Chemistry of vinylidene complexes
X*. Synthesis and characterization of the vinylidene bridged complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ with chelating diphosphine ligands P–P = dppm, dppe or dppp at the platinum atom

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Abstract

The binuclear μ-vinylidene complex $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ reacts with diphosphines $P\text{–}P = Ph_2P(CH_2)_nPPh_2$, where $n = 1$ (dppm), 2 (dppe) or 3 (dppp), at room temperature to give new complexes of the type $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ with chelating disphosphine ligands P–P at the Pt atom in quantitative yields. All complexes are characterized by IR and ^1H, ^{13}C and ^{31}P NMR spectra. The influence of the nature of the ligands at the Pt atom on the bonding between Pt and the semi-bridging carbonyl group is discussed.

Introduction

Polynuclear heterometallic complexes containing unsaturated organic ligands, in particular, vinylidenes [2, 3], may be used as 'building blocks' for construction of clusters with a higher nuclearity. Evidently, the nature of other ligands at the transition metal atoms must have an influence on the reactivity of such complexes, but this problem, to our knowledge, has attracted little attention.

Recently we have found a dramatic change in the courses of reactions between $Fe_2(CO)_9$ and μ-vinylidene Mn–Pt complexes occurring when two monodentate phosphorus ligands at the Pt atom were displaced by a bidentate chelating diphosphine. Thus, while complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$, where L is PPh_3 or $P(OPr^i)_3$, react with $Fe_2(CO)_9$ to yield the trimetallic μ_3-vinylidene complexes $CpMnPtFe(\mu_3\text{-}C{=}CHPh)(CO)_6L$ and $CpMnPtFe(\mu_3\text{-}C{=}CHPh)(CO)_5L_2$ [4], the treatment of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppe)$ with $Fe_2(CO)_9$ under the same conditions does not give analogous species. Instead, the elimination of the $[Cp(CO)_2Mn]$ fragment occurred and the tetranuclear μ_4-vinylidene cluster $(dppe)PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ was obtained [1, 5].

These observations stimulated us to synthesize a series of bimetallic μ-vinylidene Mn–Pt compounds with chelating diphosphine ligands P–P at the Pt atom and to study in detail their properties.

Most of the known heterometallic complexes including the Pt atom chelated by the diphosphine P–P have been prepared from the mononuclear platinum compounds which already maintain the P–P ligands (see, for example, ref. 6). In addition, the reactions between free P–P and heteronuclear complexes, in which the Pt atom bears easily displaced ligands such as CO, ethylene or cyclooctadiene, have also been used (e.g. ref. 7).

We describe here the use of reactions between $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (I) and diphosphines P–P (P–P is $Ph_2P(CH_2)_nPPh_2$, where $n = 1$ (dppm), 2 (dppe) or 3 (dppp)) as a very convenient synthetic route to chelated complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ and report spectral features of the new bimetallic phenylvinylidene complexes. The results of a study of their reactions with $Fe_2(CO)_9$ will be published in a following communication.

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Experimental

In this work absolute solvents saturated with argon were used. All operations were carried out under argon atmosphere. The course of reactions was followed by means of TLC on Silufol plates and IR spectroscopy.

The IR spectra were recorded on a Specord IR-75 spectrometer. The ^1H NMR spectra were recorded on a Tesla BS-567 A (100 MHz) instrument, and the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra on a Bruker WP-200 SY (50.31 and 81.01 MHz, respectively) instrument.

The complex $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (**I**) was obtained by treating $Cp(CO)_2Mn{=}C{=}CHPh$ with $Pt(PPh_3)_4$ [8]. The synthesis of $Cp(CO)_2Mn{=}C{=}CHPh$ was performed by UV irradiation of $CpMn(CO)_3$ and $PhC{\equiv}CH$ in benzene, followed by the acetylene–vinylidene rearrangement in the presence of hexamethylentetramine as a catalyst, as described in ref. 9.

Synthesis of $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppm)$ (**II**)

To a solution of 0.500 g (0.5 mmol) of complex **I** in 20 ml of benzene, 0.230 g (0.6 mmol) of $Ph_2P(CH_2)PPh_2$ (dppm) was added and the mixture was stirred for 0.5 h at 20 °C. The bright-orange solution was filtered through *c.* 1 cm alumina pad, and the filtrate was evaporated *in vacuo*. The oily residue was dissolved in 5 ml of diethyl ether, and the solution was kept overnight at −18 °C. Then the residual crystals were separated from the mother liquor, washed with cold ether and then with pentane and dried *in vacuo* at 50 °C. Orange crystals of complex **II** with m.p. 186–188 °C (dec.) were obtained; yield 0.385 g (90%). *Anal.* Found: C, 56.30; H, 4.10. Calc. for $C_{40}H_{33}O_2P_2MnPt$: C, 55.98; H, 3.85%.

The crystalline orange complexes **III** and **IV** were prepared in analogous way in yields of *c.* 90%.

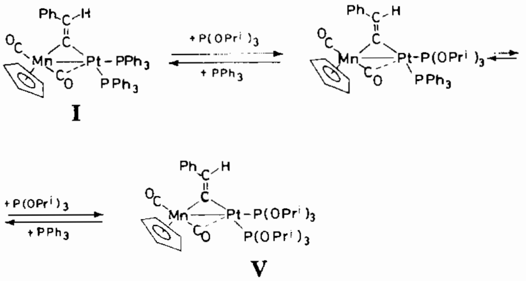
$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppe)$ (**III**), m.p. 213–214 °C (dec.). *Anal.* Found: C, 56.40; H, 4.34. Calc. for $C_{41}H_{35}O_2P_2MnPt$: C, 56.45; H, 4.02%.

$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(dppp)$ (**IV**), m.p. 211–212 °C (dec.). *Anal.* Found: C, 56.70; H, 4.70. Calc. for $C_{42}H_{37}O_2P_2MnPt$: C, 56.92; H, 4.18%.

The spectral characteristics of all complexes are summarized in Tables 1–3.

Results and discussion

In Part V of this series [10] we reported that in vinylidene-bridged complexes of the type $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ the monodentate phosphorus ligands L at the Pt atom easily undergo exchange for free phosphine or phosphite, e.g.

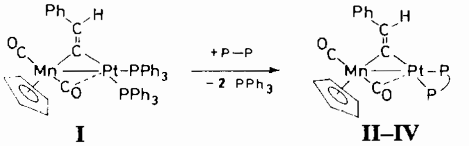


I

V

(1)

Now we have found that the PPh$_3$ ligands in **I** may be readily substituted not only for monodentate phosphite molecules, but also for bidentate diphosphines P–P.



I

II–IV

(2)

P–P = dppm (**II**), dppe (**III**), dppp (**IV**).

Reactions **2** proceed in benzene solutions at room temperature and are completed, in contrast to the reversible reactions of type (1), in 30–45 min to give (at the molar ratio **I**:P–P equal 1:1.2) chelate complexes **II–IV** in quantitative yields. Most probably, reactions (2), like (1), occur in two steps, but the substitution of the second PPh$_3$ ligand occurs so rapidly, that we did not observe any signs of formation of heteroligand intermediates with monodentately coordinated diphosphine P–P. When the lack of P–P was used, both TLC and IR spectra identified the presence of only the parent complex **I** in solution, besides **II**, **III** or **IV**, respectively.

Orange crystalline compounds $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (**II–IV**) are air-stable both as solids and in solutions and have high thermal stability. They are rather insoluble in aliphatic hydrocarbons and moderately soluble in polar organic solvents and benzene.

A comparison of the ^1H and ^{13}C NMR spectra of **I–V** (Tables 1 and 2) indicates that the substitution of two monodentate phosphorus ligands at the Pt atom for a chelating diphosphine does not provoke any significant change in the parameters of the methylendimetallacyclopropane system $MnPt(\mu\text{-}C{=}CHPh)$. The signals of the vinylidene proton $=C\textit{H}Ph$ in the ^1H NMR spectra of **II–IV**, as well as those of **I** and **V**, lie in a low field (δ *c.* 8 ppm) and are split into a triplet; J(PH) 12–15 Hz, J(PtH) 23–26 Hz. In the ^{13}C NMR spectra of complexes **I–V** the resonances of the C^1 and C^2 nuclei of the vinylidene group $C^1{=}C^2HPh$ are observed in narrow intervals of chemical shifts at δ 260–271 and 140–142 ppm, respectively, which are typical for dimetal vinylidene-bridged complexes [2].

TABLE 1. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra (in $CDCl_3$; δ, ppm [J, Hz]) of the complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$ (I), $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$, where P–P is dppm (II), dppe (III) and dppp (IV), and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OPr^i)_3]_2$ (V)

Complex	^{1}H NMR spectra			^{31}P NMR spectra	
	=CH	C_5H_5	Other groups	P^1	P^2
I[a]	7.92t [J(PH) 12.5; J(PtH) 25.6]	4.12s	7.45–6.80m (35H, C_6H_5)	43.5d [J(PtP) 4414; J(PP) 17]	27.4d [J(PtP) 2607; J(PP) 17]
II	8.33t [J(PH) 15.3; J(PtH) 23.2]	4.68s	7.85–6.98m (25H, C_6H_5) 4.30m (2H, PCH_2)	−8.6d [J(PtP) 3261; J(PP) 32]	−17.4d [J(PtP) 2177; J(PP) 32]
III	8.27t [J(PH) 11.7; J(PtH) 24.9]	4.49s	7.90–7.00m (25H, C_6H_5) 2.21m (4H, PCH_2)	52.1d [J(PtP) 3815; J(PP) 33]	49.4d [J(PtP) 2545; J(PP) 33]
IV	[b]	4.18s	8.00–6.98m (26H, =CH, C_6H_5) 2.96 and 2.44m (4H, PCH_2) 1.60m (2H, CH_2)	18.2d [J(PtP) 4030; J(PP) 3]	10.7d [J(PtP) 2365; J(PP) 3]
V	8.64dd [J(PH) 14.9 and 20.2; J(PtH) 23.7]	4.68s	7.75–7.30m (5H, C_6H_5) 4.74m (6H, OCH) 1.35d and 1.33d (36H, CH_3)	142.1d [J(PtP) 6640; J(PP) 11]	145.3d [J(PtP) 4020; J(PP) 11]

[a] In C_6D_6 solution; the signal of C_5H_5 in $CDCl_3$ solution is at δ 4.15 ppm. [b] The signal is masked by resonances of C_6H_5 groups.

It is noticeable that ^{1}H resonances of the Cp ring depend on the ligands P–P and shift regularly upfield as the size of the chelate cycle $\overline{PtP(CH_2)_nP}$ increases in the order II<III<IV. Since this shift is due to the influence of magnetic anisotropy of the phosphorus-bound phenyl groups [10], it may be concluded that distances between the Cp group coordinated to the Mn atom and the phenyl substituents of the platinum-bound PPh_2 unit, which is *cis* to Mn, decrease on going from II to IV. Perhaps, molecule II has the greatest valent angle $MnPtP^2$ (P^2 *cis* to Mn) among complexes of this type.

The ^{31}P NMR spectra of complexes II–IV (Table 1) each show doublet signals of two non-equivalent phosphorus nuclei; the values of chemical shifts and spin–spin coupling constants J(PtP) indicate that a chelate cycle $\overline{PtP(CH_2)_nP}$ is present in all species. As found earlier [8, 10], the signal with the minor value of the J(PtP) constant can be assigned to P^2 (*trans* to the μ-C atom of the vinylidene group). Interestingly, the values of J(PtP) for dimetal complexes are approximately twice those for mononuclear compounds $R_2Pt(P\text{–}P)$ [11, 12].

Altering the ligands at the Pt atom in the studied complexes exerts a noticeable influence on the IR and ^{13}C NMR parameters of the carbonyl groups of the $[Cp(CO)_2Mn]$ fragment. Earlier [8, 10], we supposed that one of the two CO groups linked to the Mn atom in molecules of this type semi-bridges the Mn–Pt bond. It is known [13] that formation of such semi-bridging carbonyl groups, CO_{sb}, reflects a tendency of the electron-rich transition-metal atom to reduce its electron density by means of back-donation into the π^* orbitals of a CO ligand linked to a neighbouring metal atom.

Unfortunately, no crystal structures of vinylidene-bridged MnPt complexes are known to date. The recent X-ray studies of the μ-vinylidene MnRh complexes have shown the presence of a bridging CO group in $Cp(CO)_2Mn\overset{}{R}h(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(PPr^i_3)$ Cp [14, 15] and of a semi-bridging CO in $Cp(CO)_2MnRh(\mu\text{-}C{=}CHPh)(Acac)(CO)$ [16]. For the latter the existence of CO_{sb} has been predicted beforehand on the basis of its IR and NMR spectra [17].

The bridging or semi-bridging CO groups have been found by X-ray studies of a series of dimetal μ-vinylidene, -carbene and -carbyne complexes involving 16-electron Pt atom, e.g. $(OC)_5WPt(\mu\text{-}C{=}CH_2)(dppm)$ [7], $Cp(CO)MnPt\{\mu\text{-}C(PMe_3)\text{-}C_6H_4Me\text{-}4\}(\mu\text{-}CO)(SC_6H_4Me\text{-}4)(PMe_3)$ [18], $[Cp(CO)_2MnPt\{(\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}(PMe_3)_2]^+ BF_4^-$ [18] and $[Cp(CO)_2MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(PMe_3)_2]^+BF_4^-$ [13]. In all of these molecules the bridging or semi-bridging carbonyl lies virtually in the plane of the dimetallacyclopropane system $\overline{MPt(\mu\text{-}C)}$ (M = W or Mn) coincident with the coordination plane of the Pt atom.

Most probably, the analogous planar location of bridging vinylidene and semi-bridging CO ligands

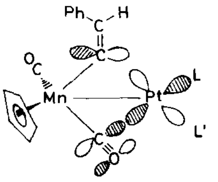
TABLE 2. ^{13}C NMR spectra of complexes I–V (in $CDCl_3$ solutions; δ, ppm [J, Hz])

Complex	μ-C^1=C^2HPh				C_5H_5	CO			Other groups
	C^1	C^2	C_6H_5			CO_t	CO_{sb}		
			C_{ipso}	C_o, C_m, C_p					
I	264.30d [J(PC) 61 and 2.5; J(PtC) 857]	141.25s, br [J(PC) 7; J(PtC) 115]	144.00t [J(PC) 13; J(PtC) 25]	127.35s 125.81s 123.05s	84.19s	229.84s	233.75br	3.91	127.46–134.74 (C_6H_5)
II	271.14d [J(PC) 61; J(PtC) 735]	141.20d [J(PC) 13; J(PtC) 93]	144.43t [J(PC) 13]	127.84s 125.59s 123.45s	86.17s	229.97s	252.42d [J(PC) 31]	22.45	128.3–133.7 (C_6H_5) 46.44t [J(PC) 28] (CH_2)
III	269.75d [J(PC) 63]	141.63br	145.02t [J(PC) 11]	127.98s 125.60s 123.57s	85.61s	230.34s	238.90br	8.56	128.8–135.1 (C_6H_5) 30.77m (PCH_2)
IV	265.96d [J(PC) 63; J(PtC) 818]	140.48br [J(PtC) 112]	144.13br	127.63s 125.83s 123.11s	83.50s	229.77s	236.99br	7.22	128.0–135.7 (C_6H_5) 29.59d [J(PC) 18] and 29.45d [J(PC) 20] (PCH_2) 19.78s (CH_2)
V	259.48d [J(PC) 92; J(PtC) 817]	141.36d [J(PC) 7; J(PtC) 118]	143.44dd [J(PC) 21 and 10; J(PtC) 26]	127.81s 126.12s 123.56s	84.40s	229.21s	231.76br	2.55	69.96s and 68.70s (OCH) 24.37s and 24.06s (CH_3)

TABLE 3. IR spectra (in CH_2Cl_2 solutions) of the complexes I–V in the CO stretching region (cm^{-1})

Complex	Ligands at Pt	$\nu(CO_t)$	$\nu(CO_{sb})$	$\Delta\nu$
I	2 PPh_3	1924	1838	86
II	dppm	1902	1768	134
III	dppe	1906	1784	122
IV	dppp	1913	1822	91
V	2 $P(OPr^i)_3$	1929	1863	66

exists in μ-vinylidene MnPt compounds. If that is so, the bonding between Pt and CO_{sb} in these complexes can be shown in terms of a localized molecular orbital representation in the following way



It is clear, that a strengthening of the Pt...CO_{sb} interaction must lower the C≡O bond order of CO_{sb}, but must have a significantly smaller influence on the terminal carbonyl group, CO_t.

The IR spectrum of each of the complexes II–IV showed two carbonyl stretching bands with different intensities: a strong band at 1913–1902 cm^{-1} and a broad medium band in the region 1822–1768 cm^{-1} (Table 3). Both the low frequency and the shape of the latter band (Fig. 1) indicate that this band may be attributed to the CO_{sb} absorption.

Earlier [10], we suggested, that the difference, $\Delta\nu$, in frequencies of $\nu(CO_t)$ and $\nu(CO_{sb})$ in the IR spectra of complexes of the type $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ with monodentate phosphorus ligands L and L' at the Pt atom may be used as a measure of the $Pt\cdots CO_{sb}$ interaction, and found that the extent of this interaction increases when the electron donating ability of the ligands attached to the Pt atom increases in the order of L, $L' = P(OPr^i)_3$, $CO < PPh_3$, $CO < 2\ P(OPh)_3 \sim 2\ P(OPr^i)_3 \sim 2\ P(OEt)_3 \ll P(OPr^i)_3$, $PPh_3 < 2\ PPh_3$.

The electronic effects of each chelating diphosphine ligand $Ph_2P(CH_2)_nPPh_2$ are close to those of the two PPh_3 groups, and the electron donating ability only slightly increases, when the number of CH_2 groups in the ligand chain increases. It is confirmed, in particular, by the lowering of the $\nu(CO)$ frequencies in the IR spectra of a series of monocarbonyl manganese complexes Cp(CO)Mn(P–P), where P–P = dppm (1842 cm^{-1}), dppe (1835 cm^{-1}), dppp (1825 cm^{-1}); a value of 1825 cm^{-1} is also found for $\nu(CO)$ of $Cp(CO)Mn(PPh_3)_2$ [19, 20].

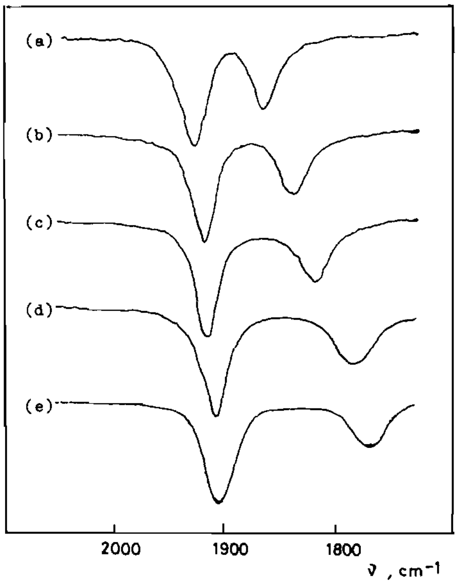


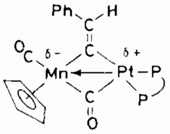
Fig. 1. IR spectra in the CO stretching region (in CH_2Cl_2 solutions) of the complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)L_2$ (I, V) and $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(P\text{–}P)$ (II–IV): (a) V, $L = P(OPr^i)_3$; (b) I, $L = PPh_3$; (c) IV, P–P = dppp; (d) III, P–P = dppe; (e) II, P–P = dppm.

The IR spectra of complexes I–IV demonstrate an opposite pattern: there is a lowering of both $\nu(CO)$ values in the order of compounds I > IV > III > II. In the same order an increase of $\Delta\nu$ values is also observed due to, in general, the shift of the $\nu(CO_{sb})$ band into the low-frequency region. The maximal shift is found for complexes II and III, where P–P ligands form with Pt four- and five-membered cycles, respectively. In these cases the CO_{sb} absorption lies, actually, in the region obvious for a bridging carbonyl group, and the $\Delta\nu$ values for both II and III are abnormally great (134 and 122 cm^{-1}, respectively).

Probably, the strengthening of the $Pt\cdots CO_{sb}$ interaction in the order of complexes I < IV < III < II is connected with a decrease in steric hindrance rendered by the phosphorus ligands: the decrease in the valent angle PPtP facilitates an approach of the CO_{sb} to the Pt atom. It is known that the PPtP angle in $(OC)_5WPt(\mu\text{-}C{=}CH_2)(dppm)$ is only 73.3° [7], whereas those in $(dppe)PtFe_2(CO)_8$ [1] and $(dppp)PtCl_2$ [21] are equal to 85.7 and 91.6°, respectively. The angle PPtP in the μ-carbene complex $Cp(CO)CoPt(\mu\text{-}CH_2)(PPh_3)_2$ involving a $Pt(PPh_3)_2$ unit is even larger (107.9°) [22].

The ^{13}C NMR spectral data also indicate the existence of a strong interaction between Pt and CO_{sb} in complexes II and III. The ^{13}C NMR spectra of compounds $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$, where L and L' are monodentate phosphorus ligands, each exhibit two separate signals of carbon nuclei of the CO groups in narrow intervals of δ 229–230 and 231–234 ppm [10]. In the spectra of **II–IV** the first signal attributed to the CO_t lies also at δ 229–230 ppm, but the second signal is shifted to the low field (see Table 2). Probably, the separation between these signals, Δδ, may be used (as well as the Δν value found from IR spectra) to measure the extent of the $Pt\cdots CO_{sb}$ interaction in complexes of this type. In the spectrum of **III** the broadened signal of CO_{sb} is seen at δ 238.90 ppm (Δδ is 8.56 ppm), and that of **II** lies at δ 252.42 ppm (Δδ is 22.45 ppm) and is split into a doublet with a *J*(PC) value of *c.* 31 Hz.

The above data show that complexes **II** and **III** may be represented as compounds in which a bridging coordination of one of the CO groups is realized. In order to satisfy the EAN rule for both metal atoms in these molecules, the electron pair of the metal–metal bond must be shifted to the Mn atom, and a partial redistribution of charges between the metal atoms must take place.



Perhaps, namely this electron shift explains the decrease in all ν(CO) frequencies in the IR spectra of the complexes studied in the order: **I** > **IV** > **III** > **II**, which is in contrast to the change in electron donating ability of the ligands linked to Pt. Moreover, a markedly higher value of the electrochemical reduction potential for complex **II** ($E_{1/2}$ −2.37 V) as compared with those for **III** and **IV** ($E_{1/2}$ −2.54 V) may be considered also as an indirect indication of the existence in **II** of a positive charge on the Pt atom. Earlier [23, 24], we observed a similar relationship between the first reduction potentials and ν(CO_{sb}) frequencies for a series of complexes $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)LL'$ and $LL'PtFe_2(CO)_8$ and noted that some weakening of the metal–metal bonding in these molecules occurs when the $Pt\cdots CO_{sb}$ interaction is strengthened.

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