_2$(CO)$_9$ and Pt(PPh$_3$)$_4$.

atom (σ component), while the role of back-donation (π component) is comparatively small (structure ***B***$_1$ in Scheme 11) [27]. The significantly smaller declination of the MnC^{1}C^2 group from linearity in **49** as compared with other μ-vinylidene complexes, in which the MnC^{1}C^2 angles are 133–145° (Table 4), can apparently be explained by the predominance of the σ component.

The IR and NMR ^{13}C data (Table 5) indicate a weak π-donor capacity of the Rh(Acac)(CO) and Rh(Hfac)(CO) groups. Complexes **49** and **50** are characterized by the highest ν(CO) frequencies of the Cp(CO)$_2$Mn fragment (1994–1975 and 1928–1902 cm^{-1}) and the largest downfield shift of the C^1 signal (291–293 ppm) in the set of dinuclear μ-vinylidene derivatives of cymantrene.

Complex **49** was shown by the NMR and IR spectra to exist in solution as two isomers, which differ in orientation of the terminal CO groups at the Mn and Rh atoms relative to the plane of the MnRh(μ-C^1) cycle [27]. In the crystal form (**49a**), the C^{4}O^4 and C^{5}O^5 groups are mutually *trans* (Fig. 3b). The minor isomer **49b** with a *cis* orientation of the C^{4}O^4 and C^{5}O^5 groups exists in solution and is in equilibrium with **49a**. Interconversion of **49a** and **49b** occurs by means of rotation of the Rh(Acac)(C^{5}O^5) fragment by 180° around the Rh/Mn=C^1 π-bond (see structure ***B***$_1$ in Scheme 11) [27]. Similar rotation of the Rh(Acac)(CO) fragment around the Rh/C=C π-bond was observed in the allene complexes (η^2-R$_2$C=C=CR$_2$)Rh(Acac)(L) (L = CO or R$_2$C=C=CR$_2$) [92].

The reactivity of **49** and **50** agrees well with their representation as rhodium π-complexes with the mangana-allene ligands [27], since the reactions result in cleavage of the bond between the Rh atom and the [Cp(CO)$_2$Mn=C=CHPh] ligand (Scheme 12).

Complexes **49** and **50** react rapidly with Ph$_3$P at 20 °C to form Cp(CO)$_2$Mn=C=CHPh (**1**) and (Acac)Rh(CO)(PPh$_3$) or (Hfac)Rh(CO)(PPh$_3$), respectively (reaction *(22)* in Scheme 12) [27]. The action of Fe$_2$(CO)$_9$ upon complex **49** (reaction *(23)*) resulted in the exchange of the [Rh(Acac)(CO)] fragment for [Fe(CO)$_4$] to give η^4-{C[Mn(CO)$_2$Cp](CO)CHPh}Fe(CO)$_3$ (**51**) (see Section 3.3).

3.1.3. Mn–Pt μ-vinylidene complexes

Phenylvinylidene complexes with the Mn–Pt bond are the most numerous and well-studied of heterometallic complexes of type ***B***. The first, Cp(CO)$_2$MnPt(μ-C=CHPh)[P(OEt)$_3$]$_2$ (**37**), was obtained from reaction *(7)* (Section 2.5.3) [22].

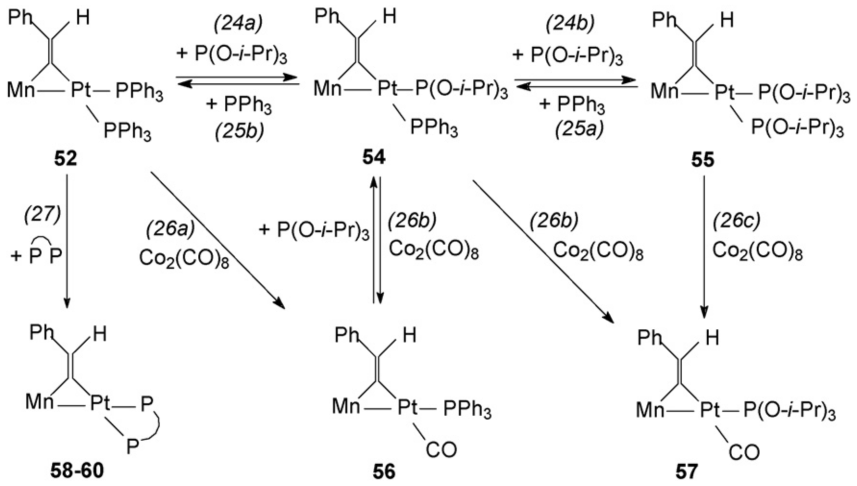
Reactions *(17)* in Scheme 10 between Cp(CO)$_2$Mn=C=CHPh (**1**) and PtL$_4$ were used to form Cp(CO)$_2$MnPt(μ-C=CHPh)(L)$_2$ (L = P(OEt)$_3$ (**37**), PPh$_3$ (**52**), P(OPh)$_3$ (**53**)) [23]. The μ-vinylidene MnPt complexes react with phosphines and phosphites without cleavage of the MnPt(μ-C^1) cycle (Scheme 13) [93,94].

The reaction *(24)* between Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (**52**) and P(O-*i*-Pr)$_3$ occurred in two consecutive stages [93]. With one eq., the mixed-ligand complex Cp(CO)$_2$MnPt(μ-C=CHPh)[P(O-*i*-Pr)$_3$](PPh$_3$) (**54**) was formed, while an excess of phosphite gave Cp(CO)$_2$MnPt(μ-C=CHPh)[P(O-*i*-Pr)$_3$]$_2$ (**55**). Treatment of **55** with Ph$_3$P gave **54** and then the initial complex **52** (reaction *(25)* in Scheme 13).

Complexes **52–55** are practically inert to the action of CO gas. The use of Co$_2$(CO)$_8$ as a source of CO allowed the tricarbonyl complexes **56** and **57** in good yield (reactions *(26)*). The CO group at the Pt atom can be easily substituted by other ligands. Substitution of both PPh$_3$ in **52** with chelating diphosphines P–P afforded Cp(CO)$_2$MnPt(μ-C=CHPh)(P–P) (P–P = dppm (**58**), dppe (**59**), dppp (**60**)) in 90–95% yields (reactions *(27)*) [94].

Orange crystalline complexes **37**, **52–55** and **58–60** are air- and thermally stable. Introduction of the CO ligand to the Pt atom somewhat reduces the stability of the MnPt(μ-C) system in complexes **56** and **57**.

Complex Cp(CO)MnPt(μ-C=CHPh)(μ-CO)(dppm) (**58**) (Fig. 4) contains a short Mn–Pt bond 2.6068(10) Å [95]. The [MnPt(μ-C=CHPh)] and [Pt(η^2-dppm)] fragments form an almost planar system. The bonds C^1=C^2 1.363(9) Å, Mn–C^1 1.924(7) Å and the MnC^{1}C^2 angle 143.3(5)° in **58** are close to those in [Cp(CO)$_2$Mn]$_2$(μ-C=CHPh) (**2**) (Table 4).



Scheme 13. Ligand substitution at the Pt atom in complexes Cp(CO)$_2$MnPt(μ-C=CHPh)(L)$_2$: Mn = [Cp(CO)$_2$Mn]; P–P = dppm (**58**), dppe (**59**), dppp (**60**)]; benzene, 20 °C, 0.5–4 h, 70–95%.

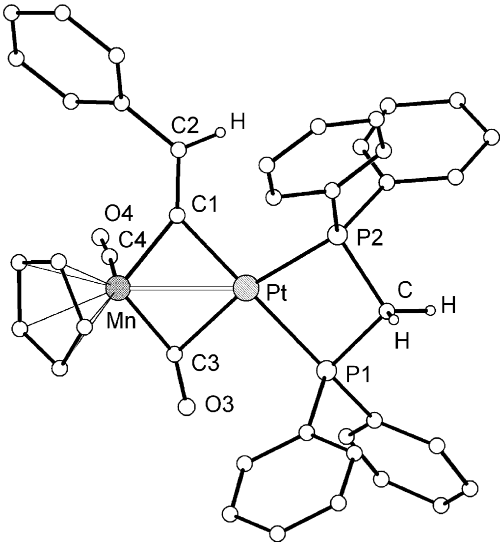


Fig. 4. Molecular structure of Cp(CO)MnPt(μ-C=CHPh)(μ-CO)(dppm) (**58**) [95].

The symmetry of the carbodimetallacycle $\overline{\text{MnMC}}^1$ is determined by the difference between the M–C^1 and Mn–C^1 bond lengths, Δ*d* (Table 4). For **2** and **58**, Δ*d* are small, viz. 0.05 and 0.067 Å, respectively, whereas Δ*d* for the MnRh complex **49** is 0.156 Å.

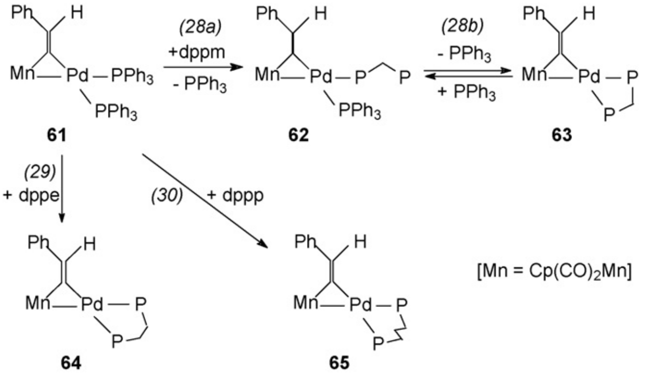
The C^1 signal at δ 260–270 ppm in the ^{13}C NMR spectrum of Cp(CO)$_2$MnPt(μ-C^1=C^{2}HPh)(L)$_2$ (**37**, **52**–**60**) is shifted appreciably upfield, and ν(CO)(Mn) in the IR spectra are lowered greatly from those of other complexes with the Mn–M bonds (M = Mn, Rh, Pd, Cu) (Table 5), due to the strong electron donor influence of the [PtL$_2$] group [104,105].

The high stability of the $\overline{\text{MnPtC}}^1$ cycle in complexes Cp(CO)$_2$MnPt(μ-C^1=C^{2}HPh)(L)$_2$ (**37**, **52**–**60**) results not only from the strong donor character of the [PtL$_2$] fragments, but also from the disposition of ligands L in the same plane as the Mn–C^1 bond (structure ***B₃*** in Scheme 11), which favors more effective transfer of electron density from Pt to the π*-MO of the Mn=C^1 bond than the perpendicular orientation of the [Rh(Acac)(CO)] fragment in complex **49** [27].

3.1.4. Mn–Pd μ-vinylidene complexes

Complexes of the "A-frame" type X$_2$MPd(μ-C=CR$_2$)(μ-dppm)$_2$ (X = Cl, Br, I; M = Ni, Pd; R = H, Cl) [4,96] and the cationic complex [(PhC≡C)PdPt(μ-C=CHPh)(PEt$_3$)$_4$]$^+$ [97] were the only palladium-containing vinylidene complexes reported before our work [28]. The μ-carbene complex Cp(CO)$_2$MnPd[μ-C(OMe)Ph](PMe$_3$)$_2$ had also been described [98].

The first MnPd vinylidene complex was Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)$_2$ (**61**) obtained from reaction *(18)* (Scheme 10) between Cp(CO)$_2$Mn=C=CHPh (**1**) and Pd(PPh$_3$)$_4$ in almost quantitative yield [28,29]. Complex **61** is less stable than Cp(CO)$_2$MnPt(μ-C=CHPh)(PPh$_3$)$_2$ (**52**). Reactions between **61** and P–P = dppe, dppp led to quite stable complexes Cp(CO)$_2$MnPd(μ-C=CHPh)(dppe) (**64**) and Cp(CO)$_2$MnPd(μ-C=CHPh)(dppp) (**65**) (reactions (29), (30)) in Scheme 14) [29,99].



Scheme 14. Ligand substitution at the Pd atom in Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)$_2$ (**61**): *(28)* benzene, 20 °C, 2 h; *(29)* and *(30)* benzene, 20 °C, 1 h, 90%.

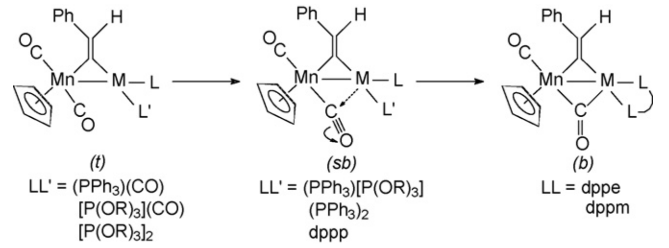
The reaction *(28)* between **61** and dppm gave two unstable compounds Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)(η^1-dppm) (**62**) and Cp(CO)$_2$MnPd(μ-C=CHPh)(η^2-dppm) (**63**) [99]. The equilibrium between **62** and **63** did not shift to the right by the addition of an excess of dppm. Stepwise substitution was observed [93] for monodentate ligands PR$_3$ at the Pt atom (reactions *(24)* and *(25)* in Scheme 13). However, we failed to isolate any complexes containing "dangling" η^1-P–P ligands in reactions *(27)* (Scheme 13), *(29)* and *(30)* (Scheme 14). Nevertheless, it is logical to assume that all the above reactions of ligand exchange at the Pt and Pd atoms occur in two stages.

The IR spectra of complexes Cp(CO)$_2$MnM(μ-C=CHPh)L$_2$ (M = Pd, Pt) show the ν(C=C) band at 1550–1545 cm^{-1}. Noticeable shifts of ν(CO) to high frequencies and downfield shift (ca. 20 ppm) of μ-C^1 for MnPd complexes compared to the MnPt analogs were observed (Table 5).

The binding in the $\overline{\text{MnPdC}}^1$ cycle corresponds to structure ***B₁*** in Scheme 11. The weaker donor power of Pd as compared to Pt should cause a decrease of the π component of the bond between the Pd atom and Mn=C^1. Probably, the σ component is also weaker, in particular, because of a greater size of the Pd atom in comparison with the Pt atom (1.49 and 1.43 Å, respectively [100]).

3.1.5. Semi-bridging CO ligands

Detailed studies of the IR spectra of complexes Cp(CO)$_2$MnM(μ-C=CHPh)L$_2$ (M = Pt (**37**, **52**–**60**) [93,94,101]; Pd (**61**–**65**) [29,99,101]) showed that the influence of the [ML$_2$] group on CO at the Mn atom is unequal. The frequency of the strongest ν(CO) band has a relatively narrow range 1944–1900 cm^{-1}, while the lower frequency band depends greatly on the nature of ligands L and is found in the broad range 1876–1768 cm^{-1}. The atom M = Pt, Pd bearing the donor L ligands tends to transfer a part of its electron density to one of the CO groups at the Mn atom by means of d$_\pi$(M) → π*(C≡O) interaction. As a result, this CO



Scheme 15. Consecutive change of the CO coordination mode from terminal *(t)* to semi-bridging *(sb)* and to bridging *(b)* in Cp(CO)$_2$MnM(μ-C=CHPh)LL′ (M = Pt, Pd).

group becomes semi-bridging (CO$_{sb}$), whereas the second CO, being weakly influenced by L, remains terminal (CO$_t$) (see Scheme 15).

The size of the splitting between two carbonyl bands $\Delta\nu = \nu(CO_t) - \nu(CO_{sb})$ has been used as an estimation of the semi-bridging interaction [101]. A gradual growth of $\Delta\nu$ from 61 to 134 cm^{-1} is observed (Table 5) as a result of a consecutive replacement of ligands LL′ at the Pt atom in the sequence: LL′ = [P(O-*i*-Pr)$_3$](CO) < (PPh$_3$)(CO) < [P(OPh)$_3$]$_2$ < [P(OEt)$_3$]$_2$ ≪ [P(O-*i*-Pr)$_3$](PPh$_3$) < (PPh$_3$)$_2$ < dppp ≪ dppe < dppm. For complexes with the monodentate ligands L, L′, such a sequence coincides with a gradual increase in the donor power of these ligands. However, the electron donor capacity of bidentate diphosphines P–P changes in the inverse order: dppp > dppe > dppm [94]. In the same order, the P–Pt–P angles decrease, e.g. 91.6° in (dppp)PtCl$_2$, 85.7° in (dppe)PtFe$_2$(CO)$_8$ and 72.8° in Cp(CO)$_2$MnPt(μ-C=CHPh)(dppm) (**58**). The P–Pt–P angle for Pt(PPh$_3$)$_2$ group reaches 108° [100c].

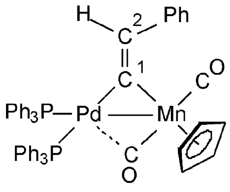
We assumed [94,101] that a gradual decrease in the steric hindrance of the ligands in the order (PPh$_3$)$_2$ > dppp > dppe > dppm, resulted in strengthening of the interaction Pt → CO$_{sb}$ at consecutive transitions L$_2$ = (PPh$_3$)$_2$ < dppp ≪ dppe < dppm. The same sequence of $\Delta\nu$ change was observed for Cp(CO)$_2$MnPd(μ-C=CHPh)L$_2$ (Table 5) [29,99,101].

The smooth change of the CO coordination mode from terminal *(t)* to semi-bridging *(sb)* and to bridging *(b)* (Scheme 15) gives an opportunity to influence the properties of the coordinated CO molecules by substituents at the metal atoms and may be useful for modification of the catalysts used in the synthesis of organic products from carbon monoxide.

3.2. Other Mn–M μ-vinylidene complexes (M = Pd, Cu, Mo, W, Fe)

3.2.1. The μ,μ$_3$-bis-vinylidene complex (dppe)PdMn(μ$_3$-C=CHPh)PdMn(μ-C=CHPh)(CO)$_4$Cp$_2$

From reaction *(29)* between Cp(CO)$_2$MnPd(μ-C=CHPh)(PPh$_3$)$_2$ (**61**) and dppe, in addition to the major product Cp(CO)$_2$MnPd(μ-C=CHPh)(dppe) (**64**) (Scheme 14), a small amount of the unusual tetranuclear complex (dppe)PdMn(μ$_3$-C=CHPh)PdMn(μ-C=CHPh)(CO)$_4$Cp$_2$ (**66**) was isolated [102].



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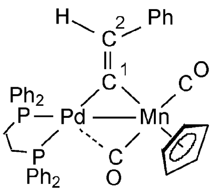

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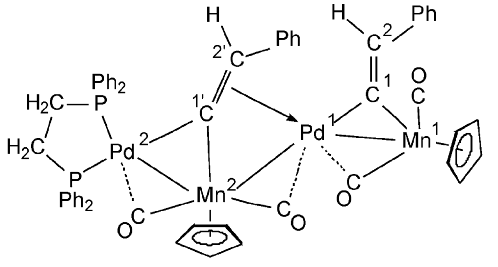


66

The structure of **66** (Fig. 5) is unique due to the presence of two vinylidene ligands linked to the chain of the alternating atoms Mn^1–Pd^1–Mn^2–Pd^2 by two different (μ$_2$ and μ$_3$) coordination modes [102]. The distances between metal atoms are Mn^1–Pd^1 2.6025(6) Å, Pd^1–Mn^2 2.8913(5) Å, Mn^2–Pd^2 2.6463(4) Å; the angles are Mn^1–Pd^1–Mn^2 140.17(2)° and Pd^1–Mn^2–Pd^2 69.36(1)°. The C=C bond length is 1.347(4) Å in the μ$_2$(η^1,η^1)-C^1=C^{2}HPh ligand and 1.372(4) Å in μ$_3$(η^1,η^1,η^2)-C$^{1\prime}$=C$^{2\prime}$HPh.

The molecule of **66** consists of two parts, viz. [Cp(CO)$_2$Mn^{1}Pd^1(μ-C^1=C^{2}HPh)] *(fragment 1)* and [Cp(CO)$_2$Mn^{2}Pd^2(μ-C$^{1\prime}$=C$^{2\prime}$HPh)(dppe)] *(fragment 2)*. Most likely, fragment (*1*) arises from **61** in the course of reaction *(29)*. Both fragments are connected with the help of π-bonding between the vinylidene C$^{1\prime}$=C$^{2\prime}$ bond of fragment (*2*) and the Pd^1 atom of fragment (*1*), and also by a long Mn^2–Pd^1 bond and semi-bridging CO group.

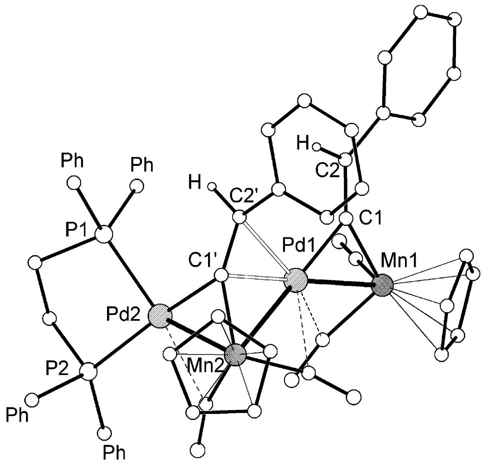


Fig. 5. Molecular structure of (dppe)PdMn(μ$_3$-C=CHPh)PdMn(μ-C=CHPh)(CO)$_4$Cp$_2$ (**66**) [102].

Earlier, the complex $[(OC)Pd(\mu\text{-}NC)Mn(CO)_2Cp']_4$ including two symmetric Mn–Pd–Pd–Mn chains [103a] and other non-vinylidene complexes containing the Mn–Pd–Pd–Mn and Mn_2Pd–Pd–Pd–Mn_2 fragments were reported [103b]. Complexes with two vinylidenes $[CpFe(CO)]_2(\mu\text{-}C{=}CH_2)_2$ [104], $[Cp(CO)_2Mn]_2Mo[\mu\text{-}C{=}C(H)COOMe]_2(CO)_2$ (**69**) (Scheme 16) [21b] and $Ir_2(\mu\text{-}C{=}CH_2)(\mu\text{-}C{=}CHPh)(\mu\text{-}dppm)_2(CO)_2I_2$ [105], where both μ-C=CHR ligands are coordinated to the metal atoms in a similar way, are also known.

Complex **66** represents the first organometallic compound containing the Pd–Mn–Pd–Mn chain, and at the same time, the first example of a compound in which two coordination types of vinylidene complexes are present in one molecule, viz. type ***B*** with the symmetric μ_2-coordination of vinylidene and type ***C*** with the μ_3-vinylidene ligand.

3.2.2. The dimeric complex $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$

Compound $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ (**67**) is the first μ-vinylidene complex with an M-Cu bond proven by X-ray analysis [30]. The structures of the known earlier complexes $(\eta^6\text{-}C_6H_6)(i\text{-}Pr_3P)OsCu(\mu\text{-}C{=}CHPh)(Cl)$ [24a] and $Cp(i\text{-}Pr_3P)RhCu(\mu\text{-}C{=}CHR)(Cl)$ (R = H, Me, Ph) [24b], were not reliably determined. Complex $TiCu\{\mu\text{-}C{=}C(SiMe_3)C_6H_3(2\text{-}NMe_2)(6\text{-}CH_2NMe_2)[\mu\text{-}(\eta^1,\eta^2)\text{-}C{\equiv}CSiMe_3]\}$ was shown by XRD not to contain a metal–metal bond [106].

We obtained dark green **67** from the reaction *(19)* (Scheme 10) between $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and CuCl in a quantitative yield [30]. The molecule **67** (Fig. 6) is a dimer, where two dinuclear fragments are linked by asymmetric chloride bridges (Cu^1–Cl^1 2.256(2) Å, Cu^1–Cl^{1a} 2.278(2) Å). The central part of each dinuclear fragment is the $MnCuC^1$ triangle with an Mn–Cu bond length of 2.438(1) Å.

The Mn–C^1 bond (1.874(5) Å) in **67** is the shortest and the declination of the Mn^1–C^1–C^2 system (157.2(4)°) from linearity is the smallest among the MnM μ-vinylidene complexes (Table 4). Unusually, all CO groups in **67** are terminal: the Mn–C–O angles are 174.7(4)° and 177.4(5)°. The IR spectrum of **67** contains two ν(CO) bands at 2005 and 1953 cm^{-1} [30] close to those of the initial complex **1**. The ^{13}C NMR spectrum of **67** showed an unusually low field C^1 resonance (δ 317.05 ppm) (Table 5). The C^1 signal of **67** differs from the C^1 in **1** by 62 ppm. The above data are consistent with **67** being a π-complex of copper with the $[Cp(CO)_2Mn{=}C^1{=}C^2HPh]$ ligand (structure $\boldsymbol{B_1}$ in Scheme 11) with weak back-bonding from Cu to Mn=C^1. The Cu–Mn and Cu–C^1 σ-bonds are also probably weak.

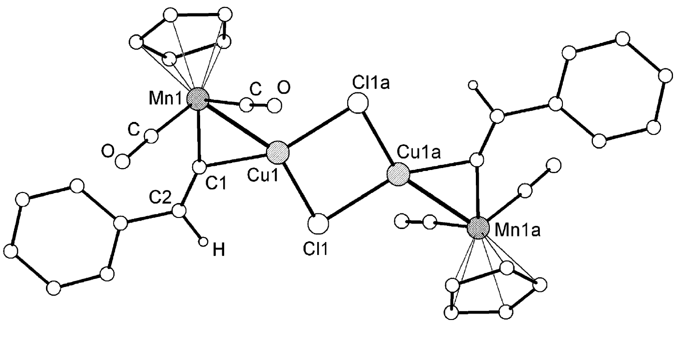


Fig. 6. Molecular structure of $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ (**67**) [30].

The properties of **67** resemble those of $Cp(CO)_2MnRh(\mu\text{-}C{=}CHPh)(Acac)(CO)$ (**49**) [27] more than those of other μ-vinylidene complexes. Reactions *(31)–(33)* in Scheme 12 result in splitting of the Mn–Cu and Cu–μ–C^1 bonds [30]. Treatment of **67** with PPh_3 affords **1**, which reacts further to give **36**. Reactions with $Fe_2(CO)_9$ and with $Pt(PPh_3)_4$ resulted in transmetalation to give **51** and **52**, respectively.

3.2.3. Mn–Mo, Mn–W and Mn–Fe μ-vinylidene complexes

Complex $Cp(CO)_2Mn{=}C{=}C(H)COOMe$ (**13**) reacted with $Mo(CO)_5(thf)$ to give the dark brown dinuclear **68** and trinuclear **69** complexes (reaction *(34)* in Scheme 16) [21b]. Complex **69** is stable up to 300 °C. The dinuclear complex **70** was isolated from a reaction *(35)* between **13** and $W(CO)_5(thf)$.

Complexes **69** and **70** were also obtained from reactions of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}COOMe)$ with $Mo(CO)_5(thf)$ and $W(CO)_5(thf)$, respectively. However, $Cr(CO)_5(thf)$ does not reacts either with $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}COOMe)$ nor with complex **13**.

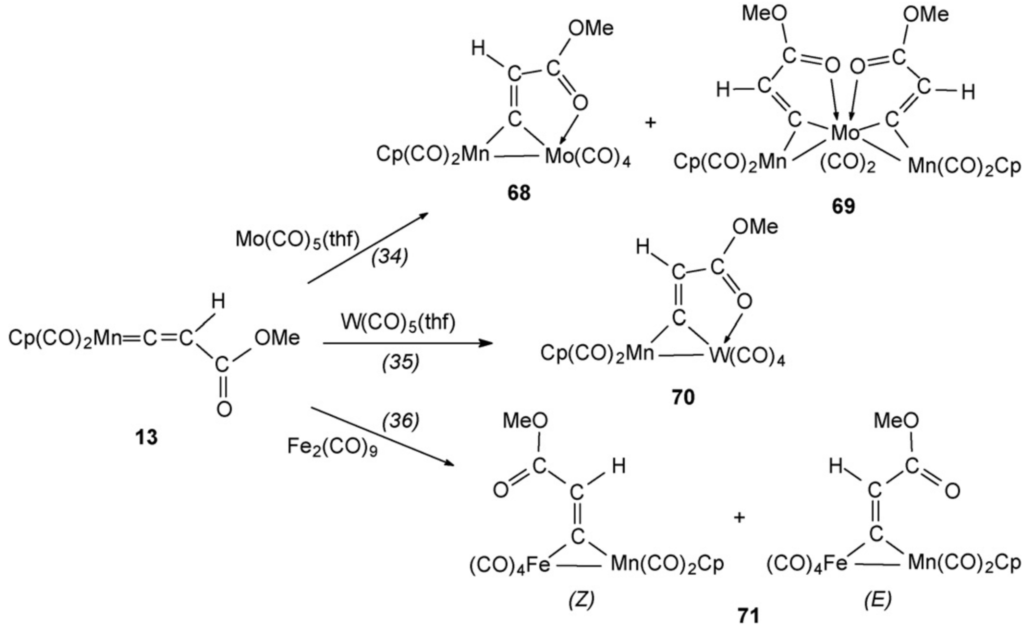
The μ-$C^1{=}C^2(H)C^3OOMe$ ligands in **69** and **70** form five-membered chelate rings by coordination $C^3{=}O{:}\rightarrow M$ (M = Mo, W). The stronger electron withdrawing power and chelate effect result in the C=C(H)COOMe bridge showing a greater constricting effect than μ-C=CHPh, with short Mn–Mo, Mn–W and Mn–C^1 bonds (Table 4). The three metal atoms in divinylidene **69** form a bent Mn–Mo–Mn chain (160.16(1)°).

Complex **13** reacts with $Fe_2(CO)_9$ to form $Cp(CO)_2MnFe[\mu\text{-}C{=}C(H)COOMe](CO)_4$ (**71**) as two air-stable red isomers, ***E*** (9%) and ***Z*** (73%) (reaction *(36)*, Scheme 16) which do not interconvert [21a]. Isomer ***Z*** was structurally characterized. The parameters of the central MnFe(μ-$C^1{=}C^2$) fragment (Table 4) are similar to those of $[(CO)_4Fe]_2(\mu\text{-}C{=}CPh_2)$ [10], $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) [7,8] and $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2)$ (**10**) [50], because of the similarly sized Mn and Fe atoms (covalent radii 1.38 and 1.34 Å, respectively [100]).

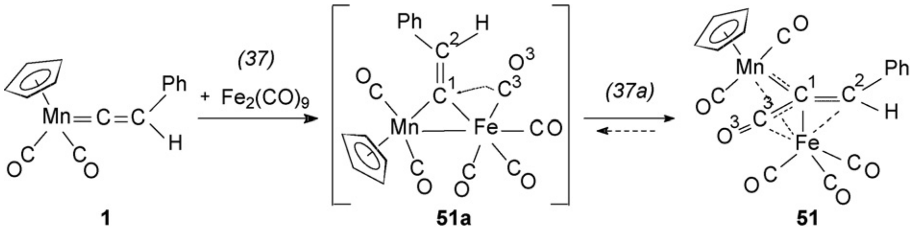
3.3. The trimethylenemethane-type complex with Mn–Fe bond

Addition of the $[Fe(CO)_4]$ unit to $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) did not give the expected μ-vinylidene $Cp(CO)_2MnFe(\mu\text{-}C{=}CHPh)(CO)_4$ (**51a**), but its isomer **51** in 50% yield (Scheme 17) [90]. Complex **51** was also obtained from the reaction between $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CPh)$ (**1a**) and $Fe_2(CO)_9$ in low yield [107].

The molecule of **51** (Fig. 7) was shown by an X-ray study [90] to contain Mn–Fe (2.760(4) Å), Mn–C^1 (2.03(2) Å) and Fe–C^1 (2.00(1) Å) bonds and the $C^1{=}C^3{=}O^3$ group with a short $C^1{=}C^3$ bond (1.45(2) Å). Addition of one of the CO groups of the $[Fe(CO)_4]$ fragment to the vinylidene C^1 atom occurs (Scheme 17). The phenylvinylidene transformed into benzylideneketene $[PhC^2H{=}C^1{=}C^3{=}O^3]$, non-existent in a free form. This organic fragment and the $[Mn(CO)_2Cp]$ group form the



Scheme 16. Synthesis of μ-vinylidene complexes from $Cp(CO)_2Mn{=}C{=}C(H)COOMe$ (**13**): *(34)* and *(35)* THF, 40–60 °C, 1 h; *(36)* hexane, 40 °C.



Scheme 17. Formation of the TMM type complex **51** from $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and $Fe_2(CO)_9$.

unusual organometallic ligand $\{C[Mn(CO)_2Cp](CO)CHPh\}$, η^4-coordinated to the Fe atom.

Complex **51** is the first heterometallic analogue of trimethylenemethane transition metal complexes. Structure **51** [90] is similar to that of classical trimethylenemethane (TMM) complexes η^4-$[C(CH_2)_3]Fe(CO)_3$ (**72**) [108a] and η^4-$[C(CH_2)_2(CHPh)]Fe(CO)_3$ (**73**) [108b]. The "trimethylenemethane" system in **51** is created by isolobal replacement of one of the $[CH_2]$ groups by $[C^3{=}O^3]$, the second $[CH_2]$—by the $[Mn(CO)_2Cp]$ group, the third substituent at the central C^1 atom being phenylmethylene [CHPh].

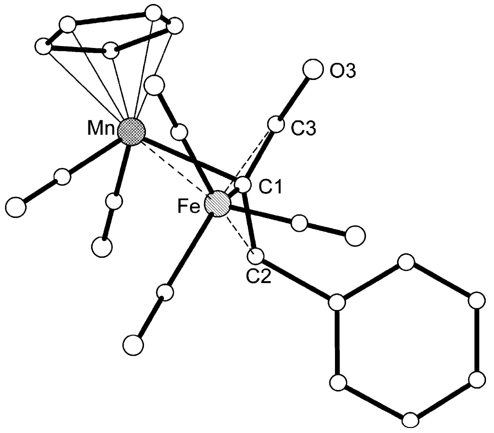
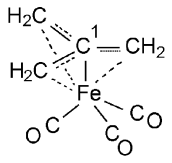


Fig. 7. Molecular structure of η^4-$\{C[Mn(CO)_2Cp](CO)CHPh\}Fe(CO)_3$ (**51**). The H atom at C2 was not located [90].



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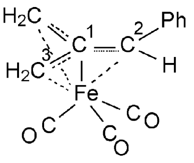

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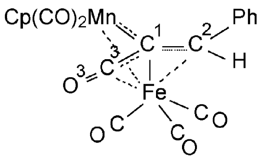
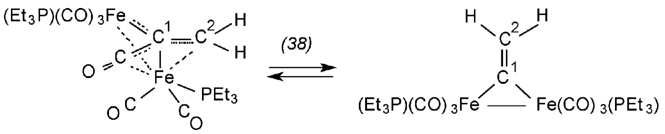


51

The $[C^1(Mn)(C^3O)C^2HPh]$ fragment in **51** is an almost planar conjugated system, and the central C^1 atom is displaced from the MnC^2C^3 plane by 0.10 Å opposite to the Fe atom [90]. In **72** and **73** such displacement is 0.3 Å [108]. The methylene groups in **72** and **73** are in a staggered conformation in relation to the CO groups. The $Fe(CO)_3$ and $C^1MnC^2C^3$ fragments in **51** are also mutually staggered (see Fig. 7). In all three compounds, the axis of the $Fe(CO)_3$ group, having the C_{3v} local symmetry, coincides with the Fe–C^1 bond. The bond angles and interatomic distances in the triangular fragments FeC^1C^2 and FeC^1C^3 of complexes **51** and **73** are similar.

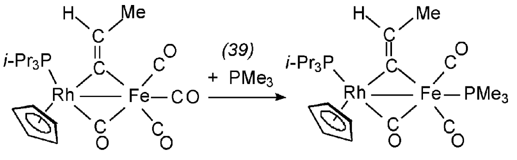
The ^1H NMR spectra of complexes **73** and **51** show resonances of the C^2H protons at δ 4.28 [108b] and 4.10 ppm, respectively. The IR spectrum of **51** contains, along with the $\nu(CO)$ bands between 2085 and 1927 cm^{-1}, the $\nu(C{=}O)$ band at 1857 cm^{-1} due to the ketene $C^3{=}O^3$ group. Some additional strong $\nu(CO)$ bands appear in the spectrum after the crystals have been kept in solution [82]. Additional signals due to μ-C=CHPh and Cp groups are also observed in the ^1H and ^{13}C NMR spectra. This suggests that two isomeric forms, viz. "trimethylenemethane" (**51**) and μ-vinylidene (**51a**), may exist in solution (Scheme 17).

A similar dynamic process *(38)* was described for **74**, whose crystal structure corresponds to the "TMM type", but which in solution is in equilibrium with the μ-vinylidene isomer **74a** [109].

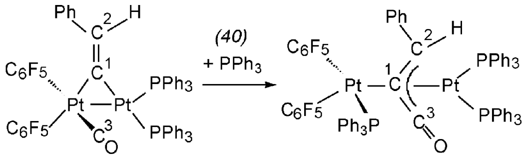


74 **74a**

Usually, the $[Fe(CO)_4]$ unit adds to the M=C^1 bond (M = Mn, Fe, Rh) of mononuclear vinylidene or allenylidene complexes to form the MFe(μ-C^1) system, but does not participate in any other interactions with an organic part of a molecule. The synthesis of stable $Cp(CO)_2MnFe[\mu\text{-}C{=}C(H)COOMe](CO)_4$ (**71**) [21a], $Cp(i\text{-}Pr_3P)RhFe(\mu\text{-}C{=}CHR)(\mu\text{-}CO)(CO)_3$ (**75**) and $(i\text{-}Pr_3P)RhFe_2(\mu_3\text{-}C{=}CHR)(\mu\text{-}CO)_2(CO)_4Cp$ (**76**) (R = H, Me, Ph) [25] serve as examples. Substitution of CO by PMe_3 in **75** did not cause any changes in the RhFe(μ-C=CHR) system (reaction *(39)*) [25].



75 **77**



78 **79**

In contrast, the substitution of CO by PPh_3 in **78** (reaction *(40)*) resulted in C^3O migration from Pt to the vinylidene C^1 atom, the Pt–Pt bond splitting and formation of the unusual complex **79** [110]. According to the X-ray study, the benzylideneketene $[PhC^2H{=}C^1{=}C^3{=}O]$ ligand in **79** serves as an η^3-allylic ligand on one of the Pt atoms, and forms a C^1–Pt σ-bond with the second Pt.

The cause of instability of μ-vinylidene complexes **51a** and **74a** and the reason why they are stabilized by CO addition to the vinylidene μ-C^1 atom are unclear. The vinylidene carbonylation reactions do not have common features. At the same time, carbonylation of carbene and carbyne (intra- and intermolecular) resulting in the formation of free ketenes, η^2-ketene, η^1- and η^2-ketenyl ligands, is well-known and has been intensively investigated [5b,110–112]. Organometallic compounds participating in similar reactions are considered as models of probable intermediates in the Fischer-Tropsch process [41a,113].

4. Formation of heteronuclear μ_3-vinylidene complexes

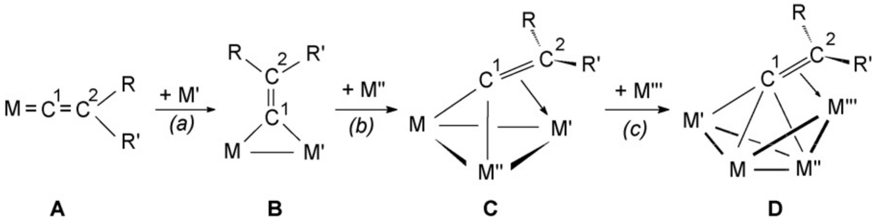
Most known μ_3-vinylidene complexes were prepared by thermal transformations of acetylide, vinyl, carbyne and other ligands on the preformed trinuclear M_3 or M_2M' cores [1–4]. A series of μ_3-vinylidene clusters with $RuCo_2$ and $MCoM'$ (M = Fe, Ru; M′ = Mo, W, Fe, Ni) cores was obtained by means of AVR of μ_3-acetylene isomers or by exchange of the Co atom in the μ_3-vinylidene $FeCo_2$ or $RuCo_2$ clusters for M′ = Mo, W, Fe, Ni [61].

A different approach to the synthesis of heterometallic clusters ***C*** and ***D*** would be by gradual building of the metal core with vinylidene complexes ***A*** and ***B*** being used as building blocks (Scheme 18).

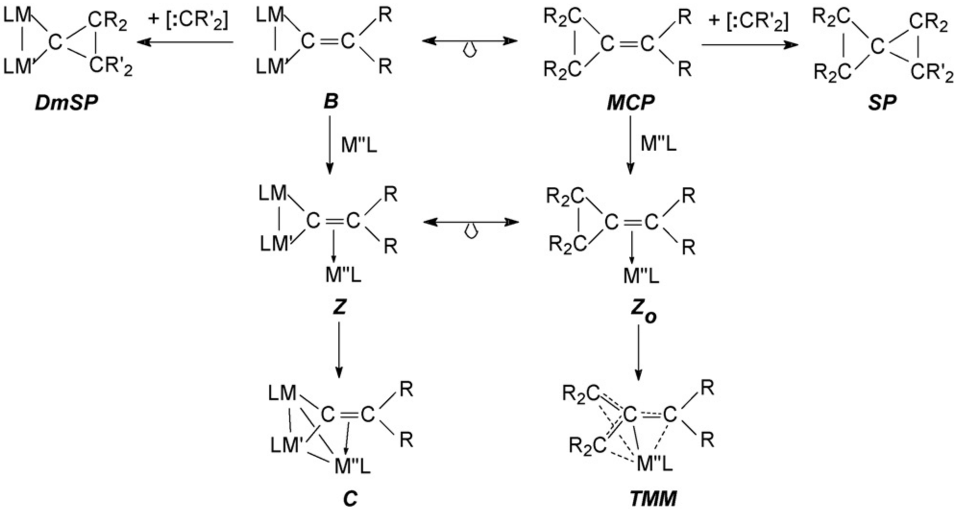
Similarities in the geometries and electronic structures of the $\overline{MM'}(\mu\text{-}C{=}CR_2)$ [114] and $\overline{CCC}{=}CR_2$ [77] systems, which are the central fragments of dinuclear μ-vinylidene complexes ***B*** and organic methylenecyclopropanes (***MCP***), respectively, allowed us to extend the isolobality concept [31] over these classes of compounds [2,32] (Scheme 19).

Carbenes $[:CR'_2]$ can be added both to the C=C bond of ***MCP*** to give spiropentanes (***SP***) [115] and to the $C^1{=}C^2$ bond of complexes ***B*** to give dimetallaspiropentanes (***DmSP***) [116] (Scheme 19). Thus, photochemical reactions of $[Cp(CO)_2Fe]_2(\mu\text{-}C{=}CHR)(\mu\text{-}CO)$ (R = H, Me) with the diazomethanes N_2CHR' (R′ = H, COOEt) gave complexes $[Cp(CO)_2Fe]_2[\mu\text{-}\overline{C(CHR)CHR'}](\mu\text{-}CO)$, where a bridging cyclic carbene together with two Fe atoms form the ***DmSP*** system [116]. The [M″L] fragments, isolobal with carbenes $[:CR_2]$, were reported to be added to the C=C bond of ***MCP*** to form η^2-olefinic complexes ($\boldsymbol{Z_o}$), such as the crystallographically characterized **80** (Scheme 26) [117] or η^4-trimethylenemethane (***TMM***) complexes [118].

The [M″L] fragment is expected to add to the $C^1{=}C^2$ bond of complex ***B*** to form η^2-derivative ***Z*** and then μ_3-vinylidene cluster ***C*** (Scheme 19). The location of π-system of the $C^1{=}C^2$ bond



Scheme 18. Development of the trimetallic ***C*** and tetrametallic ***D*** cluster cores from the vinylidene ***A*** and ***B*** building blocks.



Scheme 19. The proof of the transformation of the dinuclear μ-vinylidene complex ***B*** into the trinuclear μ_3-vinylidene cluster ***C*** based on the isolobal nature of the organometallic complexes with the corresponding organic compounds.

of complexes ***B*** in the plane perpendicular to the $\overline{MM'(\mu\text{-}C^1)}$ cycle plane favors the formation of MM′M″ clusters ***C*** in this way.

Stone and co-workers were the first to use the unsaturation of dinuclear μ-vinylidene complexes to synthesize mixed-metal clusters [119]. They studied the reactions of $[Cp(CO)Fe]_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)$ with $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Mn_3(\mu\text{-}H)_3(CO)_{12}$, and the only vinylidene cluster $CpFeCo_3(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7$ (**81**) was isolated in the first case, whereas other reactions gave μ_3-methylcarbyne clusters. The reactions of $[Cp(CO)Co]_2(\mu\text{-}C{=}CH_2)$ with $HMn(CO)_5$ and $HMo(CO)_3Cp$ also gave μ_3-methylcarbyne clusters [120].

Our first attempts to prepare the trimetal MnMM′ complexes from $Cp(CO)_2MnRh(\mu\text{-}C{=}CHPh)(Acac)(CO)$ (**49**) or $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(L_2)$ (**52**, **54**, **55**, **59**) were also unsuccessful. Thus, reaction *(23)*, Scheme 12 resulted in replacement of the [Rh(Acac)(CO)] fragment by $[Fe(CO)_4]$ [27]. Reactions *(26)*, Scheme 13 led to the replacement of L at the Pt atom by CO [93]. The action of $Fe_2(CO)_9$ on $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppe)$ (**59**) gave the tetranuclear μ_4-vinylidene cluster $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**) [34] (see Section 5.2.1). It is likely that the above reactions occurred through corresponding trimetal MnFeRh, MnCoPt or MnFePt intermediates (type ***Z***, Scheme 19) [35,93].

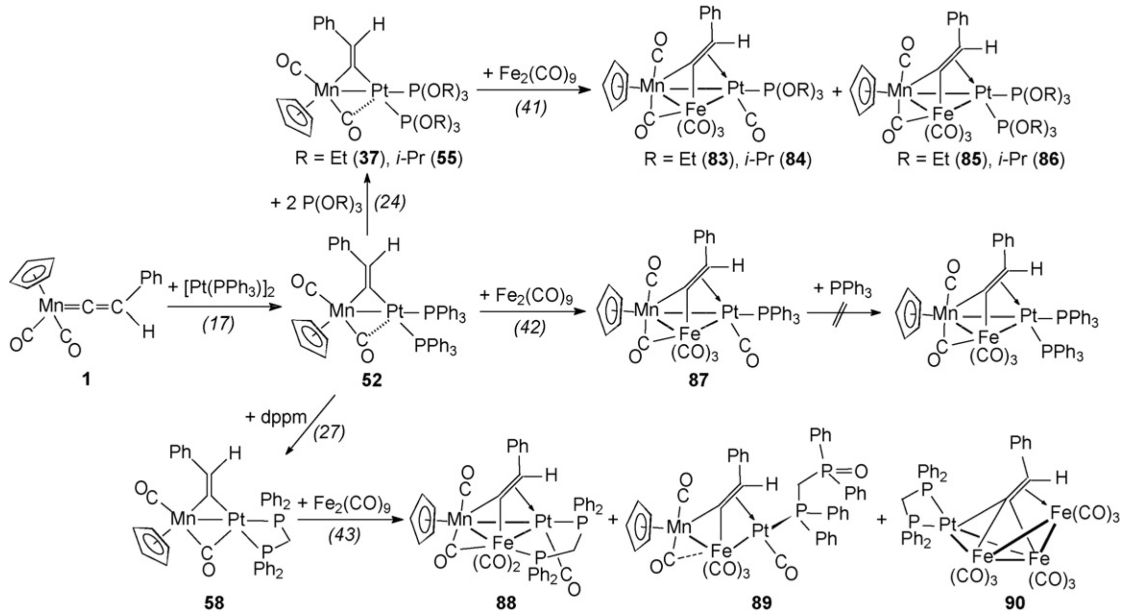
The following Sections describe successful syntheses of the trinuclear MnFePt and $MnFe_2$ μ_3-vinylidene clusters from various vinylidene precursors.

4.1. MnFePt μ_3-vinylidene clusters

Unlike $Cp(CO)_2MnRh(\mu\text{-}C{=}CHPh)(Acac)(CO)$ (**49**) and $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ (**67**), complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(L)_2$ containing ligands L = PPh_3 or $P(OR)_3$ on Pt do not undergo transmetalation with $Fe_2(CO)_9$. Complexes **37** and **55** react smoothly to add an iron carbonyl fragment forming air-stable dark green μ_3-vinylidene clusters of two kinds, namely $CpMnFePt(\mu_3\text{-}C{=}CHPh)(L)(CO)_6$ (**83**, **84**, 45%) and $CpMnFePt(\mu_3\text{-}C{=}CHPh)(L)_2(CO)_5$ (**85**, **86**, 30%) (reaction *(41)*, Scheme 20) [32].

Only $CpMnFePt(\mu_3\text{-}C{=}CHPh)(PPh_3)(CO)_6$ (**87**) was formed from $Fe_2(CO)_9$ and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**52**) (reaction *(42)*) or $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)(CO)$ (**56**) in quantitative yield. Complexes **85** and **86** can be prepared from **83** and **84** by the substitution of the CO group at the Pt atom by the appropriate phosphite $P(OR)_3$ (benzene, 40–50 °C). However, the CO group in **87** is not substituted by the more bulky PPh_3 [100c] even in boiling benzene [32] (Scheme 20).

From the reaction *(43)* between $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppm)$ (**58**) and $Fe_2(CO)_9$, three types of complexes, viz. the trinuclear μ_3-vinylidenes $CpMnFePt(\mu_3\text{-}C{=}CHPh)(\mu\text{-}dppm)(CO)_5$ (**88**, 46%) and $CpMnFePt(\mu_3\text{-}C{=}CHPh)(CO)_6[\eta^1\text{-}Ph_2PCH_2P({=}O)Ph_2]$ (**89**, 2%) and tetranuclear μ_4-vinylidene $(dppm)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**90**, 4%) have been isolated [33] (Scheme 20). The yield of **90** reached 40% when six equivalents of $Fe_2(CO)_9$ were used [99].



Scheme 20. *(41)–(43)* Benzene, 20 °C, 1–3 h.

Complex **89** (Fig. 8) represents the first structurally characterized organometallic compound with an MnFePt framework and the first example of vinylidene complex with a core in the form of a chain of three different metal atoms [33]. It is a derivative of the triangular MnFePt cluster **88** and it results from cleavage of the Mn–Pt and Fe–P bonds and oxidation of the uncoordinated P atom. A small amount of **89** was obtained by chromatography of **88** on an alumina [99]. Similarly, $Cp(CO)_2Mn[\eta^1\text{-}Ph_2PCH_2CH_2P({=}O)Ph_2]$ was obtained by chromatography of $Cp(CO)_2Mn(\eta^1\text{-dppe})$ [121].

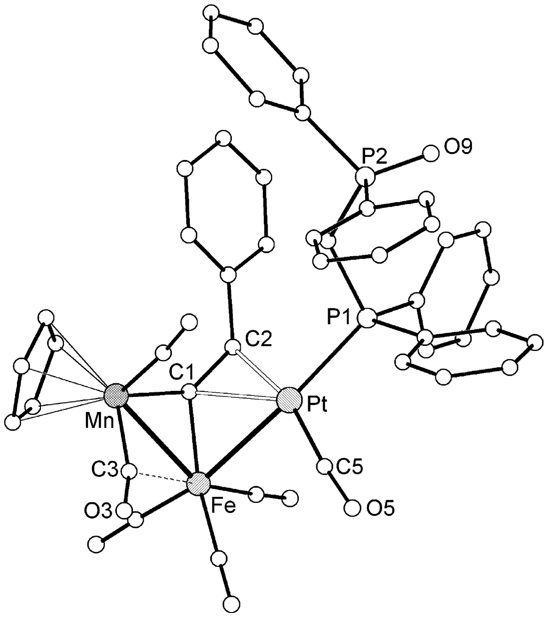


Fig. 8. Molecular structure of $CpMnFePt(\mu_3\text{-}C{=}CHPh)[\eta^1\text{-}Ph_2PCH_2P({=}O)Ph_2](CO)_6$ (**89**). The H atom at C2 was not localized [33].

The Pt···Mn distance is 3.512(3) and 3.718(3) Å in two independent molecules **89** [33]. The MnFePt angle is 83.14(9)° and 88.57(9)°.

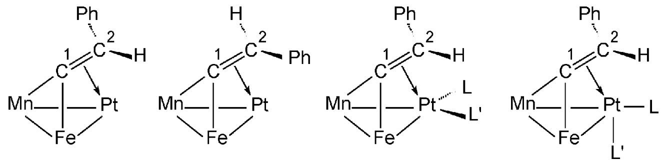
The $\mu_3\text{-}C^1{=}C^2HPh$ ligand is η^1-coordinated to Mn and Fe and η^2-coordinated to the Pt atom. The $C^1{=}C^2$ bond in **89** (1.42(2) Å) is longer than that of triangular clusters, such as $CpMnFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8$ (**91**) (av. 1.31 Å) [37] and $Fe_3(\mu_3\text{-}C{=}CHPh)(\mu\text{-}CO)(CO)_9$ (**92**) (1.38 Å) [122]. The C^1 and C^2 atoms in **89** are almost equally distant from the Pt atom (Pt–C^1 2.24(1), 2.23(1) Å; Pt–C^2 2.24(1), 2.18(1) Å). The Pt atom has a strictly square-planar configuration in one of two independent molecules **89** [33,99]. Its coordination plane consists of the Fe, C^5, P^1 atoms and a middle of the $C^1{=}C^2$ bond. In the second molecule **89**, the Fe atom is inclined to this plane by ∼10°.

Similar features were observed for $(i\text{-}Pr_3P)RhFe_2(\mu_3\text{-}C^1{=}C^2H_2)(\mu\text{-}CO)_2(CO)_4Cp$ (**76**) with a core as the Rh–Fe–Fe chain, where the RhFeFe angle is 85.6°, the Rh–C^1 (2.18 Å) and Rh–C^2 (2.22 Å) bonds differ from each other a little and the configuration of the Rh atom is close to square-planar [25]. The above data are consistent with **89** [33] and **76** [25] being isolobal with η^2-olefinic derivatives of platinum and rhodium, respectively.

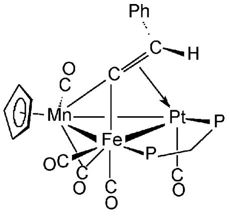
The ^{13}C NMR spectra of **84–88** show the C^1 and C^2 signals at δ 297–312 and 93–94 ppm. The $={C^2}H$ proton of **83–89** resonates between δ 6 and 8 ppm.

According to the ^1H, ^{13}C and ^{31}P NMR spectra, two isomers, (a) and (b), with identical central $[MnFePt(\mu_3\text{-}C{=}CHPh)]$ fragments, are present in solutions of each of complexes **83–88** [32,33,99].

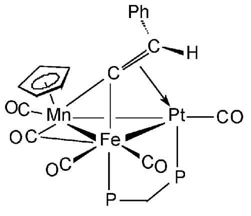
The isomerism of **83–87** with terminal ligands L, $L' = P(OR)_3$, PPh_3, CO at the Pt atom may be caused by a site exchange of the Ph and H substituents at the vinylidene C^2 atom, or by a change in the position of the L and L' ligands relative to the MnFePt plane [32]. Such isomerism does not show up in the ν(CO) region of the IR spectra, since the mutual orientation of the CO groups at the Mn and Fe atoms is the same in both isomers. Thus, the spectra of pentacarbonyl complexes **85** and **86** contain five ν(CO) bands [32].



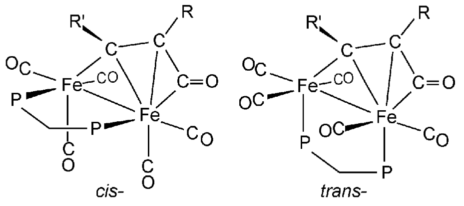
In contrast, the presence of nine ν(CO) bands in the spectrum of pentacarbonyl CpMnFePt(μ_3-C=CHPh)(μ-dppm)(CO)$_5$ (**88**) can be explained by a different orientation of the CO groups at the Pt, Fe and Mn atoms in isomers **88a** and **88b** with respect to vinylidene and μ-dppm. According to the ^{31}P NMR spectrum, dppm bridges the Fe-Pt bond in both isomers **88** [33,99]. Probably, the **88a** and **88b** isomers differ by the arrangement of μ-dppm with respect to the MnFePt triangular plane (coplanar or perpendicular to it) and being either *cis* or *trans* with respect to the vinylidene ligand.



88a



88b



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A similar isomerism caused by *cis* or *trans* position of μ-dppm in relation to a bridging organic ligand was reported by Knox et al. for complexes Fe$_2$[μ-C(O)CRCR′](μ-dppm)(CO)$_5$ (**93**) [123].

4.2. MnFe$_2$ μ_3-vinylidene cluster

Trinuclear cluster CpMnFe$_2$(μ_3-C=CHPh)(CO)$_8$ (**91**) was obtained in two ways, viz. the transmetalation of Cp(CO)$_2$MnPd(μ-C=CHPh)(η^2-P–P) (**64**, **65**) with Fe$_2$(CO)$_9$ [29,36,37] and, in low yield, by addition of two Fe-carbonyl groups to Cp(CO)$_2$Mn=C=CHPh (**1**) [37] (Scheme 21).

Treatment of **1** with Fe$_2$(CO)$_9$ at 20–90 °C affords η^4-[Cp(CO)$_2$MnC(CO)CHPh]Fe(CO)$_3$ (**51**) solely (Section 3.3) [37,90]. The sharp contrast between the conditions required for the formation of **91** from **1** (98 °C, 10%) and from **64** (20 °C, 71%) suggests a specific role of palladium in the easy formation of **91** in reaction *(44)*.

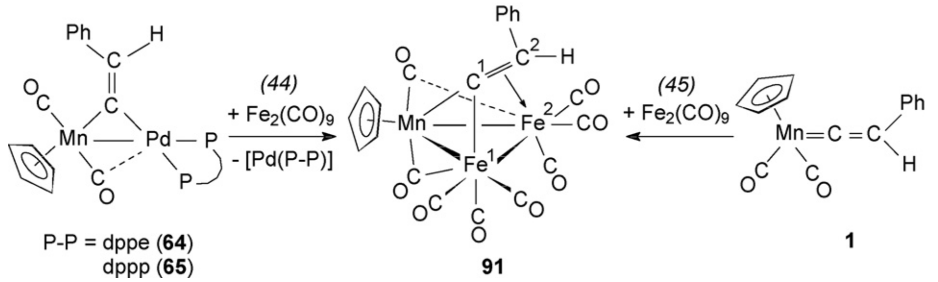
The ^{13}C NMR spectrum of **91** exhibited signals for C^1 at δ 306.18 ppm and C^2 at δ 97.01 ppm. The =C^{2}H proton resonates at δ 7.85 ppm. A molecular ion in the mass spectrum of **91** eliminated sequentially eight CO groups, and then the Mn and Fe atoms [37].

Complex **91** was studied both by powder [78b] and single-crystal XRD [37].

The Fe and Mn atoms in molecule **91** (Fig. 9) form an isosceles triangle (Mn–Fe^1 2.653(2) Å, Mn–Fe^2 2.669(2) Å, Fe^1–Fe^2 2.569(2) Å) [37]. The C^1=C^{2}HPh ligand is located above the MnFe$_2$ triangle and disordered over two positions with equal occupancies. Molecule **91** in the crystal can be considered as a superposition of two molecules. In the first, the vinylidene is σ-bonded with the Mn and Fe^1 and π-bonded with the Fe^2 atom, whereas in the second molecule it is σ-bonded with the Mn and Fe^2 and π-bonded with the Fe^1 atom.

Cluster **91** is characterized by the strongly pronounced asymmetry of the π-bonding of C^1=C^{2}HPh with the Fe atom. The bonds Fe^1–C$^{2\prime}$ (2.45(2) Å) and Fe^2–C^2 (2.35(2) Å) are substantially weaker than Fe^1–C^1 (1.877(11) Å) and Fe^2–C^1 (1.896(10) Å). The C^1=C^2 bond lengths are 1.35(2) and 1.26(2) Å in two molecules **91**. Similar structural features were found for Ru$_3$(μ_3-C^1=C^{2}HPh)(μ-H)$_2$(CO)$_9$, where a difference between the Ru–C^1 and Ru–C^2 bonds averaged 0.25 Å, and the C^1=C^2 distances are 1.36 and 1.19 Å in two independent molecules [124]. It is likely that **91** is fluxional, the vinylidene ligand showing the common "windscreen-wiper" motion (Scheme 22).

Similar rotatory movement of vinylidene C=CR$_2$ was found for the cation [(CO)$_9$Co$_3$CCHR]$^+$. The calculated difference in energy between the side-bonded (μ_3,η^2) and the central symmetric (μ_3,η^1) configurations of the vinylidene ligand is 10.5 kcal/mol [125].



Scheme 21. *(44)* Benzene; P–P = dppe, 20 °C, 3 h, 71%; P–P = dppp, 50–70 °C, 0.5 h, 53%; *(45)* heptane, 98 °C, 1 h, 10%.

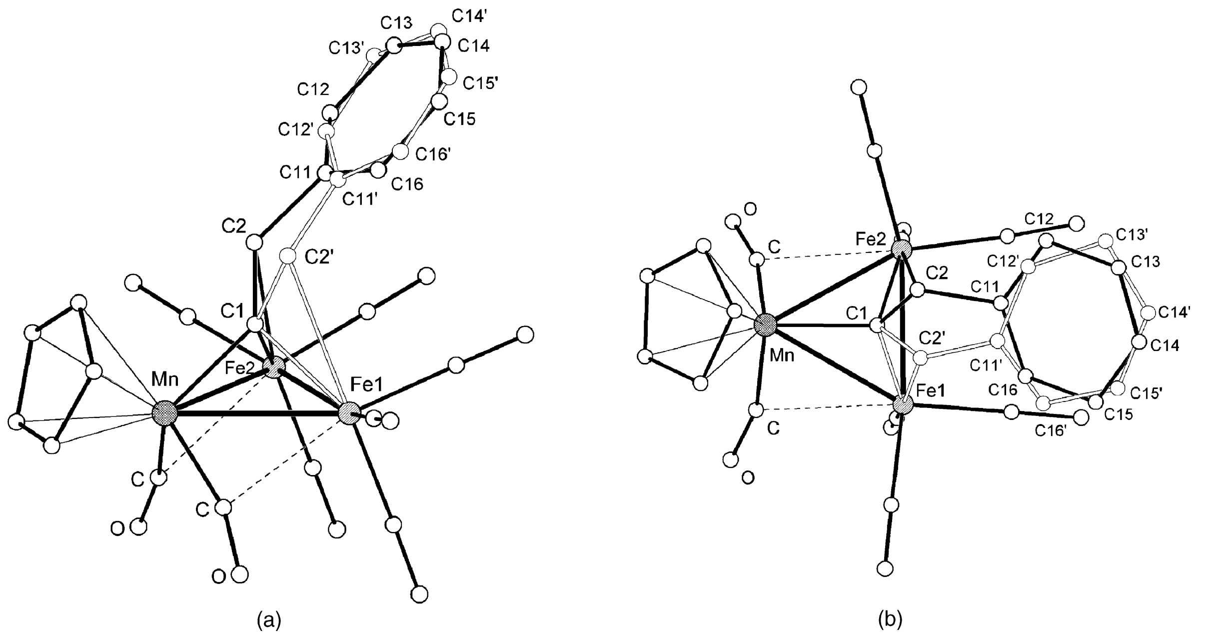
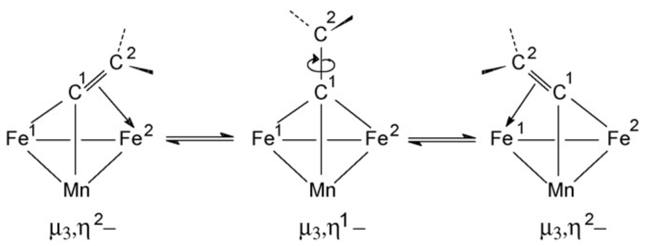


Fig. 9. Molecular structure of $CpMnFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8$ (**91**): (a) overall view of the molecule and (b) projection onto the plane of the $MnFe_2$ triangle. The second position of the $\mu_3\text{-}C{=}CHPh$ ligand is indicated by empty lines. The H atom at C2 was not located [37].



Scheme 22. The motion of the μ_3-vinylidene ligand over the $MnFe_2$ triangle in cluster **91**.

5. Formation of tetranuclear clusters

5.1. *Transformations of phenylvinylidene on an $MnOs_3$ cluster*

We have shown for the first time that not only 14- and 16-electron units $[ML_n]$ (M = Fe, Mn, Re, Rh, Pd, Pt, Cu), but also an unsaturated cluster, such as $(\mu\text{-}H)_2Os_3(CO)_{10}$ may be joined to the Mn=C=C system. The main product of the reaction between $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and $(\mu\text{-}H)_2Os_3(CO)_{10}$ was the dark-red tetranuclear cluster $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (**94**, 60%) [126,127]. Simultaneously, the trinuclear clusters $Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**95**), $(\mu\text{-}H)_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$ (**96**) and $(\mu\text{-}H)Os_3(\mu\text{-}CH{=}CHPh)(CO)_{10}$ (**97**) were isolated in 5–10% yields (Scheme 23, reaction *(46)*).

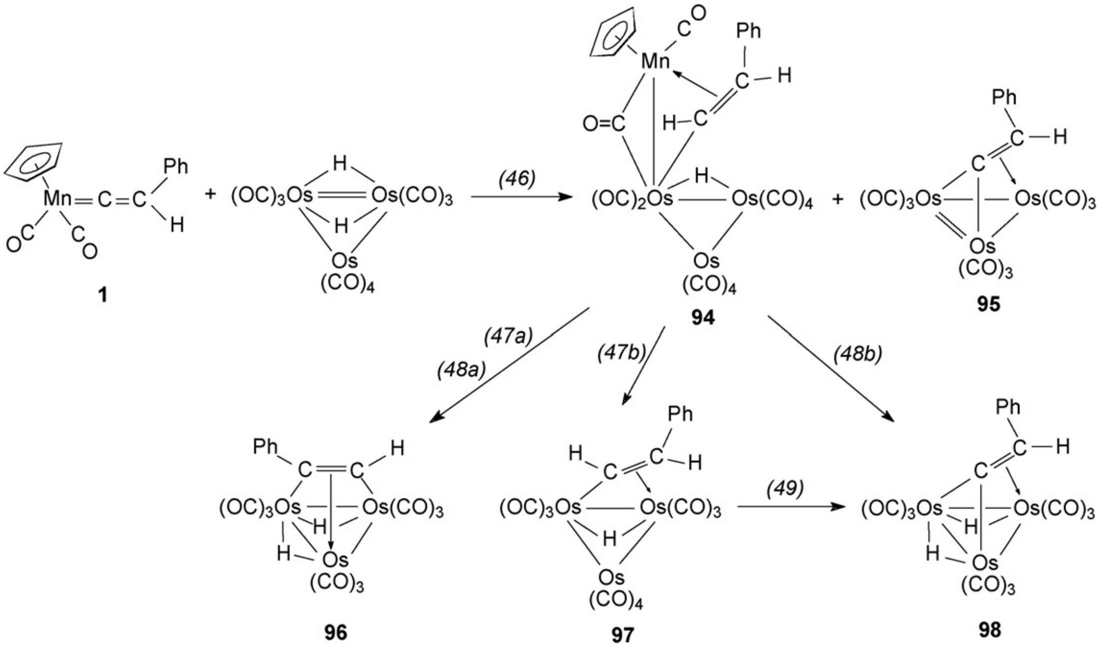
Cluster **94** (Fig. 10) belongs to a rare structural type of "spiked" cluster as its metal core consists of the Os_3 triangle and the Mn atom linked to the Os^1 atom [127]. The Os^1–Os^2 (2.851(2) Å) and Os^2–Os^3 (2.889(1) Å) bonds are substantially shorter than Os^1–Os^3 (3.069(1) Å) bridged by the μ-H ligand (δ – 22.2 ppm in the ^1H NMR spectrum). The Mn–Os^1 bond (2.765(4) Å) is bridged by $\mu\text{-}C^4O^4$ (ν(C=O) 1790 cm^{-1}) and $\mu\text{-}C^1H{=}C^2HPh$, which is σ-bonded to the Os^1 atom and asymmetrically π-bonded to the Mn atom (Mn–C^1 2.08(3) Å, Mn–C^2 2.28(2) Å).

The $C^1{=}C^2$ bond length is 1.46(4) Å. Both bridging C^1MnOs^1 and C^4MnOs^1 fragments are practically coplanar (dihedral angle 173°). Significant strain in the planar bicyclic $MnC^1Os^1C^4$ system with very small bond angles at the Os^1 atom ($MnOs^1C^1$ 48.1(9)°, $MnOs^1C^4$ 42.9(9)°) causes easy cleavage of the Mn–Os^1 bond.

In solution, **94** eliminates $CpMn(CO)_3$ and is converted into the carbonylhydride Os_3 complexes with unsaturated organic ligands, whose nature depends on the temperature (Scheme 23) [126,127]. At 20 °C in pentane (reactions *(47a)* and *(47b)*), the μ_3-alkyne complex $(\mu\text{-}H)_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$ (**96**) (64%) and μ-vinyl complex $(\mu\text{-}H)Os_3(\mu\text{-}CH{=}CHPh)(CO)_{10}$ (**97**) (32 %) were formed. At 120 °C in octane (reactions *(48a)* and *(48b)*), the isomeric μ_3-alkyne $(\mu\text{-}H)_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$ (**96**) and μ_3-vinylidene $(\mu\text{-}H)_2Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**98**) were formed in 2:1 ratio.

The synthesis of $(\mu\text{-}H)_2Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**98**) from $(\mu\text{-}H)Os_3(\mu\text{-}CH{=}CHPh)(CO)_{10}$ (**97**) (octane, 120 °C, 88%) was described earlier [128]. The reaction *(49)* in Scheme 23 proved the intermediate participation of μ-vinyl **97** in the formation of μ_3-vinylidene **98** from cluster **94**.

Consequently, the phenylvinylidene underwent a series of transformations in the course of the formation of cluster $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (**94**) and its decomposition. α-Hydrogenation of vinylidene by addition of $(\mu\text{-}H)_2Os_3(CO)_{10}$ to $Cp(CO)_2Mn{=}C_\alpha{=}C_\beta HPh$ (**1**) led to the formation of the phenylvinyl $\mu\text{-}C_\alpha H{=}C_\beta HPh$. Isomerization of C=CHPh into HC≡CPh was a result of α-hydrogenation of the phenylvinylidene *(46)* and following β-dehydrogenation of the $\mu\text{-}C_\alpha H{=}C_\beta HPh$ group *(47a)*.



Scheme 23. Transformations of phenylvinylidene on the $MnOs_3$ cluster system: *(46)* CH_2Cl_2, 20 °C, 6 h; *(47)* pentane, 20 °C, 24 h; *(48)* and *(49)* octane, 120 °C, 1 h.

Consecutive α-hydrogenation of the C=CHPh ligand *(46)*, *(47b)* and α-dehydrogenation of $C_\alpha H{=}C_\beta HPh$ *(49)* were concluded by transfer of vinylidene from the Mn atom to the Os_3 cycle:

$$\mathbf{1}\xrightarrow{(46)}\mathbf{94}\xrightarrow{(47b)}\mathbf{97}\xrightarrow{(49)}\mathbf{98}$$

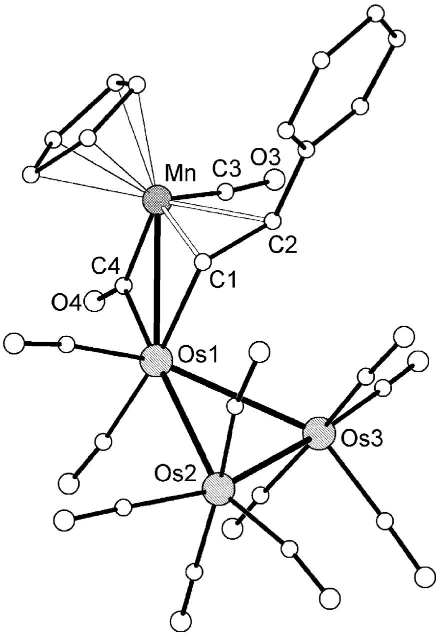


Fig. 10. Molecular structure of $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (**94**). The H atoms at the C1 and C2 atoms and H atom bridging the Os1—Os3 bond were not located [127].

The mechanism of formation of unusual bronze-red cluster $Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**95**) is unclear. Its structure based on the mass spectrum (*m/z* 926 $[P]^+$), the IR and NMR data [126] and corresponds with its electrochemical behaviour (see Section 7).

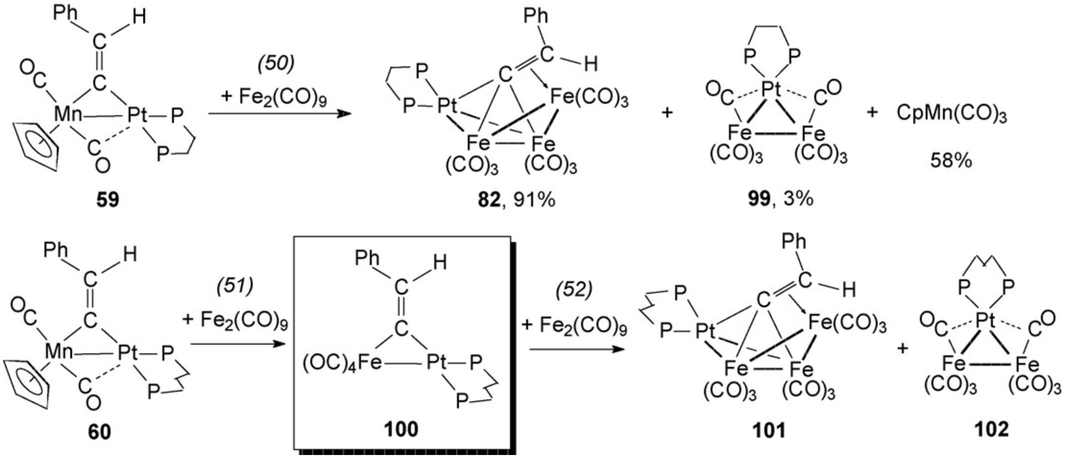
The formation of clusters **95** and **98** containing the $[Os_3(\mu_3\text{-}C{=}CHPh)]$ group starting from $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) showed for the first time a possibility of transfer of an unsaturated carbene from a mononuclear system to trinuclear cluster [126,127].

5.2. *Formation of the butterfly MFe_3 μ_4-vinylidene clusters and triangular MFe_2 clusters (M = Pd, Pt)*

The μ_4-vinylidene clusters ***D*** are the least numerous type among vinylidene complexes [2,4,76]. The first μ_4-vinylidene clusters containing platinum [34a] and palladium [36] have been synthesized starting from the dinuclear complexes $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(dppe)$ (M = Pt, Pd). Below, the formation, structure and spectroscopic characteristics of $(P\text{–}P)MFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (P–P = dppe, dppp; M = Pt, Pd) are considered.

5.2.1. *$(P\text{–}P)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ and $(P\text{–}P)PtFe_2(CO)_8$ clusters*

Interaction of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(\eta^2\text{-}P\text{–}P)$ (P–P = dppe (**59**), dppp (**60**)) with $Fe_2(CO)_9$ resulted exclusively in products of cleavage of the Mn–Pt bond, namely, μ_4-vinylidene clusters $(P\text{–}P)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (P–P = dppe (**82**), dppp (**101**)), non-vinylidene clusters $(P\text{–}P)PtFe_2(CO)_8$ (P–P = dppe (**99**), dppp (**102**)) and $CpMn(CO)_3$ [34,35] (Scheme 24). No signs of any



Scheme 24. *(50–52)* C_6H_6, 20 °C, 2–4 h.

MnFePt clusters have been seen in reactions *(50)* and *(51)*.

The tetranuclear clusters (P–P)$PtFe_3(\mu_4$-C=CHPh)$(CO)_9$ (P–P = dppm (**90**), dppe (**82**), dppp (**101**)) form black-green crystals stable up to 200–230 °C. The structure of (dppe)$PtFe_3(\mu_4$-C=CHPh)$(CO)_9$ (**82**) (Fig. 11) [34b] is considered in Section 5.2.2.

The lemon-yellow dinuclear complex (dppp)PtFe(μ-C=CHPh)$(CO)_4$ (**100**) was isolated in 13% yield from reaction *(51)*, along with **101** and **102** [35]. Complex **100** appeared as a result of transmetalation of **60**, originating from $Cp(CO)_2Mn$=C=CHPh (**1**) (Schemes 10 and 13). Consecutive transformations **1** → **60** → **100** resulted in vinylidene transfer from Mn onto the dinuclear PtFe system.

Treatment of complex **100** with $Fe_2(CO)_9$ afforded clusters **101** (50%) and **102** (2%) (reaction *(52)* in Scheme 24). These observations shed some light on the mechanism of formation of (P–P)$PtFe_3(\mu_4$-C=CHPh)$(CO)_9$, where P–P = dppm (**90**), dppe (**82**) and dppp (**101**) (see Section 5.3). We supposed that after η^2-coordination of the $[Fe(CO)_4]$ unit to the C^1=C^2 bond of the MnPt(μ-C^1=C^2HPh) system to form trimetal intermediate **Z** (Schemes 19 and 26), similar to complex **80** [117], exchange of the $[Mn(CO)_2Cp]$ group for $[Fe(CO)_4]$ occurs to give complex **100** [35]. The latter adds two additional iron carbonyl groups to yield the $PtFe_3$ cluster **101**. Intermediate complexes [(P–P)PtFe(μ-C=CHPh)$(CO)_4$] (P–P = dppm, dppe) possibly form in reactions *(43)*, Scheme 20 and *(50)*, Scheme 24. However, we failed to find them, since they are more reactive towards $Fe_2(CO)_9$ than their dppp analog **100**, and transform rapidly into the corresponding $PtFe_3$ clusters **90** and **82**.

The bright red clusters (P–P)$PtFe_2(CO)_8$ (**99**, **102**) are apparently formed in reactions *(50–52)* from intermediates [(P–P)PtFe(μ-C^1=CHPh)$(CO)_4$] by the cleavage of the Pt–Fe and Pt–μ-C^1 bonds and joining of the fragment [(η^2-P–P)Pt] with two $[Fe(CO)_4]$ units present in a reaction solution [35]. Cluster (dppe)$PtFe_2(CO)_8$ (**99**) was obtained earlier in 5% yield from the reaction between $Pt(dppe)_2$ and $Fe_2(CO)_9$ [129a]. The central fragment of **99** is an isosceles $PtFe_2$ triangle [34b]. The dppe ligand chelates the Pt atom (P–Pt–P angle 84.9(8)°). A semi-bridging interaction of one of the CO groups on each Fe atom with the Pt atom occurs. The crystallographically characterized $(Ph_3P)(CO)PtFe_2(CO)_8$ [129b], and a series of related complexes $L_2PtFe_2(CO)_8$ ($L_2 = (PPh_3)_2$, $[P(OR)_3]_2$, etc.) [129c,d] were also reported.

5.2.2. *(P–P)$PdFe_3(\mu_4$-C=CHPh)$(CO)_9$ and (P–P)$PdFe_2(CO)_8$ clusters*

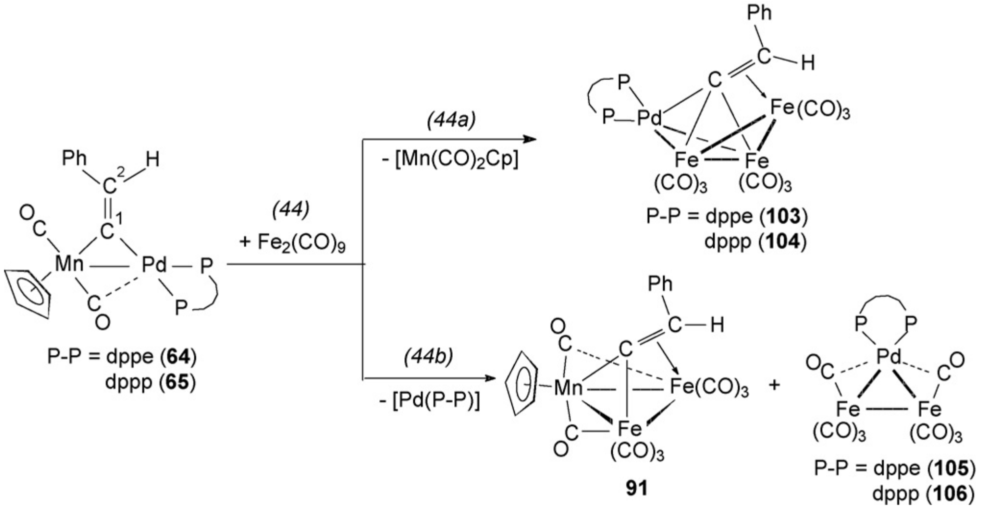
Distinctions between the chemical behaviour of $Cp(CO)_2$MnPd(μ-C=CHPh)(L_2) ($L_2 = (PPh_3)_2$, dppm, dppe, dppp) and their MnPt analogues revealed by their reactions with $Fe_2(CO)_9$ [29,36–38,99], are briefly considered in this section.

In contrast to the smooth transformation of $Cp(CO)_2$MnPt(μ-C=CHPh)$(PPh_3)_2$ (**52**) into CpMnFePt(μ_3-C=CHPh)$(PPh_3)(CO)_6$ (**87**) (Scheme 20) [32], only $CpMn(CO)_3$ and $(PPh_3)Fe(CO)_4$ were isolated from the reaction of $Cp(CO)_2$MnPd(μ-C=CHPh)$(PPh_3)_2$ (**61**) with $Fe_2(CO)_9$ [99]. Complex $Cp(CO)_2$MnPd(μ-C=CHPh)(dppm) (**63**) also decomposed under action of $Fe_2(CO)_9$.

The compounds $Cp(CO)_2$MnPd(μ-C=CHPh)(P–P) (P–P = dppe (**64**), dppp (**65**)) showed a new mode of chemical behaviour of the dinuclear μ-vinylidene complexes ***B***. Two parallel and competitive transmetalations of the MnPd(μ-C^1=C^2HPh) system were observed in reactions with $Fe_2(CO)_9$ (Scheme 25) [29,36–38].

In the way *(44a)*, the Pd-vinylidene bond remains intact, the $[Cp(CO)_2Mn]$ fragment being substituted for $[Fe(CO)_4]$ and the subsequent addition of two further iron carbonyl groups resulting in the black-green μ_4-vinylidene clusters (P–P)$PdFe_3(\mu_4$-C=CHPh)$(CO)_9$ (P–P = dppe (**103**), dppp (**104**), 10–30%). Probably, the initial products of transmetalation were the intermediates [(P–P)PdFe(μ-C=CHPh)$(CO)_4$] analogous to (dppp)PtFe(μ-C=CHPh)$(CO)_4$ (**100**) in Scheme 24.

In the prevailing direction *(44b)*, the Mn-vinylidene bond was retained, the [Pd(P–P)] fragment was replaced by $[Fe(CO)_4]$, and the final product was the brown μ_3-vinylidene cluster $CpMnFe_2(\mu_3$-C=CHPh)$(CO)_8$ (**91**) (50–71%) (see Section 4.2). The formation of **91** does not have an analogy in chemistry of the MnPt μ-vinylidene complexes and is specific for the MnPd compounds. The [Pd(P–P)] fragment adds two $[Fe(CO)_4]$ groups to form the violet clusters (P–P)$PdFe_2(CO)_8$ (P–P = dppe (**105**),



Scheme 25. Formation of the $PdFe_3$ and $MnFe_2$ clusters as a result of the two parallel directions of transmetalation of the $MnPd(\mu\text{-}C{=}CHPh)$ system in the reactions with $Fe_2(CO)_9$.

dppp (**106**), 2–4%). The ratio between the competitive processes *(44a)* and *(44b)* depends on the P–P ligands. The Pd–Mn and Pd–μ–C bonds in $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (**63–65**) become stronger as the donor ability of the P–P ligands increases in the order dppm < dppe < dppp [37,99].

Consecutive conversions of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) into $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (**58–60**, **64**, **65**) and $(P\text{–}P)MFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**, **90**, **101**, **103**, **104**) led to vinylidene transfer from Mn to the tetranuclear $PtFe_3$ and $PdFe_3$ systems.

The structures of $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**) (Fig. 11) [34b] and $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**) (Fig. 12) [38] are similar. The MFe_3 cores (M = Pt, Pd) adopt a butterfly shape. The Fe^1 and M atoms are located at the tips of the "butterfly wings". The M atoms are chelated by diphosphines (P^1–Pt–P^2 angle 84.9(8)° in **82**; P^1–Pd–P^2 92.69(2)° in **104**). The bonds Pd–Fe^2 and Pd–Fe^3 (av. 2.668 Å) in **104** [38] are somewhat longer than Pt–Fe^2 and Pt–Fe^3 (av. 2.655 Å) in **82** [34b].

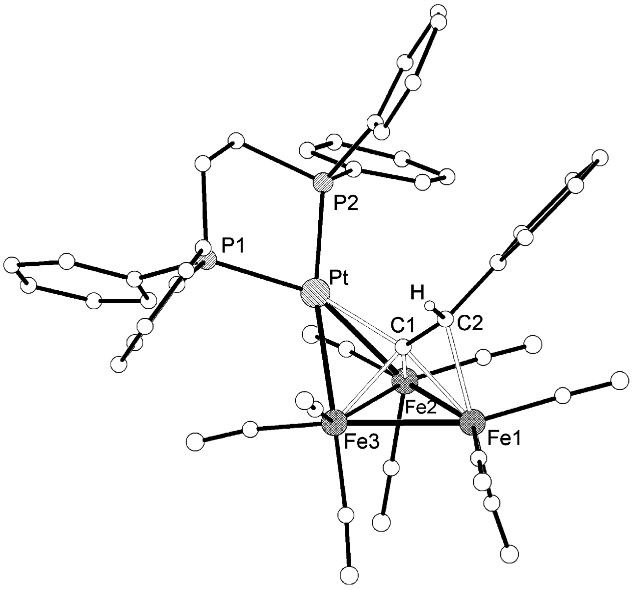


Fig. 11. Molecular structure of $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**) [34b].

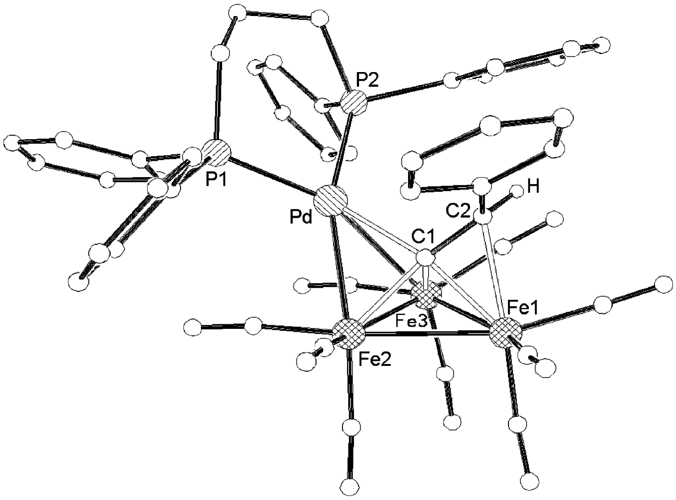


Fig. 12. Molecular structure of $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**) [38].

The $\mu_4\text{-}C^1{=}C^2HPh$ ligands in both clusters are σ-bonded to the M, Fe^2 and Fe^3 atoms and π-bonded to the Fe^1 atom. The Pd–μ–C^1 bond (2.134(2) Å) in **104** is also somewhat longer than Pt–μ–C^1 in **82** (2.100(8) Å) [34b] and in $(dppe)PtRu_3[\mu_4\text{-}C{=}C(H)t\text{-}Bu](CO)_9$ (2.120(10) Å) [130]. The $C^1{=}C^2$ bond length is 1.403(3) Å in **104** and 1.422(10) Å in **82**. A large asymmetry of π-bonding of the $\mu_4\text{-}C^1{=}C^2HPh$ ligand is characteristic of complex **104**, where the difference between the Fe^1–C^2 (2.182(3) Å) and Fe^1–C^1 (1.946(2) Å) distances amounts to 0.236 Å. Similar values are 0.202 Å for **82** [34b] and 0.174 Å for $(dppe)PtRu_3[\mu_4\text{-}C{=}CH(t\text{-}Bu)](CO)_9$ [130].

The ^{13}C NMR spectra of $(P\text{–}P)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**, **90**, **101**) [33–35] and $(P\text{–}P)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**103**, **104**) [29,37,99] contain signals at δ 316–331 (C^1) and 88–93 (C^2). The vinylidene proton $=C^2H$ resonates in the ^1H NMR spectra at δ 6.2–6.6 ppm.

Unlike the extensively studied triangular clusters $L_2PtFe_2(CO)_8$ (L_2 = P–P, $(PPh_3)(CO)$, $(PPh_3)_2$, $[P(OR)_3]_2$, etc.) [34b,35,129] (see Section 5.2.1), none of the Pd-analogs $L_2PdFe_2(CO)_8$ were known before our work [29,36,37]. The only reported $PdFe_2$ clusters were $(\mu\text{-dppm})_2PdFe_2(CO)_6$, where both dppm ligands bridge the Pd–Fe bonds [131], and $[Me_3NCH_2Ph^+]_2[Fe_4Pd(CO)_{16}]^{2-}$ which has a *spiro*-structure consisting of two $PdFe_2$ triangles with a common Pd vertex [132]. The structure and mechanism of formation of $(dppe)PdFe_2(CO)_8$ (**105**) and $(dppp)PdFe_2(CO)_8$ (**106**) [29,37] are obviously similar to those of $(dppe)PtFe_2(CO)_8$ (**99**) [34b,35].

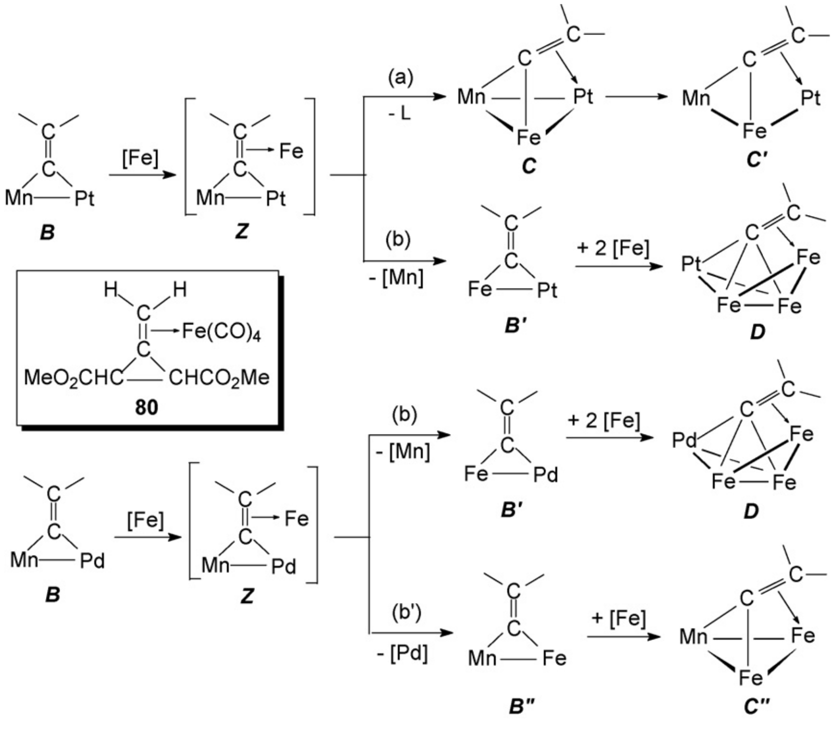
An increase in the ν(CO) frequencies is characteristic of palladium compounds, as compared to platinum analogs. This is rather noticeable for $Cp(CO)_2MnM(\mu\text{-C=CHPh})(P\text{–}P)$, where the electronic effect of atom M = Pt, Pd is transmitted only to two CO groups at the Mn atom (Table 5). In contrast, for clusters $(P\text{–}P)MFe_2(CO)_8$ and $(P\text{–}P)MFe_3(\mu_4\text{-C=CHPh})(CO)_9$, where the electronic effect of the M atom extends through the M–Fe bonds to eight or nine CO groups at the Fe atoms, the increase in ν(CO) frequencies when passing from Pt to Pd is hardly noticeable. Thus, the IR spectra of $(P\text{–}P)PdFe_3(\mu_4\text{-C=CHPh})(CO)_9$ and $(P\text{–}P)PtFe_3(\mu_4\text{-C=CHPh})(CO)_9$ in the ν(CO) region are almost identical.

5.3. Some regularities in heterometallic cluster formation from μ-vinylidene precursors

An interest in the synthesis of vinylidene clusters by means of the addition of new metal atoms to metallvinylidene precursors arose at an early stage of the development of vinylidene complexes chemistry [2,4]. For the first time, the synthesis of tetranuclear μ_4-vinylidene cluster ***D*** from dinuclear μ-vinylidene complex ***B***, i.e. $CpFeCo_3(\mu_4\text{-C=CH}_2)(\mu\text{-CO})_2(CO)_7$ (**81**) from $[Cp(CO)Fe]_2(\mu\text{-C=CH}_2)(\mu\text{-CO})$, was realized by Stone and co-workers in 1981–1983 [119]. Soon after, reports [133,134] concerning transformations of μ_3-vinylidene clusters into μ_4-vinylidenes by addition of the fourth metal atom appeared, i.e. ***C*** → ***D*** (Scheme 18). Sappa et al. obtained $CpNiOs_3[\mu_4\text{-C=CH}(t\text{-Bu})](\mu\text{-H})(CO)_9$ from reaction between $(\mu\text{-H})_2Os_3[\mu_3\text{-C=CH}(t\text{-Bu})](CO)_9$ and $[Cp(CO)Ni]_2$ [133]. Mathieu and Attali showed that $[HFe_3(\mu_3\text{-C=CHR})(CO)_9]^-$ (R = H, Ph) reacted with $[RhCl(CO)_2]_2$ in the presence of $TlBF_4$ to form $(\mu\text{-H})Fe_3Rh(\mu_4\text{-C=CHR})(CO)_{11}$ [134]. In the case of R = Ph, addition of the rhodium-containing fragment occurred in almost quantitative yield.

We were the first to show consecutive assemblage of a metal framework around the vinylidene C=CHR, starting from mononuclear system (Mn), through dinuclear (MnPt), to trinuclear (MnFePt) (Scheme 20, transition ***A*** → ***B*** → ***C***) [32,33,99]. In addition, transmetalation to give new dinuclear systems MnM′ (M′ = Fe) or MM′ (M = Pd, Pt; M′ = Fe) was found to be characteristic of the dinuclear μ-vinylidene systems MnM (M = Rh [26,27], Cu [30], Pd [29,36,37] and Pt [34,35]). Further metalation of the MM′ (M = Pd, Pt; M′ = Fe) systems led to the μ_4-vinylidene clusters ***D*** [29,34–38]. Two parallel reactions were observed for the MnPd complexes, leading to the $MnFe_2$ and $PdFe_3$ clusters [29,36–38,99]. These results are summarized in Scheme 26.

Most likely, the first step is η^2-coordination of the $[Fe(CO)_4]$ unit to the C=C bond of the dinuclear MnM μ-vinylidene complex ***B*** to form an intermediate [***Z***] isolobal with complex **80** [117].



Scheme 26. The Cp, CO, PR_3, P–P ligands are omitted for clarity.

Stabilization of [***Z***] may be achieved by formation of new Fe-metal bonds, which demands vacant coordination sites and may be realized in one of the following ways:

(a) by removal of one ligand L/L′ from atom M, subsequent reorganization of bonds and regrouping of ligand environment to give the trimetal clusters ***C***.

(b/b′) by replacement of one metal-containing fragment by a Fe-containing fragment to give ***B***′ (similar to **100**) or ***B***″ (similar to **51a**). Further interaction of ***B***′ or ***B***″ with an excess of $Fe_2(CO)_9$ results in the final polynuclear products ***D*** or ***C***″, respectively.

A way of stabilization of intermediate [***Z***] is determined by the ratio of two factors, viz. the strength of the M–L/M–L′ bond and the strength of the metal-μ–C bonds in the $\overline{\text{Mn-M-C}}\text{=C}$ cycle. The latter depends on the electronic properties of the MLL′ fragment and comparative dimensions of the M and Mn atoms.

For (a), the strong carbodimetallacycle $\overline{\text{Mn-M-C}}$ and easily displaced ligands L/L′ at atom M in the initial molecule ***B*** are necessary. Thus, the presence of strong Mn–Pt and Mn–μ–C bonds and the readily displaced monodentate ligands L, L′ = CO, PPh_3, $P(OR)_3$ in complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ favors the stabilization of [***Z***] by (a), with the μ_3-vinylidene MnFePt clusters (***C***) as the end-products. In the case of LL′ = η^2-dppm, the subsequent cleavage of the Mn–Pt bond in the $\overline{\text{MnFePt}}$ metallocycle results in the formation of the trimetal Mn–Fe–Pt chain (***C***′).

Otherwise, for (b), stabilization of [***Z***] by replacement of a fragment, such as $[Cp(CO)_2Mn]$ or [MLL′], which is less strongly connected to vinylidene, by the $[Fe(CO)_4]$ group, is preferred.

The lesser stability of the systems $\overline{\text{Mn-M-C}}\text{=C}$, where M = Rh, Cu, Pd, as compared with $\overline{\text{Mn-Pt-C}}\text{=C}$, can be explained by a weaker π-donor ability of groups Rh(Acac)(CO), CuCl and PdL_2, than that of PtL_2 (see Section 3; Scheme 11). The greater difference in dimensions of atoms Mn (covalent radius 1.38 Å) and M = Rh (1.46 Å), Pd (1.49 Å), Re (1.51 Å) [100] also contributes to weakening of the Mn–M bonds. Comparison of properties of very stable homodinuclear $[Cp(CO)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (**2**) and $[Cp(CO)_2Re]_2(\mu\text{-}C{=}CHPh)$ (**7**) with their ephemeral heterometallic "relative" $Cp_2(CO)_4MnRe(\mu\text{-}C{=}CHPh)$ (**47**) [20] is most indicative in this respect (see Section 3.1.1).

Complexes $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)L_2$, having no strong Mn–Pd bonds, cannot be used for the synthesis of MnFePd clusters. However, they serve as intermediates in the vinylidene transfer from the Mn atom onto the $PdFe_3$ cluster system.

6. Vinylidene transfer reactions

While studying the addition of unsaturated units containing metals M′ and M″ to $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) and subsequent transformations of heterometallic derivatives, we found for the first time transfer of vinylidene from atom M = Mn to the other metal M′ = Re [20] and onto polymetallic systems M′M″ = FePt [35], $M'_3 = Os_3$ [126,127], $M'M_3'' = PdFe_3$ [29,36–38,99] and $PtFe_3$ [33–35] (Scheme 27).

All processes shown in Scheme 27 proceed in several stages. The first stages occur at room temperature. Heterometallic compounds formed in the first stage are stable and may be isolated in good yields (60–95%), except $Cp_2(CO)_4MnRe(\mu\text{-}C{=}CHPh)$ (**47**) [20] (Section 3.1.1). Subsequent stages, as a rule, also proceed under mild conditions (20–50 °C). The exception is reaction *(48b)*, which occurs at 120 °C (Section 5.1), and reaction *(44a)* in the case of transformation of $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)(dppp)$ (**65**) into cluster $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**), which goes more smoothly at 70 °C (Section 5.2.2).

Reactions *(15)*, *(21)* and *(46)*, *(48b)* show the possibility of vinylidene transfer from Mn to Re and to the Os_3 triangle. These processes are of theoretical interest, but have no practical importance since they give $Cp(CO)_2Re{=}C{=}CHPh$ (**6**) and $(\mu\text{-}H)_2Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**98**) in small yields. More rational ways to **6** [16] and **98** [128] are known (Sections 2.1 and 5.1).

Reaction *(51)* giving $(dppp)PtFe(\mu\text{-}C{=}CHPh)(CO)_4$ (**100**) in 13% yield and reactions *(43)*, *(44a)* resulting in $(dppm)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**90**), $(dppe)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**103**) and $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**) in 10–40% yields, were used by us for synthetic purposes, since other methods of preparation of these compounds are unknown.

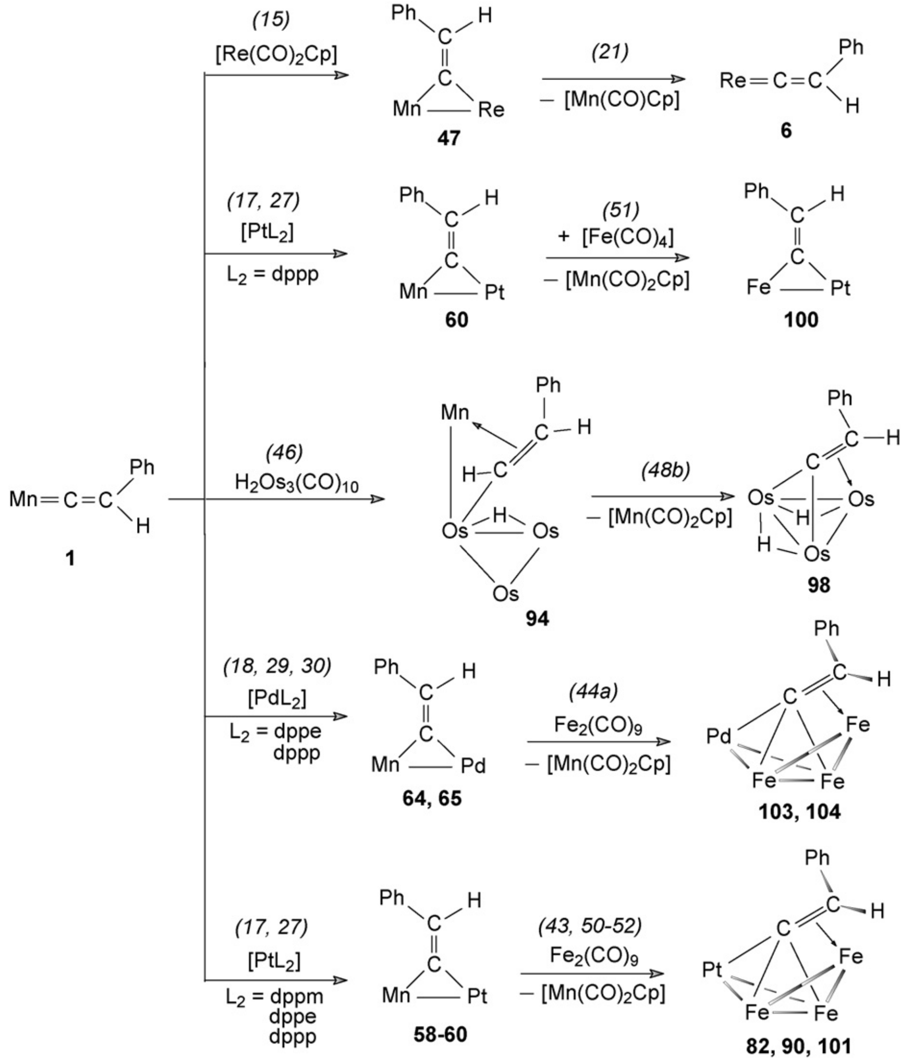
Finally, the reactions *(50–52)* afford the μ_4-vinylidene clusters $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**) [34b] and $(dppp)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**101**) [35] in almost quantitative yields and may be used as preparative methods for these heterometallic compounds.

The first example of the parent vinylidene $C{=}CH_2$ transfer is described in [49b]. The reaction between $Cp(i\text{-}Pr_3P)Rh{=}C{=}CH_2$ and $Ir(Cl)[P(i\text{-}Pr_3)_2]$ (benzene, 50 °C, 2 h) led to an unstable dinuclear RhIr complex, which splits up into mononuclear fragments. Complex $(i\text{-}Pr_3P)_2(Cl)Ir{=}C{=}CH_2$ can be isolated in 77% yield.

7. Electrochemistry of $Cp(CO)_2Mn{=}C{=}CHPh$ and polynuclear complexes

Electrochemical studies of the η^2-alkyne, η^1-vinylidene derivatives of cymantrene and complexes ***B***, ***C*** and ***D*** by means of classical and switching polarography, controlled-potential electrolysis and CV were described in refs. [135–142]. The electrochemical characteristics were obtained with a dropping Hg electrode or a stationary Pt electrode, in MeCN containing 0.1 M $[Et_4N]BF_4$. The cyclic voltammograms were measured varying the potential scan rate from 0.01 to 1.00 V/s. Potentials are given versus Ag/0.1 M $AgNO_3$ in MeCN; they can be converted to V versus SCE by adding 0.337 V.

Polarographic reduction of $Cp(CO)_2Mn(\eta^2\text{-}RC{\equiv}CPh)$ (R = H (**1a**), Ph_3Ge (**1b**), Ph_3Si (**1d**), Ph) proceeds in three stages [135,137]. The first irreversible one-electron wave of **1a** ($E_{1/2}$ − 2.38 V) is shifted to higher potential compared with



Scheme 27. Vinylidene transfer from Mn to Re (*15*; *21*) and to FePt (*17*, *27*; *51*), Os$_3$ (*46*; *48b*), PdFe$_3$ (*18*, *29*, *30*; *44a*) and PtFe$_3$ (*17*, *27*, *43*; *50–52*). The Cp, CO, PR$_3$, P–P ligands are omitted for clarity.

CpMn(CO)$_3$ (−2.70, −2.90 V) and with PhC≡CH (−2.80, −2.93 V). Two subsequent reversible waves (−2.78, −2.90 V) coincide with those of free PhC≡CH. Alkyne elimination from the complex in the first stage is confirmed by the isolation of PhC≡CPh after the electrolysis of Cp(CO)$_2$Mn(η^2-PhC≡CPh) at the potential of the first reduction wave [135].

Reversible one-electron reduction of Cp(CO)$_2$Mn=C^1=C^{2}HPh (**1**) proceeds more easily (−1.99 V) as compared with Cp(CO)$_2$Mn(η^2-HC≡CPh) (**1a**) [136,137], since the LUMO of **1** is located at lower energy than the LUMO of the isoelectronic **1a**. Most probably, the C^1 atom contributes significantly into the LUMO of **1**, whereas such a clearly defined electrophilic center is absent in **1a**. The higher stability of the radical anion [Cp(CO)$_2$Mn=C=CHPh]$^{\bullet-}$ as compared to [CpMn(CO)$_2$(HC≡CPh)]$^{\bullet-}$ seems to be due to the delocalization of electron density in the Mn=C=C system.

Redox chemistry of mononuclear complexes (L)$_n$M=C=CHR and bis-vinylidenes (L)$_n$M=C=CRCR=C=M(L)$_n$ (M = Mn, Re, etc.) was reviewed in detail by Ustynyuk and co-workers [42c]. Mutual redox transformations of Cp′(L)Mn=C=CPhCPh=C=Mn(L)Cp′ (**29**) and [Cp′(L)Mn≡CCPh=CPhC≡Mn(L)Cp′]$^{2+}$ (L = dmpe) were studied by Berke and co-workers [75]. The electrochemistry of carbene, vinylidene, allenylidene, carbyne and alkynyl species was extensively published by Pombeiro [79d,143].

Complex [Cp(CO)$_2$Mn]$_2$(μ-C^1=CHPh) (**2**) is reduced in two stages: reversible two-electron (−1.81 V) and irreversible one-electron (−2.23 V) [136,137]. Keeping in mind that the LUMO in [Cp(CO)$_2$Mn]$_2$(μ-CH$_2$) is localized on the Mn–Mn bond [114b], one can suppose that two electrons come into a similar orbital of **2**. The addition of one more electron to dianion [Cp$_2$(CO)$_4$Mn$_2$(μ-C^1=CHPh)]$^{2-}$ cleaves the Mn–Mn and Mn–μ-C^1 bonds. A more difficult splitting of the Mn–Mn bond in **2** compared with other dimanganese complexes, such as Mn$_2$(CO)$_{10}$ (−1.60 V), corresponds with the higher strength of the Mn–Mn bond in **2** (2.734 Å) than in Mn$_2$(CO)$_{10}$ (2.904 Å) [8].

The dimeric complex [Cp(CO)$_2$MnCu(μ-C=CHPh)(μ-Cl)]$_2$ (**67**) (Fig. 6) shows two two-electron reductions (−0.78 and −2.08 V) and a two-electron oxidation (−0.16 V)

[138]. Both processes are irreversible with the consecutive cleavage of Cu–Cl and Mn–Cu bonds and formation of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**). Reduction of **67** gives metallic Cu and Cl^- ions, while oxidation forms Cu^{2+} and Cl^- ions. The formation of **1** was confirmed with controlled-potential electrolysis of **67** at $E_{1/2}$ −2.20 V. The polarogram of the solution showed a reduction wave at $E_{1/2}$ −1.99 V for **1** [136,137] (see above). In the IR spectrum of this solution, ν(CO) bands at 2008 and 1948 cm^{-1} belonging to **1** [15] were found. Chemical transformations of **67** also result in the elimination of **1** (Section 3.2.2; Scheme 12) [30].

The one-electron reduction of $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(LL')$ (M = Pt [136,137,139], Pd [29,140]) proceeds in one stage at $E_{1/2}$ between −2.10 and −2.60 V (Table 5). The irreversible reduction is typical of complexes $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(LL')$ (**37**, **52–57**), where L, L′ = PPh_3, $P(OR)_3$, CO. More stable $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (P–P = dppe, dppp) (**59**, **60**, **64**, **65**) are reduced reversibly. The reduction of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppm)$ (**58**) is quasi-reversible and proceeds more easily (−2.37 V) than $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (P–P = dppe (**59**), dppp (**60**)) (−2.54 V) [137]. At the same time, the $E_{1/2}$ values for **58** and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**52**) (−2.37 V) coincide. It is possible that the four-membered $\overline{PtP(CH_2)P}$ cycle in **58** is cleaved, and dppm becomes monodentate.

Such splitting of the $\overline{PtP(CH_2)P}$ cycle was observed by transformation of **58** into **89** (Scheme 20) [33]. The products of electrolysis of $Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)(LL')$ (M = Pt, Pd) are $CpMn(CO)_3$, $PhC{\equiv}CH$ and fragments containing Pt or Pd [140].

The reduction of μ_3-vinylidene $CpMnFePt(\mu_3\text{-}C{=}CHPh)[P(O\text{-}i\text{-}Pr)_3]_2(CO)_5$ (**86**), $CpMnFePt(\mu_3\text{-}C{=}CHPh)(PPh_3)(CO)_6$ (**87**) and $CpMnFePt(\mu_3\text{-}C{=}CHPh)(\mu\text{-}dppm)(CO)_5$ (**88**) gives rise to three waves: the first two-electron ($E_{1/2}$ −1.84, −1.66, −1.70 V, respectively), the second (−2.72 V) and the third (−2.92 V) are one-electron [137,139]. As found by CV at a hanging mercury drop at a potential scan rate v of 1 V/s, the first reduction stages are quasi-reversible. The splitting of the first waves into two waves of unequal heights (the ratio ~2:1) is apparently caused by the presence of isomers (see Section 4.1).

The polarograms of μ_4-vinylidene clusters $(\eta^2\text{-}P\text{–}P)MFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (M = Pt; P–P = dppm (**90**), dppe (**82**), dppp (**101**) [136,137,139]; M = Pd; P–P = dppe (**103**), dppp (**104**) [29,140]) show two two-electron waves. The first stage (between −1.14 and −1.43 V) is reversible in all cases. A larger number of metal atoms in a molecule facilitates its reduction and enhances the stability of the substances formed, which is shown in a reversible two-electron reduction of tri- and tetranuclear clusters.

Triangular clusters $(P\text{–}P)PtFe_2(CO)_8$ (**99**, **102**) and $(P\text{–}P)PdFe_2(CO)_8$ (**105**, **106**) (P–P = dppe, dppp) are reduced in three stages, attaching two electrons at the first reversible stage; the subsequent processes are one-electron reductions [29,137,139,140]. The polarography of clusters $(L)(L')PtFe_2(CO)_8$ (L, L′ = PPh_3, $AsPh_3$, $SbPh_3$, $P(OR)_3$, CO) was also reported [136,141].

Comparison of the platinum compounds with their palladium analogues shows a small decrease of the reduction potentials [29,140]. The distinctions in the electrochemical and IR and ^{13}C NMR spectroscopic data (see Table 5 and Section 5.2.2) for the appropriate series of complexes with the cores MnM, MFe_2, MFe_3 (M = Pd, Pt) are caused by a smaller electron donor capacity of the Pd atom than that of the Pt atom.

The electrochemical behaviour of the Os_3-containing clusters **94–98** (see Scheme 23) is considered in ref. [142]. Reduction of $Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ (**95**) occurs irreversibly in three stages (−1.20, −1.35, −2.80 V). The anodic shift of the first potential at 0.55 V relative to $E_{1/2}$ for $Os_3(CO)_{12}$ indicates that the introduction of vinylidene μ_3-C=CHPh greatly facilitates the reduction process.

The presence of the μ-H ligands in **96–98** is responsible for more difficult reductions, and therefore the $E_{1/2}$ values are shifted by 0.20–0.92 V compared with **95**. The isomeric μ_3-alkyne **96** and μ_3-vinylidene **98** clusters are reduced in the same way in three irreversible stages. The anodic shift of a potential of the first wave for **98** (−1.92 V) compared with **96** (−2.12 V) is due to the electron-acceptor influence of vinylidene μ_3-C=CHPh. The subsequent reductions involve the addition of electrons to the $[(\mu\text{-}H)_2Os_3(CO)_9]^{2-}$ dianion and to free $PhC{\equiv}CH$.

The cluster $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (**94**) is reduced in four successive stages at −1.72, −2.15, −2.52 and −2.80 V [142]. The first two-electron stage is reversible, as found by switching polarography and CV (scan rate 0.5 V/s: versus $Ag/AgNO_3$). Comparison of the $E_{1/2}$ values for clusters **94**, $(\mu\text{-}H)_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$ (**96**) and $(\mu\text{-}H)Os_3(\mu\text{-}CH{=}CHPh)(CO)_{10}$ (**97**) shows that the dianion $[CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}]^{2-}$ formed in the first stage, then decomposes into $[CpMn(CO)_2]^{2-}$ and **97**, which is then converted into **96**. Finally, addition of electrons to cluster **96** takes place. These data are in accordance with the chemical behaviour of cluster **94** (Section 5.1; Scheme 23) [126,127].

8. Structural and spectroscopic features of η^1-, μ-, μ_3- and μ_4-vinylidene complexes

In spite of an abundance of publications concerning the synthesis and reactivity of vinylidene complexes, not enough attention has been paid to their structural and spectroscopic features. The X-ray and NMR parameters of vinylidene clusters were cited in the reviews [2,4], when the number of such compounds was still rather limited. Comparative studies of the IR and NMR spectroscopic data for Ru and Os complexes with the $\mu_2\text{-}C{=}CH_2$ and $\mu_3\text{-}C{=}CH_2$ ligands were performed [144].

Our systematic research into vinylidene complexes ***A***, ***B***, ***C*** and ***D*** containing the C=CHPh ligand allowed a study of the changes in structural and spectroscopic characteristics of the C=CHPh group as its coordination mode changes $\eta^1 \rightarrow \mu_2 \rightarrow \mu_3 \rightarrow \mu_4$. The influence of the metal atoms M, M′

and M″ and surrounding ligands on the structural, spectroscopic and electrochemical characteristics of complexes was investigated as well. We systematized our own and extensive literature data on the IR and NMR spectra and X-ray analysis of η^1-vinylidene complexes of manganese and other transition metals (***A***) and also homo- and heteronuclear complexes with bridging vinylidenes (***B***, ***C***, ***D***). The results are given in Table 6.

The presence of the vinylidene $C^1{=}C^2RR'$ in complexes of all types is unequivocally proved by the location of the C^1 signal in a very low field of the ^{13}C NMR spectra, between δ 230 and 400 [2–5]. We noticed that the transition from one structural type to another causes changes not only in the C^1 and C^2 chemical shifts, but also in the difference between them $\Delta\delta = \delta(C^1) - \delta(C^2)$ [2]. As evident from Table 6, the $\Delta\delta$ value decreases twice during the transition from complexes ***A*** to ***B***, and begins to grow again during further increase in amount of metal atoms around vinylidene (***B*** → ***C*** → ***D***) owing to a low-field shift of signal C^1 and simultaneous high-field shift of signal C^2. We inferred that a splitting $\Delta\delta$ between chemical shifts of C^1 and C^2 is most characteristic of each coordination mode of $C^1{=}C^2RR'$, rather than the δ regions for C^1 and C^2.

In the frequent cases, where single crystal XRD is impossible, the $\Delta\delta$ value coupled with other physico-chemical parameters may be used to attribute a structural type to any complex. For instance, we exactly defined the structural formulas of $Cp(CO)MnPt(\mu\text{-}C{=}CHPh)(\mu\text{-}CO)(dppm)$ (**58**) [94], $CpMnFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8$ (**91**) [36], $(dppe)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**103**) [36] and $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**) [37] using the $\delta(C^1)$, $\delta(C^2)$ and $\Delta\delta$ values, coupled with the ^1H NMR and IR data. Later X-ray analyses completely confirmed the structures of **58** (Fig. 4) [95], **91** (Fig. 9) [37] and **104** (Fig. 12) [38].

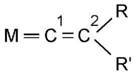
The resonance of the vinylidene proton C=CHR in a wide interval δ 5.5–9.0 depends on the nature of metals and surrounding ligands and is not characteristic.

According to the X-ray data, the C=C bond length of vinylidene increases by 0.03 Å on average due to a gradual decrease in its multiple character during the transition from mononuclear ***A*** and dinuclear ***B*** to trinuclear ***C*** complexes, where vinylidene is involved in η^2-coordination and donates four electrons. There is also a gradual lowering of the ν(C=C) stretching frequencies by ~350 cm^{-1} on going from ***A*** to ***B*** and then to ***C*** complexes. In tetranuclear clusters ***D***, where two electrons of the C^1 atom participate in the formation of σ-bonds with three M atoms, there is apparently a transfer of part of electron density from vinylidene π-orbitals to the orbitals of metal atoms of suitable symmetry, resulting in an increase of 0.07 Å in C=C distance on average, compared with complexes of ***C*** type.

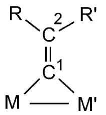
An important structural characteristic of μ_3- and μ_4-vinylidene complexes is the degree of symmetry of η^2-bonding of the $C^1{=}C^2R_2$ ligand with the M atom, determined as the difference between the M–C^2 and M–C^1 bond lengths, Δd. A considerably stronger interaction of the η^2-coordinated M atom with the C^1 atom as compared with C^2 is typical for μ_3-vinylidene triangular clusters ***C***. An average Δd value for this type of complexes is 0.25 Å (Table 6). Our complex $CpMnFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8$ (**91**) (Fig. 9), for two independent molecules of which the Δd values are 0.58 and 0.45 Å [37], stands out sharply against the statistical average picture. On the contrary, in μ_3-vinylidene complexes with a "chain" metal core, an almost symmetrical η^2-bonding of vinylidene with the M atom is observed. Thus, the Δd values are 0.00 and 0.05 Å for two independent molecules of $CpMnFePt(\mu_3\text{-}C{=}CHPh)(CO)_6[\eta^1\text{-}Ph_2PCH_2P({=}O)Ph_2]$ (**89**) (Fig. 8) [33]. For $(i\text{-}Pr_3P)RhFe_2(\mu_3\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_4Cp$ (**76**) containing the Fe–Fe–Rh chain, the Δd difference between the Rh–C^1 and Rh–C^2 bond lengths is 0.04 Å [25].

In μ_4-vinylidene clusters ***D*** with "butterfly" and "rhombus" frameworks, the η^2-bonding of the $C^1{=}C^2RR'$ ligand is close to symmetrical and Δd averages 0.09 Å. The greatest differences are found in $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**82**) (Fig. 11) [34b], $(dppe)PtRu_3[\mu_4\text{-}C{=}CH(t\text{-}Bu)](CO)_9$ [130] and $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**104**) (Fig. 12) [38], for which Δd reaches 0.17–0.24 Å. It is remarkable that $(P\text{–}P)MM'_3(\mu_4\text{-}C{=}CHR)(CO)_9$ (M = Pd, Pt; M′ = Fe, Ru) containing chelating diphosphine ligands at the M atom *trans* to vinylidene, have 60 cluster valence electrons (c.v.e.), whereas most known μ_4-vinylidene clusters have 62 or 64 c.v.e.

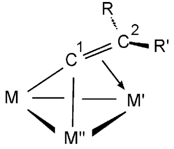
Table 6
^{13}C NMR, IR spectroscopic and X-ray structural parameters of transition metal complexes with η^1-, μ_2-, μ_3- and μ_4-$C^1{=}C^2RR'$ ligands



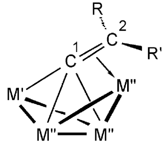
A (η^1)
2 e⁻



B [μ_2 (η^1,η^1)]
2 e⁻



C [μ_3 (η^1,η^1,η^2)]
4 e⁻



D [μ_4 (η^1,η^1,η^1,η^2)]
4 e⁻

Type	^{13}C NMR, δ (ppm)			X-ray, d (Å)				IR, ν (cm^{-1})
	C^1	C^2	$\Delta\delta$	$C^1{=}C^2$	$(C^1{=}C^2)$av.	Δd(M–C^1)[a]	(Δd)av.	$C^1{=}C^2$
A (η^1)	360–400	95–150	260	1.31–1.35	1.33	–	–	1680–1570
B (μ_2)	235–295	120–150	130	1.29–1.38	1.34	–	–	1600–1500
C (μ_3)	250–315	70–135	180	1.25–1.43	1.36	0.19–0.33	0.25	1390–1300
D (μ_4)	285–330	60–100	220	1.39–1.48	1.43	0.00–0.23	0.09	–

[a] Difference between the M–C^2 and M–C^1 distances $\Delta d = |(M\text{–}C^2)\text{–}(M\text{–}C^1)|$ for η^2-coordinated vinylidenes.

9. Conclusions

Rapid progress in the vinylidene complexes chemistry over the last decades has resulted from the development of convenient methods of synthesis from alkynes. The acetylene-vinylidene rearrangement has become a common phenomenon and represents a key reaction in stoichiometric and catalytic syntheses of many valuable organic and organometallic products from alkynes. Nevertheless, this reaction is hindered in some cases and demands the presence of a catalyst, e.g. the rearrangement of $Cp(CO)_2Mn(\eta^2\text{-}HC{\equiv}CPh)$ into $Cp(CO)_2Mn{=}C{=}CHPh$. The mechanism of AVR is still not clear for many real alkyne complexes. It is obvious that the realization of the new theoretical and experimental studies directed at the search of conditions, which would facilitate the course of AVR on simple, accessible and reasonably cheap metal systems, is a current challenge.

A high degree of unsaturation of the $M{=}C^1{=}C^2$ system and its strongly pronounced electrophilic center, at C^1, drives the various reactions of vinylidene complexes. In our opinion, three groups of processes with the vinylidene participation will be the most promising for studying in the near future:

(i) C–C coupling reactions and further growth of the carbon chain to give the cycles and other carbon-rich species.
(ii) Inclusion of functional groups and heteroatoms into the vinylidene ligand with the subsequent isolation of organic products from the complexes.
(iii) Metalation and transmetalation reactions allowing designed syntheses of dinuclear and cluster compounds containing several different metal atoms, including the platinum Group metals.

The processes (i) were reported to be characteristic for such metals as Ru, Rh, etc. However, for Mn they are still poorly studied.

Selective stoichiometric synthesis of styrylphosphonates $PhCH{=}CHP(O)(OR)_2$ allowed us to show the possibility for an efficient use of the Mn=C=C system in processes (ii). It should be expected that the catalytic syntheses of vinylphosphonates from alkynes and phosphites would proceed on other metal centers.

At present, the Mn=C=C system is the most successfully used in an initial stage of processes (iii), viz. preparation of the dinuclear μ-vinylidene MnM complexes. However, further metalation resulting in trimetal clusters is still limited to the synthesis of the MnFePt series. It is important to solve the problem of stabilization of the dinuclear MM' systems in order to avoid their further transmetalation, and to search for M'' fragments which might enter into the trimetal $MM'M''$ systems. Thorough research into the behaviour of the C=CHR ligands on polynuclear heterometallic centers, which will result in new opportunities in organic catalysis, is required.

Certainly, new reactions for the M=C=C systems and their polynuclear derivatives will soon appear, and new properties of vinylidene complexes useful for application in fine chemical synthesis, as catalysts of homogeneous and heterogeneous processes, as precursors of new materials and in other areas of modern chemical technology will be developed.

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