

## Reaction products of CO with square-planar platinum(II)-(N,N-chelate) complexes: synthesis and reactivity

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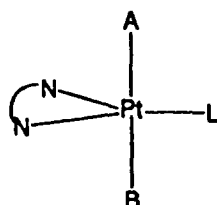
### Abstract

Carbon monoxide adds to [PtCl(R)(N-N)] (R = hydrocarbyl group; N-N = chelating N,N-ligand) to afford neutral five-coordinate [PtCl(R)(CO)(N-N)] or cationic four-coordinate [Pt(R)(CO)(N-N)]<sup>+</sup> complexes, depending on the sterical crowding of the N,N-ligand. For R-aryl, a migratory insertion process follows under mild conditions and the corresponding acyl species are obtained. Some reactions of the five-coordinate adducts with nucleophiles are reported, and a substitution at the metal or an addition to the coordinated carbon monoxide are described.

**Keywords:** Platinum(II); Square-planar complexes; Carbonyls; Five-coordinate complexes; Synthesis

### 1. Introduction

Most coordinatively saturated platinum(II) complexes have the general formula [Pt(A)(B)(L)(N-N)] and display a trigonal-bipyramidal arrangement [1], where N-N = chelating N,N-ligand.



A large variety of the axial ligands A and B can be present including neutral or anionic species [1,2] but only a restricted list of equatorial groups. In particular, N-N must chelate and have suitable steric requirements and L is an  $\eta^2$  moiety with both good  $\sigma$ -donor and  $\pi$ -acceptor properties [1,3]. The  $\eta^1$  ligand CO shows comparable electronic properties and several attempts to

synthesize the corresponding Pt(II) five-coordinate adducts have been made [4]. Recently, two complexes [PtI<sub>2</sub>(CO)(dmphen)] [5] and [PtClMe(CO)(dmphen)] [6] (dmphen = 2,9-dimethyl-1,10-phenanthroline) have been described and characterized by X-ray structural analysis. However, only the latter complex is a 'true' five-coordinate trigonal-bipyramidal compound, at least in the solid state, with dmphen and CO in the equatorial plane. The di-iodo derivative is substantially four-coordinate with monodentate dmphen.

In this paper we report the interaction between neutral or cationic complexes [PtR(Cl/MeCN)(N-N)]<sup>0/+</sup> (R = hydrocarbyl group) and CO, in order to ascertain the influence of the ancillary ligands and the complex charge on CO coordination in a five- or a four-coordinate environment. The reactivity of these products in migratory insertion processes and towards nucleophiles has also been examined.

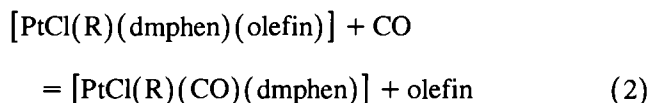
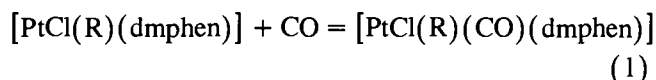
### 2. Results and discussion

#### 2.1. 2,9-Dimethyl-1,10-phenanthroline complexes

The CO adducts [PtCl(R)(CO)(dmphen)] (R = Me, Et, or 4-MeOPh) can be easily obtained through CO

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uptake by the corresponding four-coordinate precursor (Eq. (1)) or by ligand exchange in a five-coordinate olefin complex (Eq. (2)).

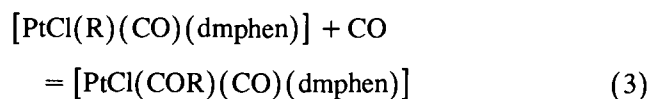


The choice of the 4-anisyl derivative instead of the simple phenyl, as representative example of a compound in which R = aryl, has been mainly dictated by the easier interpretation of the spectra in the  $^1\text{H}$  NMR-monitored experiments. Some exploratory tests showed no significant differences in the chemical behaviour of the aryl complexes. Complexes of ethylene and propene are the most suitable for the exchange reaction (2), since five-coordinate complexes containing olefins with electron-withdrawing substituents are unreactive. The exchange is reversible and a  $pK$  of about 1.5 has been evaluated for the reverse process in the case of olefin = ethylene and R = Me at 30°C in chloroform solution. This value indicates that the equilibrium is markedly shifted towards the CO coordination. This behaviour is consistent with that reported [7] for square-planar  $\text{Pt}^{\text{II}}$ -ethylene complexes.

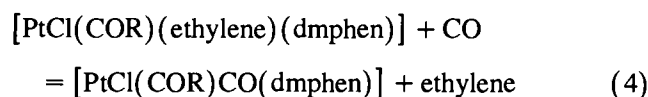
In the solid state, complexes  $[\text{PtCl}(\text{R})(\text{CO})(\text{dmphen})]$  form pale-yellow crystals, which are unaffected by long standing. They are also stable in solutions of chlorinated solvents and no appreciable CO release is observed. The compounds are not conducting in chloroform or nitromethane solution. The  $^1\text{H}$  NMR spectra of all complexes show the equivalence of the two halves of dmphen and a chemical shift for the Pt-CH protons which is intermediate between the values reported for the parent four-coordinate and the corresponding ethylene five-coordinated complexes (e.g. 0.64 vs. 1.34 and -0.07  $\delta$ , respectively, in the case of R = Me).  $^{13}\text{C}$ -enriched samples were prepared by isotopic exchange and used to identify the resonance of the  $\eta^1$  CO in the  $^{13}\text{C}$  NMR spectra (see Table 1). Although the chemical shift does not show significant differences from the values reported [8] in the case of square-planar  $\text{Pt}^{\text{II}}$ -carbonyl complexes, the  $^1J(^{195}\text{Pt}-^{13}\text{C})$  is markedly higher (2500–2700 Hz) than that measured in a four-coordinate environment (less than 2000 Hz). This enhancement has already been observed [1] for the olefin carbon resonances in five-coordinate  $\text{Pt}^{\text{II}}$ -olefin complexes and can be attributed (at least in part) to strengthening of the metal-olefin bond that corresponds, in our case, to an increased  $\pi$ -backdonation. The IR spectra show an intense absorption band at about 2010–2020  $\text{cm}^{-1}$  due to  $\nu(\text{CO})$ . The  $\nu(\text{CO})$  frequencies in neutral four-coordinate *trans*- $[\text{PtCl}_2(\text{CO})(\text{L})]$  occur in the range

2150–2050  $\text{cm}^{-1}$  [9]. In our case, the observed shift to lower frequencies is indicative of a higher metal-to-CO  $\pi$ -backdonation. The close spectral similarities allow to assign similar geometries to all complexes  $[\text{PtCl}(\text{R})(\text{CO})(\text{dmphen})]$ , as shown [6] by the X-ray structural analysis for R = Me.

When the above compounds are allowed to stand in solution under CO, a migratory insertion process takes place.

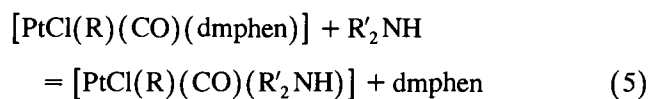


In the cases of R = Et and 4-MeOPh the five-coordinate acyl complex is quantitatively obtained after 48 h and 12 h, respectively. When R = Me, a low conversion is observed, even at 10 bar CO pressure after 48 h. The same complexes can be prepared independently by CO-ethylene exchange on the appropriate five-coordinate acyl precursors [6].



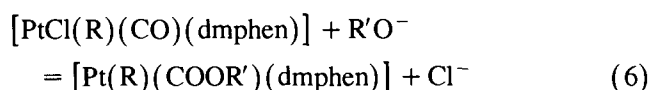
These complexes show  $\nu(\text{CO})$  and  $^1J(^{195}\text{Pt}-^{13}\text{C})$  (see Table 1) that are consistent with a five-coordination, as above discussed. The acyl complexes are stable in the solid state, as well in solution, with the exception of the anisoyl derivative. In this case, a very slow decarbonylation process takes place in solution, with reversion to the starting anisyl compound. This peculiar behaviour has already been reported [2a] for the corresponding five-coordinate aroyl-olefin complexes.

Nucleophilic addition to the coordinated CO was attempted. Different behaviours were observed, according to which N-, O- or C-nucleophiles were used. In particular, an aliphatic amine substitutes the coordinate dmphen affording a square-planar complex.

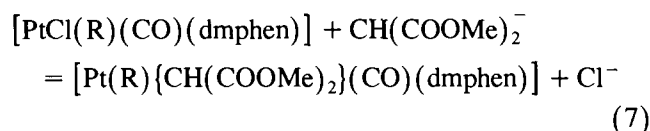


The reaction requires a large excess of the amine (at least 6:1 with the respect to the dmphen compound) since the substitution equilibrium favours the chelating ligand. In fact, the analytically pure square-planar complex was recovered in an only 35% yield, whereas more than 80% exchange was estimated by the  $^1\text{H}$  NMR analysis of the reaction mixture. It is reasonable to assume a *cis* arrangement of the R and CO groups, but we have no firm evidence to assign the exact location of the other two groups. The lack of reactivity of CO in the five-coordinate environment towards amines is consistent with its low stretching frequency [10]. A comparable behaviour was observed with the corresponding five-coordinate olefin complexes [11].

In contrast, alkoxydes react easily affording square-planar Pt-carboalkoxy derivatives.



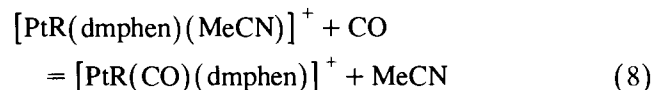
A C-nucleophile such as  $\text{CH}(\text{COOMe})_2^-$  causes chlorine substitution and a new five-coordinate CO adduct was isolated.



The five-coordinate structure of this latter species was inferred using the characterization data reported above for the parent halo complex. This new five-coordinate compound is stable in the solid state, but decomposes in solution of chlorinated solvents with release of dmphen and malonic ester. In methanol, immediate formation of free malonic ester and of a carboxylato Pt<sup>II</sup> complex analogous to that reported in Eq. (6) takes place. An ethereal anhydrous solvent is suitable for recrystallization purposes.

The synthesis of cationic species was attempted by three different routes: (i) chloride abstraction by  $\text{AgBF}_4$  in MeCN starting from  $[\text{PtClR}(\text{CO})(\text{dmphen})]$  complexes; (ii) CO addition to cationic square-planar  $[\text{PtR}(\text{dmphen})(\text{MeCN})]^+$ , (iii) CO-ethylene exchange in cationic five-coordinate  $[\text{PtR}(\text{ethylene})(\text{dmphen})(\text{MeCN})]^+$  compounds. The same square-planar cationic CO adduct was obtained in all cases, for example, through route (ii).

(dmphen)(MeCN)]<sup>+</sup>, (iii) CO-ethylene exchange in cationic five-coordinate  $[\text{PtR}(\text{ethylene})(\text{dmphen})(\text{MeCN})]^+$  compounds. The same square-planar cationic CO adduct was obtained in all cases, for example, through route (ii).



The five-coordinate arrangement of the ligands can be restored upon LiCl addition to the above cationic species. The square-planar ionic complexes are characterized by a conductivity of about  $70\text{--}80 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  (in  $\text{CH}_3\text{NO}_2$ ) which is consistent with a 1:1 electrolyte [12]. In the <sup>1</sup>H NMR spectra a distinct non-equivalence of the two halves of the symmetric dmphen is observed, which is particularly pronounced in the case of the anisyl derivative. Conceivably, an interaction with the phenyl ring current is responsible for the marked highfield shift (about 1 ppm) of the resonance of the adjacent methyl group of the dmphen.

The <sup>13</sup>C NMR spectra on <sup>13</sup>CO-enriched samples show a small (about 2 ppm) downfield shift of the Pt-bound CO resonance with the respect to the five-coordinated species, <sup>1</sup>J(<sup>195</sup>Pt-<sup>13</sup>C) being of a magnitude comparable to that reported for a square-planar geometry [8]. The reduced electron density on the metal in the cationic species causes a lower Pt-to-CO π-backdonation.

Table 1  
Selected <sup>1</sup>H [<sup>13</sup>C] NMR and IR data for five-coordinate  $[\text{PtClR}(\text{dmphen})(\text{CO})]$  (A) and square-planar  $[\text{PtR}(\text{dmphen})(\text{CO})]\text{BF}_4$  (B)

Type	R	Pt-R	Pt- <sup>13</sup> CO	Me-C(Het)	Others	ν(CO)
A <sup>b</sup>	Me <sup>c</sup>	0.64(67, s)		3.42(s)		2010
		[−19.6(550)]	[161.0(2490)]	[28.0(27)]		
	MeCO	2.30(24, s)		3.50(s)		2020, 1650(acyl)
		[193.0(CO), 45.9]	[160.5(2695)]	[28.5(25)]		
	Et	0.93(61, t); 1.50(78, q)		3.45(s)		2020
		[7.5(542); 19.5]	[162.8(2560)]	[28.7(25)]		
EtCO	0.74(t); 2.64(q)		3.47(s)		2020; 1670(acyl)	
	6.35(d, 2H); 6.90 (54, d, 2H)	[158.8(2460)]	3.50(s)	3.57(s, OMe)	2020	
4-MeOph	[156.9(C4); 136.5(33, C3, C5); 114.1(55, C2, C6)]	[158.8(2460)]	[28.1(24)]	[54.9(OMe)]		
	6.85(d, 2H); 7.88(d, 2H)	[160.1(2530)]	[28.5(25)]	3.44(s)	3.83(s, OMe)	2020; 1660(acyl)
4-MeOphCO	[191.1(CO); 131.9(C3, C5); 113.3(C2, C6)]	[160.1(2530)]	[28.5(25)]	[55.4(OMe)]		
	1.54(74, s)		3.13(s); 3.25(s)		2110	
B <sup>d</sup>	Me	[−16.2(515)]	[163.3(1990)]	[28.9, bs]		
		2.74(20, s)		3.04(s)		2120; 1670(acyl)
	Et	1.29(66, t); 2.39(85, q)		3.19(bs)		2110
		[2.1(519); 18.9]	[164.7(2090)]	[28.6, bs]		
	COEt	1.10(t); 2.97(q)		3.03(s)		2100; 1680(acyl)
		6.90(d, 2H); 7.35(50, d, 2H)	[161.2(2035)]	2.33(s); 3.24(s)	3.82(s, OMe)	2110
4-MeOph	[138.8(32, C3, C5); 116.5 (54, C2, C6)]	[161.2(2035)]	[29.1, bs]	[56.0(OMe)]		
	7.09(d, 2H); 8.22(d, 2H)	[161.0(2139)]	[29.8(bs)]	3.90(s, OMe)	2110; 1590(acyl)	
4-MeOphCO	[194.6(771, CO); 134.2 (C3, C5); 115.7(C2, C6)]	[161.0(2139)]	[29.8(25)]	[56.7(OMe)]		

<sup>a</sup> NMR spectra recorded in  $\text{CDCl}_3$  (A, reference  $\delta$  7.26,  $\text{CHCl}_3$  [ $77.0, ^{13}\text{CDCl}_3$ ]) or in  $\text{CD}_2\text{HNO}_2$  (B, reference  $\delta$  4.33,  $\text{CD}_2\text{HNO}_2$  [ $62.8, ^{13}\text{CD}_2\text{HNO}_2$ ]); the coupling constants with <sup>195</sup>Pt (Hz) are in parentheses; abbreviations: s(singlet), bs(broad singlet), d(doublet), t(triplet), q(quartet). IR spectra recorded in Nujol mulls. <sup>b</sup> The aromatic protons [carbons] of the dmphen resonate in the ranges 8.35–8.25(d, 2H), 7.85–7.75(s, 2H), 7.80–7.60(d, 2H) [160(25,C2,C9), 143(C11,C12), 138(C4,C7), 128(C13,C14), 126(C3,C5,C6,C8)]. <sup>c</sup> See also Ref. [6]. <sup>d</sup> The aromatic protons [carbon] of the dmphen resonate in the ranges 8.80–8.75(2H), 8.20–8.10(2H), 8.00–8.05(2H) [162(C2,C9), 142(C4,C7), 131(C13,C14), 129 and 128(C3,C5,C6,C8)].

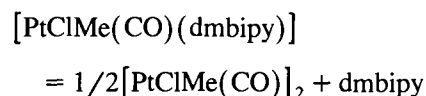
tion, as shown by the higher  $\nu(\text{CO})$  (about  $2100 \text{ cm}^{-1}$ ). Therefore, the above results imply that a marked electronic factor is significant in the stabilization of the five-coordinate arrangement. A similar conclusion has already been reached in the case of the corresponding olefin complexes [13]

In the presence of an excess of CO, the corresponding acyl derivatives  $[\text{Pt}(\text{COR})(\text{CO})(\text{dmphen})]^+$  can be isolated. In contrast to the parent compounds  $[\text{PtR}(\text{CO})(\text{dmphen})]^+$ , the two halves of the dmphen appear to be equivalent in the  $^1\text{H}$  NMR spectra of the acyl species when recorded at room temperature. This equivalence is removed at  $-30^\circ\text{C}$ . A dmphen in a symmetric environment is also observed for the species  $[\text{PtR}(\text{CO})(\text{dmphen})]^+$  on raising the complex concentration from 0.01 to 0.1 M at room temperature. This indicates an intermolecular associated exchange [14]. Traces of free CO or of water in the solvent, or the counterion could be responsible for this process. In addition, when solutions of  $[\text{Pt}(\text{COR})(\text{CO})(\text{dmphen})]^+$  were treated with  $^{13}\text{C}$  CO in order to detect clearly the  $^{13}\text{C}$  resonance of the  $\eta^1$ -coordinate carbon monoxide, a small labeling of the  $\text{CO}_{\text{acyl}}$  was also observed.

## 2.2. Other N-N ligands complexes

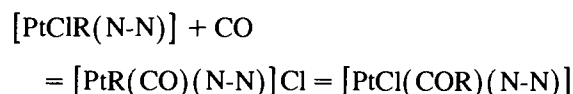
Attempts to synthesize other five-coordinate CO complexes were made by using the N-N ligands depicted in Fig. 1. They differ mainly from dmphen in the skeletal rigidity (1) or in the steric 'in plane' crowding (2 and 3) or in both (4). The procedure shown in Eq. (1) was generally adopted. In the case of N-N = 1 and 4, CO-ethylene exchange (Eq. (2), R = Me) on the corresponding ethylene complexes was also satisfactory. A

CO adduct was always obtained, but the experimental data rule out the clear assignment of a five-coordinate *tbp* structure to any species, at least in solution, with only one exception. When 1 (dmbipy) was used, a yellow microcrystalline compound was formed whose characterization data ( $\nu(\text{CO}) = 2010 \text{ cm}^{-1}$ ,  $\delta_{\text{Pt-Me}} = 0.7 \text{ ppm}$ ) are quite similar to those reported for the corresponding five-coordinate dmphen complex. However, an approximate 20% dissociation is observed in solution at room temperature, according the equilibriums law.



When the chlorine atom is substituted by iodine in the coordination sphere, a noticeable decrease of dissociation is detected in solution. The reduced platinum-to-CO  $\pi$ -backdonation in the dinuclear species can explain this, in spite of the better bridging ability of the iodide [15].

By using 2 and 3, solid orange CO adducts were obtained that were identified as the ionic square-planar complexes  $[\text{PtMe}(\text{CO})(\text{N-N})]\text{Cl}$ . This was clearly inferred from the spectroscopic parameters ( $\nu(\text{CO}) = 2100 \text{ cm}^{-1}$ ,  $\delta_{\text{Pt-Me}} = 1.5 \text{ ppm}$ ) and conductivities (in  $\text{CH}_3\text{NO}_2$   $\Lambda = 75$  and  $60 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  for N-N = 2 and 3 respectively) consistent with 1:1 electrolytes [12]. Similar results were obtained by using the species in which R = 4-MeOPh. In this last case, and when N-N = 3, the initial formation in chloroform solution of the ionic adduct is followed by an insertion process and the neutral four-coordinate anisoyl derivative is also detected in solution.



When the reaction was performed in  $\text{CH}_3\text{NO}_2$ , only the ionic derivative was identified, while the neutral acyl complex was obtained in chloroform. Well-characterized square-planar ionic species of the type  $[\text{MR}(\text{CO})(\text{N-N})]^+$  are rare, although they have been proposed as intermediates in the CO insertion into the M-R bond [16].

A more complex reaction pattern was observed when the five-coordinate complex  $[\text{PtClMe}(\text{ethylene})(\text{N-N})]$  (N-N = 4) was allowed to react with CO. The reaction has been monitored by  $^1\text{H}$  NMR spectroscopy and the fast ethylene-CO exchange was followed by the formation of a mixture of products, in which the presence of free N-N and square-planar mononuclear and dinuclear platinum complexes were detected. The change of the coordination number is clearly shown by the downfield shift of the Pt-bound methyl signal compared with the value reported in the case of the 'true' five-coordinate

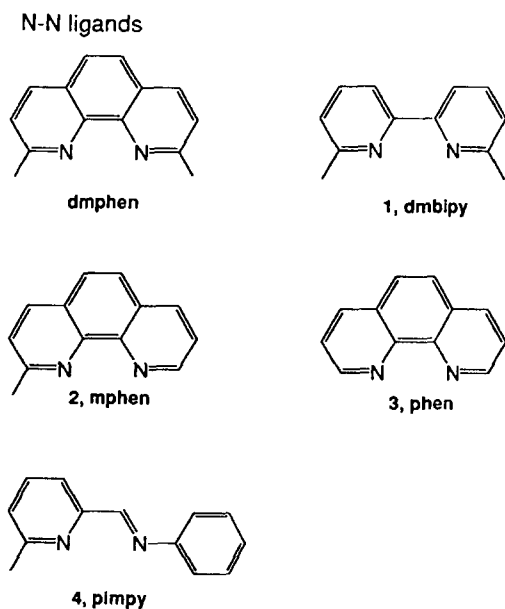
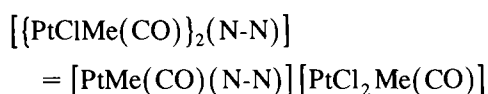
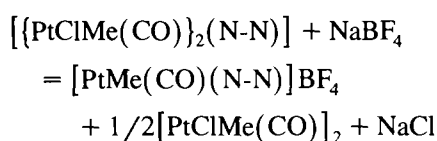


Fig. 1. N-N ligands.

dmphen adduct. The most abundant product was isolated and the elemental analysis and the molecular weight determination are consistent with the formula  $[\text{Pt}_2\text{Cl}_2\text{Me}_2(\text{CO})_2(\text{N-N})]$ . This species is non-conducting in chloroform and a dinuclear structure in which the N-N binds two platinum atoms can be inferred from the analysis of the  $^1\text{H}$  NMR spectrum. However, the nitromethane solution is conducting and the complex behaves as a 1 : 1 electrolyte. This is consistent with the solvent-dependent equilibrium.



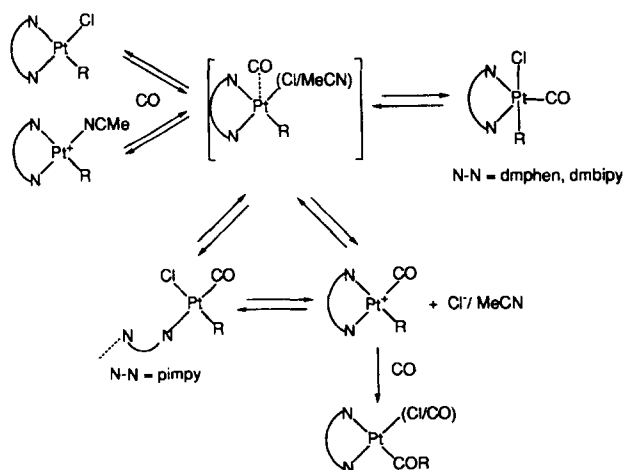
When a nitromethane solution of the above complex was allowed to react with  $\text{NaBF}_4$ , the following reaction took place.



### 3. Conclusions

The electronic and steric conditions that the ancillary ligands must satisfy in order to confer thermodynamic stability on the coordinatively saturated complexes  $[\text{Pt}(\text{A})(\text{B})(\text{CO})(\text{N-N})]$  are even more demanding than those required [1] in the case of the corresponding alkene derivatives. The small size of CO and the reduced the platinum-to-CO  $\pi$ -backdonation in the *tbp* arrangement require a rigid and crowded equatorial N-N ligand and strong  $\sigma$ -donor axial groups. The results obtained when CO is added to complexes  $[\text{PtR}(\text{Cl}/\text{MeCN})(\text{N-N})]^{0/+}$  ( $\text{R}$  = hydrocarbyl) are depicted in the comprehensive Scheme 1.

Stable five-coordinate adducts are obtained only when



N-N is a 2,9-disubstituted-1,10-phenanthroline or part in a 6,6'-disubstituted-2,2'-bipyridine and the axial ligand is a halogen. If only one of these conditions is not fulfilled, the formation of square-planar ionic  $[\text{Pt}(\text{R})(\text{CO})(\text{N-N})]^+$  complexes is generally preferred. When a flexible N-N ligand is used, a square-planar species with monodentate N-N can also form. The ionic compounds  $[\text{Pt}(\text{R})(\text{CO})(\text{N-N})]^+$  undergo a migratory insertion process when allowed to stand under CO, with the ultimate formation of the acyl species  $[\text{Pt}(\text{COR})(\text{Cl}/\text{CO})(\text{N-N})]^{0/+}$ . A similar cationic complex may also be the intermediate [16] when CO insertion occurs into the five-coordinate  $[\text{PtClR}(\text{CO})(\text{dmphen})]$  complexes. Mechanisms involving the five-coordinate *tbp* species itself or a square-planar compound with monodentate dmphen seem to be unlikely [16]. A dissociative equilibrium of the N-N ligand, that has been clearly shown in the case of the dmbipy five-coordinate adduct, affords a highly unsaturated  $\{\text{PtClR}(\text{CO})\}$  fragment that can be a suitable substrate for the insertion process.

### 4. Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian XL-200 or on Bruker AC-270 spectrometers.  $^1\text{H}$  NMR chemical shifts are reported in  $\delta$  (ppm) relative to the solvent ( $\text{CHCl}_3$ , 7.26;  $\text{CD}_2\text{HNO}_2$ , 4.33). The reported data refer to spectra recorded at 25°C. The following abbreviations are used in descriptions of NMR multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened;  $J_{\text{PtH}}$  is the coupling constant to  $^{195}\text{Pt}$  (when satellite peaks are unambiguously detected). IR spectra were recorded on a Perkin Elmer 457 spectrophotometer in Nujol mulls. Conductivity measurements were made with a Crison MicroCM 2200. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany. Solvents and reagents were of AnalR grade and, unless otherwise stated, were used without further purification. The N-N ligands dmphen and **3** (phen) are commercially available, while **1** (dmbipy) [17], **2** (mphen) [18] and **4** [19] are prepared according to known procedures. The complexes  $[\text{PtClR}(\text{N-N})]$  [20,21],  $[\text{PtCl}(\text{COR})(\text{N-N})]$  [2a],  $[\text{PtR}(\text{MeCN})(\text{N-N})]\text{BF}_4$  [21,13],  $[\text{PtClR}(\text{ethylene})(\text{N-N})]$  [20,21],  $[\text{PtCl}(\text{COR})(\text{ethylene})(\text{dmphen})]$  [2a] and  $[\text{PtR}(\text{ethylene})(\text{MeCN})(\text{dmphen})]\text{BF}_4$  [21,13] were synthesized as described. Characterization data of previously unreported complexes are available from the authors.

#### 4.1. Synthesis of $[\text{PtClR}(\text{CO})(\text{dmphen})]$

*Method A.* CO was bubbled through a solution of 0.10 g of  $[\text{PtClR}(\text{dmphen})]$  dissolved in 4 ml of

dichloromethane at room temperature. After 10 min, the solution was concentrated under vacuum and the product isolated by careful addition of diethyl ether, giving pale yellow crystals (yield 80–90%).

**Method B.** The title complexes can be obtained in 70–80% yield by treating compounds [PtClR(ethylene)(dmphen)] with CO, under the above conditions. In the case of R = Et, 24 h standing under CO is required in order to complete the exchange reaction. Anal. Found (R = Et): C, 40.95; H, 3.34; N, 5.46. C<sub>17</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 41.18; H, 3.46; N, 5.65%. Found (R = 4-MeOPh): C, 46.22; H, 3.40; N, 4.62. C<sub>22</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 46.04; H, 3.34; N, 4.88%.

#### 4.2. Determination of the equilibrium constant of CO–ethylene exchange reaction.

The complex [PtClMe(CO)(dmphen)] (11.5 mg, 0.024 mmol) was dissolved in 2.6 ml of CDCl<sub>3</sub> in a gas-tight NMR tube of volume 2.6 ml. Free ethylene was added (about 0.020 mmol ml<sup>-1</sup>) and the solution kept at 30°C until no more changes in the <sup>1</sup>H NMR spectrum were observed. The relative concentrations of the free olefin and the two five-coordinate species were then measured by integration of the corresponding signals. The free CO concentration was assumed to be equal to that of the ethylene complex. Five different experiments gave comparable values of the equilibrium constant.

#### 4.3. Synthesis of [PtCl(COR)(CO)(dmphen)]

The title complexes were prepared in 70–80% yield by CO addition to the corresponding [PtCl(COR)(ethylene)(dmphen)] compounds (Method B of Section 4.1). An alternative procedure starting from the parent [PtClR(CO)(dmphen)] is effective for R = 4-MeOC<sub>6</sub>H<sub>4</sub> and Et. A solution of [PtClR(CO)(dmphen)] (0.10 g) in 4 ml of dichloromethane was treated with CO (1.5 bar) at room temperature. After 12 h (48 h in the case of R = Et) the solution was concentrated under vacuum and the complex crystallized by careful addition of diethyl ether (yield 70–80%). Anal. Found (R = Et): C, 41.35; H, 3.34; N, 5.23. C<sub>18</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 41.27; H, 3.27; N, 5.35%. Found (R = 4-MeOPh): C, 46.04; H, 3.25; N, 4.45. C<sub>23</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>3</sub>Pt. Calc.: C, 45.89; H, 3.18; N, 4.65%.

#### 4.4. Reaction of [PtClMe(CO)(dmphen)] with diisopropylamine

To a solution of the title complex (0.100 g, 0.21 mmol) in 4 ml of dry dichloromethane, freshly distilled <sup>1</sup>Pr<sub>2</sub>NH was added (0.127 g, 1.26 mmol). After 2 h the brown solution was concentrated to a small volume and the product separated by chromatography on silica gel, by elution with dichloromethane. [PtClMe(CO)(<sup>1</sup>Pr<sub>2</sub>NH)] was obtained in 35% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ):

3.41(m, 2H, 2CH), 3.05(br, NH), 1.39(d, 6H, 2Me), 1.33(d, 6H, 2Me), 1.11(s, Pt–Me, <sup>2</sup>J<sub>PtH</sub> = 72 Hz). IR(Nujol, cm<sup>-1</sup>): 3220 (NH), 2060 (CO). Anal. Found: C, 25.55; H, 4.80; N, 3.85. C<sub>8</sub>H<sub>18</sub>ClNO<sub>2</sub>Pt. Calc.: C, 25.64; H, 4.84; N, 3.74%.

#### 4.5. Reaction of [PtClMe(CO)(dmphen)] with sodium methoxide

To a yellow solution of the five-coordinate complex (0.100 g, 0.21 mmol) in 4 ml of dry methanol, 0.6 ml of 1.6 M methanol solution of NaOMe (0.96 mmol) was added dropwise under dinitrogen. After a few minutes the dark orange solution was filtered through a thin layer of Celite. The volume of filtrate was reduced under vacuum to about 1 ml and the yellow complex [PtMe(COOMe)(dmphen)] crystallized by slow addition of diethyl ether. (yield 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 8.33(d, 1H), 8.28(d, 1H), 7.76(s, 1H), 7.75(s, 1H), 7.61(d, 2H), 3.69(s, COOMe, 3H <sup>4</sup>J<sub>PtH</sub> = 8 Hz), 3.09(s, Me, 3H), 2.86(s, Me, 3H), 1.09(s, Pt–Me, 3H, <sup>2</sup>J<sub>PtH</sub> = 89 Hz). IR(Nujol, cm<sup>-1</sup>): 1660 (CO). Anal. Found: C, 43.67; H, 3.76; N, 5.93. C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 42.77; H, 3.80; N, 5.87%.

#### 4.6. Reaction of [PtClMe(CO)(dmphen)] with potassium dimethylmalonate

To a white suspension of K[CH(COOMe)<sub>2</sub>], obtained by adding CH<sub>2</sub>(COOMe)<sub>2</sub> (0.247 g, 1.87 mmol) to solution of KO<sup>t</sup>Bu (0.209 g, 1.87 mmol) in 5 ml of dry THF, solid [PtClMe(CO)(dmphen)] (0.150 g, 0.315 mmol) was added portionwise. After 30 min stirring the yellow suspension was filtered and the residue was washed with 4 ml of the same solvent. The volume of the combined filtrates was reduced under vacuum to about 4 ml and the yellow complex [PtMe{CH(COOMe)<sub>2</sub>}(CO)(dmphen)] crystallized by slow addition of dry diethyl ether. (yield 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 8.30(d, 2H), 7.83(s, 2H), 7.75(d, 2H), 3.30(s, 2COOMe, 6H, <sup>5</sup>J<sub>PtH</sub> = 10 Hz), 3.18(s, 1H, CH), 3.03(2Me, 6H), 0.34(Pt–Me, 3H, <sup>2</sup>J<sub>PtH</sub> = 50 Hz). IR(Nujol, cm<sup>-1</sup>): 2000 (CO), 1750 (COOMe). Anal. Found: C, 43.51; H, 3.74; N, 4.70. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>Pt. Calc.: C, 43.68; H, 3.84; N, 4.85%.

#### 4.7. Synthesis of [PtR(CO)(dmphen)]BF<sub>4</sub>

**Method A.** To a solution of [PtClR(CO)(dmphen)] (1 mmol) in 10 ml of a 1:1 dichloromethane–acetonitrile mixture, 4 ml of 0.25 M solution of AgBF<sub>4</sub> in the same solvent was added dropwise at 0°C. After 10 min stirring, the mixture was filtered through a thin layer of Celite. The volume of the filtrate was reduced under vacuum. Addition of diethyl ether afforded the ionic product as white crystals (yield: 70–80%).

**Method B.** CO was bubbled through a solution of

[PtR(ethylene)(MeCN)(dmphen)]BF<sub>4</sub> (0.100 g) in 5 ml of nitromethane at room temperature. After 10 min stirring the solution was concentrated under vacuum. Addition of diethyl ether caused the crystallization of the product (yield: 70–80%). The same experimental procedure was used successfully starting from [PtR(MeCN)(dmphen)]BF<sub>4</sub> (Method C). Anal. Found (R = Me): C, 36.24; H, 2.92; N, 5.28. C<sub>16</sub>H<sub>15</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 36.04; H, 2.84; N, 5.25%. Found (R = Et): C, 37.45; H, 3.15; N, 5.30. C<sub>17</sub>H<sub>17</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 37.31; H, 3.13; N, 5.12%. Found (R = 4-MeOPh): C, 42.25; H, 3.18; N, 4.55. C<sub>22</sub>H<sub>19</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 42.26; H, 3.06; N, 4.48%.

#### 4.8. Synthesis of [Pt(RCO)(CO)(dmphen)]BF<sub>4</sub>

The title complexes were obtained in 60–70% yield starting from the parent species [(PtCl(RCO)(CO)(dmphen)] by the Method A of Section 4.7. An alternative procedure (see Section 4.3.) can be adopted, starting from compounds [PtR(CO)(dmphen)]BF<sub>4</sub>. Anal. Found (R = Me): C, 36.40; H, 2.65; N, 5.08. C<sub>17</sub>H<sub>15</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 36.38; H, 2.69; N, 4.99%. Found (R = Et): C, 37.29; H, 3.09; N, 4.56. C<sub>18</sub>H<sub>17</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 37.58; H, 2.98; N, 4.87%. Found (R = 4-MeOPh): C, 41.56; H, 2.92; N, 4.26. C<sub>23</sub>H<sub>19</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>3</sub>Pt. Calc.: C, 42.29; H, 2.93; N, 4.29%.

#### 4.9. Reaction of [PtClMe(ethylene)(dmbipy)] with CO

The title complex was obtained adapting a reported procedure [20] (<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.98(d, 2H), 7.84(t, 2H), 7.45(d, 2H), 3.14(s, 2Me), 2.93(m, 2H, <sup>2</sup>J<sub>PtH</sub> = 88 Hz), 2.20(m, 2H, <sup>2</sup>J<sub>PtH</sub> = 65 Hz), -0.10(s, Pt-Me, <sup>2</sup>J<sub>PtH</sub> = 70 Hz)). CO was bubbled through a solution of this complex (0.100 g, 0.22 mmol) in 5 ml of dichloromethane at room temperature. After 10 min stirring the solution was concentrated under vacuum to about 1 ml. Addition of diethyl ether afforded yellow-brown crystals of the product [PtClMe(CO)(dmbipy)] (yield: 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.86(m, 4H), 7.41(d, 2H), 3.01(s, 2Me), 0.7(br, Pt-Me, <sup>2</sup>J<sub>PtH</sub> = 70 Hz). IR(Nujol, cm<sup>-1</sup>): 2100 (CO). Anal. Found: C, 38.43; H, 3.37; N, 6.25. C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 36.73; H, 3.30; N, 6.12%.

#### 4.10. Synthesis of [PtClMeCO(dmbipy)]

To a solution of [PtClMe(CO)(dmbipy)] (0.050 g, 0.109 mmol) in 2 ml of dichloromethane, 3 ml of a saturated solution of NaI in water was added. After 2 h the organic phase was separated, washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under vacuum to afford the product (yield: 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.92(d, 2H), 7.83(t, 2H), 7.41(d, 2H), 3.08(s, 2Me), 0.71(s, Pt-Me, <sup>2</sup>J<sub>PtH</sub> = 68 Hz).

IR(Nujol, cm<sup>-1</sup>): 2100 (CO). Anal. Found: I, 22.95. C<sub>14</sub>H<sub>15</sub>IN<sub>2</sub>O<sub>2</sub>Pt. Calc.: I, 23.10%.

#### 4.11. Reaction of [PtClMe(N-N)] (N-N = mphen or phen) with CO

A solution of [PtClMe(N-N)] (0.100 g) in the minimum amount of dichloromethane was treated under CO pressure (1.5 bar) at room temperature. After a few minutes an orange precipitate began to form. The suspension was stirred for 15 min, and the precipitate was collected, washed with dichloromethane and dried under vacuum to afford [PtMe(CO)(N-N)]Cl (yield: 90%).

N-N = mphen, <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, δ): 9.35(d, 1H, <sup>3</sup>J<sub>PtH</sub> = 42 Hz), 9.01 (d, 1H), 8.82(d, 1H), 8.25(s, 1H), 8.22(s, 1H), 8.30–8.15(m, 2H), 3.22 (s, Me), 1.57(s, Pt-Me, <sup>2</sup>J<sub>Pt-H</sub> = 68 Hz); IR(Nujol, cm<sup>-1</sup>): 2100 (CO); Anal. Found: C, 38.45; H, 2.76, N, 5.80. C<sub>15</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 38.51; H, 2.80; N, 5.99%.

N-N = phen, <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, δ): 9.35(d, 2H, <sup>3</sup>J<sub>Pt-H</sub> = 34 Hz), 9.02(d, 2H), 8.30(s, 2H), 8.25(m, 2H), 1.50(s, Pt-Me, <sup>2</sup>J<sub>Pt-H</sub> = 68 Hz); IR(Nujol, cm<sup>-1</sup>): 2100 (CO); Anal. Found: C, 36.90; H, 2.55; N, 6.03. C<sub>14</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>Pt. Calc.: C, 37.05; H, 2.44; N, 6.17%.

#### 4.12. Reaction of [PtCl(4-MeOPh)(N-N)] (N-N = mphen or phen) with CO

N-N = mphen. By using the procedure reported in Section 4.11 a yellow solution was obtained when CO was added to a suspension of the title complex in dichloromethane. The crude amorphous reaction product [Pt(4-MeOPh)(CO)(mphen)]Cl was isolated by concentrating the solution in vacuo and washing the residue with diethyl ether. <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, δ): 8.94(d, 1H), 8.85(d, 1H), 8.32(d, 1H, <sup>3</sup>J<sub>PtH</sub> = 40 Hz) 8.27(s, 1H), 8.23(s, 1H), 8.22(m, 1H), 7.98(m, 1H), 7.55(d, 2H-Ar, <sup>3</sup>J<sub>PtH</sub> = 47 Hz), 7.01(d, 2H-Ar), 3.87(s, OMe), 3.31(s, Me). IR(Nujol, cm<sup>-1</sup>): 2100 (CO). Λ (CH<sub>3</sub>NO<sub>2</sub>) = 60 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>. The chemical identification of the product is supported by comparison of the reported data with those of [Pt(4-MeOPh)(CO)(mphen)]BF<sub>4</sub> independently synthesized by CO-exchange in the related MeCN complex.

N-N = phen. By adding CO to a suspension of the title complex in a chlorinated solvent, a solution containing the starting compound and two different reaction products was obtained even at 100 bar CO pressure. No analytically pure compounds could be isolated. However, the two products could be identified as [Pt(4-MeOPh)(CO)(phen)]<sup>+</sup> and [PtCl(4-MeOPhCO)(phen)] by comparison with the <sup>1</sup>H NMR data of authentic samples independently synthesized. In a run performed in CDCl<sub>3</sub> (10 bar CO pressure, 24 h) these two species were obtained in 50 and 25% yield respectively. When the reaction was carried out in nitromethane, only the cationic product was detected in quantitative yield.

$^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ ,  $\delta$ ),  $[\text{Pt}(4\text{-MeOPh})(\text{CO})(\text{phen})]^+$ : 9.45(d, 1H,  $^3J_{\text{PtH}} = 20$  Hz), 9.08 (d, 1H), 8.98(d, 1H), 8.42(d, 1H,  $^3J_{\text{PtH}} = 40$  Hz) 8.33(s, 1H), 8.31(s, 1H), 8.25(m, 1H), 8.05(m, 1H), 7.55 (d, 2H–Ar), 7.00(d, 2H–Ar,  $^3J_{\text{PtH}} = 45$  Hz), 3.87(s, OMe).

#### 4.13. Reaction of $[\text{PtClMe}(\text{ethylene})(\text{pimpy})]$ with CO

The title complex was obtained by a reported procedure [20] ( $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 9.09(s, 1H,  $^3J_{\text{PtH}} = 34$  Hz), 7.92(d, 1H), 7.89(t, 1H), 7.75(d, 1H), 7.60–7.40(m, 5H), 3.12(s, Me), 2.95(br, 2H); 2.30(br, 2H); –0.04(s, Pt–Me,  $^2J_{\text{PtH}} = 68$  Hz)). CO was bubbled through an orange solution of this complex (0.100 g, 0.21 mmol) in 5 ml of dichloromethane at room temperature. After 5 min, the resulting yellow solution was concentrated to dryness, affording an orange solid. This residue was washed twice with 1 ml diethyl ether and recrystallized from chloroform–pentane. Pale-yellow microcrystals of  $[\{\text{PtClMe}(\text{CO})\}_2(\text{pimpy})]$  were obtained in 60% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 9.87(s, 1H,  $^3J_{\text{PtH}} = 62$  Hz), 8.61(d, 1H), 8.19(t, 1H), 7.78(d, 1H), 7.52–7.42(m, 5H), 2.96(s, Me), 1.01 (s, Pt–Me,  $^2J_{\text{PtH}} = 76$  Hz), 0.97(s, Pt–Me,  $^2J_{\text{PtH}} = 68$  Hz). IR(Nujol,  $\text{cm}^{-1}$ ): 2110, 2060 (CO). Anal. Found: C, 27.45; H, 2.50; N, 3.70.  $\text{C}_{17}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}_2$ . Calc.: C, 27.47; H, 2.44; N, 3.77%. Mol. wt. (osmometric,  $\text{CHCl}_3$ ) Found: 754. Calc.: 743.4.

$^1\text{H}$  NMR ( $\text{CD}_3\text{NO}_2$ ,  $\delta$ ): 9.24(s, 1H,  $^3J_{\text{PtH}} = 68$  Hz), 8.35(t, 1H), 8.20(d, 1H), 8.05(d, 1H), 7.60(m, 3H), 7.40(m, 2H), 3.02(s, Me), 0.96(s, Pt–Me,  $^2J_{\text{PtH}} = 70$  Hz), 0.88(s, Pt–Me,  $^2J_{\text{PtH}} = 80$  Hz).  $\Lambda(\text{CH}_3\text{NO}_2) = 73 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .

A nitromethane solution (3 ml) of the dinuclear complex (30 mg) was treated with an equimolar amount of  $\text{NaBF}_4$ . After overnight stirring, the suspension was filtered and the residue analysed for chlorine. The yellow solution was concentrated to dryness. The residue was extracted with nitromethane- $d_3$ . The  $^1\text{H}$  NMR spectrum was exactly superimposable on that reported above, except for the absence of the resonance at 0.88  $\delta$ . A signal at 1.13  $\delta$  was detected, attributable to  $[\{\text{PtClMe}(\text{CO})\}_2]$  [22].

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#### References

- [1] V.G. Albano, G. Natile and A. Panunzi, *Coord. Chem. Rev.*, **133** (1994) 67.
- [2] (a) V. De Felice, B. Giovannitti, A. Panunzi, F. Ruffo and D. Tesauero, *Gazz. Chim. Ital.*, **123** (1993) 65; (b) V.G. Albano, C. Castellari, V. De Felice, M. Monari, A. Panunzi and F. Ruffo, *Organometallics*, **11** (1992) 3665; (c) M.E. Cucciolito, V. De Felice, F. Giordano, A. Panunzi and F. Ruffo, *J. Chem. Soc. Dalton Trans.*, (1993) 3421.
- [3] (a) V. De Felice, A. De Renzi, F. Giordano and D. Tesauero, *J. Chem. Soc. Dalton Trans.*, (1993) 1927; (b) M.E. Cucciolito, V. De Felice, A. De Renzi, F. Ruffo and D. Tesauero, *J. Organomet. Chem.*, **493** (1995) 1.
- [4] (a) J.D. Oliver and P.E. Rush, *J. Organomet. Chem.*, **104** (1976) 117; (b) H.C. Clark and M.A. Mesubi, *J. Organomet. Chem.*, **215** (1981) 131.
- [5] F.P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, *J. Chem. Soc. Chem. Commun.*, (1992) 333.
- [6] V. De Felice, M.L. Ferrara, F. Giordano and F. Ruffo, *Gazz. Chim. Ital.*, **124** (1994) 117.
- [7] F.R. Hartley, in *Comprehensive Organometallic Chemistry*, Vol. 6, Pergamon, Oxford, 1982, Chapter 39, p. 489.
- [8] (a) D.G. Cooper and J. Powell, *Inorg. Chem.*, **16** (1977) 142; (b) W.J. Cherwinski, B.F.G. Johnson, J. Lewis and J.R. Norton, *J. Chem. Soc. Dalton Trans.*, (1975) 1156.
- [9] G.A. Foulds, P.S. Hall and D.A. Thornton, *Polyhedron*, **6** (1987) 85.
- [10] R.J. Angelici, *Acc. Chem. Res.*, **5** (1972) 335.
- [11] A. De Renzi, A. Panunzi, A. Saporito and A. Vitagliano, *Gazz. Chim. Ital.*, **107** (1977) 549.
- [12] W.J. Geary, *Coord. Chem. Rev.*, **7** (1971) 81.
- [13] C. Castellari, V. De Felice, A. Panunzi, A. Sanchez and A. Vitagliano, *J. Organomet. Chem.*, **388** (1990) 243.
- [14] J.P. Jesson and E.L. Meutterties, in *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, London, 1975, Chapter 8.
- [15] M. Herberhold, *Metal  $\pi$ -Complexes*, Vol. II part 2, Elsevier, Amsterdam, 1974, p. 161.
- [16] R. van Asselt, E.E.C.G. Gielen, R.E. Rulke, K. Vrieze and C.J. Elsevier, *J. Am. Chem. Soc.*, **116** (1994) 977.
- [17] E. Breitmaier and T. Rode, *Synthesis*, **6** (1987) 574.
- [18] W.T. Nauta, P.J. Pijper, H. Timmerman and H. Van der Goot, *Eur. J. Med. Chem.-Chim. Ther.*, **5** (1984) 399.
- [19] G. van Koten and H. van der Poel, *Inorg. Chem.*, **20** (1981) 2950.
- [20] M.E. Cucciolito, V. De Felice, A. Panunzi and A. Vitagliano, *Organometallics*, **8** (1989) 1180.
- [21] V. De Felice, A. De Renzi, D. Tesauero and A. Vitagliano, *Organometallics*, **11** (1992) 3669.
- [22] J.D. Scott and R.J. Puddephatt, *Organometallics*, **5** (1986) 1253.