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Stable five-coordinate $[\mathrm{Pt}(\overline{\mathrm{N\ N'}})(\mathrm{olefin})(\mathrm{R})\mathrm{X}]$ complexes formed by oxidative addition to $[\mathrm{Pt}(\overline{\mathrm{N\ N'}})(\mathrm{olefin})]$ precursors

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Abstract

The oxidative addition of an electrophilic reagent such as a halogen or an alkyl halide to a suitable three-coordinate species of the type $[\mathrm{Pt}(\overline{\mathrm{N\ N'}})(\mathrm{olefin})]$ ($\overline{\mathrm{N\ N'}}$ = chelating *N,N*-ligand) affords a five-coordinate product. The reaction provides a new versatile route to the synthesis of trigonal bipyramidal complexes of general formula $[\mathrm{Pt}(\mathrm{X})(\mathrm{Y})(\overline{\mathrm{N\ N'}})(\mathrm{olefin})]$ (X = halide; Y = hydrocarbyl or halide). This is apparently the first widely applicable oxidative addition process to three-coordinate M(0) organometallic derivatives of group 10 elements to give isolable five-coordinate M(II) products. Some general features of the addition and preliminary observations on the reaction mechanism are described.

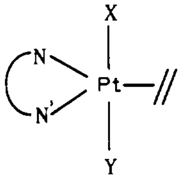
Introduction

Oxidative addition reactions play a crucial role in most stoichiometric and catalytic processes promoted by transition metals [1]. Stoichiometric processes of this type generally give the expected coordinatively saturated species [2]. This is not the case, however, for well known processes [3] involving $16e^-$ three-coordinate precursors. These reactions are expected to give five-coordinate $18e^-$ products, as depicted in eq. 1:

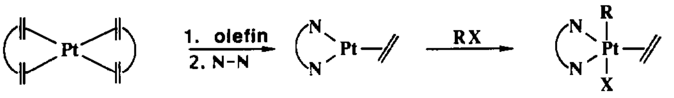
$$\underset{\mathrm{I}}{\mathrm{L_3M}} + \mathrm{AB} \rightarrow \underset{\mathrm{II}}{\mathrm{L_3M(A)(B)}} \qquad (1)$$

The addition process, however, is usually followed by another reaction *, and the final product can be formed from II by loss of one ligand [4], by an insertion [5], or by a reductive elimination [6].

In seeking to isolate type II stable compounds formed according to eq. 1 we took account of previous observations [7,8] on the stabilization of five-coordinate species of the type [M(X)(Y)($\overline{N\ N'}$)(olefin)] (M = Pd, Pt; X = halide; Y = halide or hydrocarbyl)



and of the procedures [9,10] used for the preparation of d^{10} M(0) olefin complexes. We report here on the synthesis of suitable three-coordinate precursors I, and on their reaction with several electrophiles to give type II products [11*]:



I II

Results

Three-coordinate precursors

Previous observations [7,8] on the stability of five-coordinate olefin complexes of palladium(II) and platinum(II) have revealed the importance of the steric requirements of the $\overline{N\ N'}$ ligands in the stabilization of five-coordinate complexes II, and would expected that these compounds could be isolable if the $\overline{N\ N'}$ ligands used are such as to bring sterically demanding substituents "in plane".

Three-coordinate platinum(0) complexes I that meet this requirement were prepared (see Scheme 1) in the first part of the present work by the procedures suggested by previous studies. Palladium compounds of the type [M($\overline{N\ N'}$) olefin] were previously reported [9,10] but no platinum species of the same type had been described [11*] as far as we know. These seem to be generally more stable than the corresponding palladium species when compounds with matching coordination environments are compared. Complexes containing olefins with electron-withdrawing substituents are fairly stable and/or inert. They can be recrystallized from CH_2Cl_2/Et_2O, and do not decompose appreciably during several hours in chloroform or methylene chloride solution. The ethylene complexes are obtained from the

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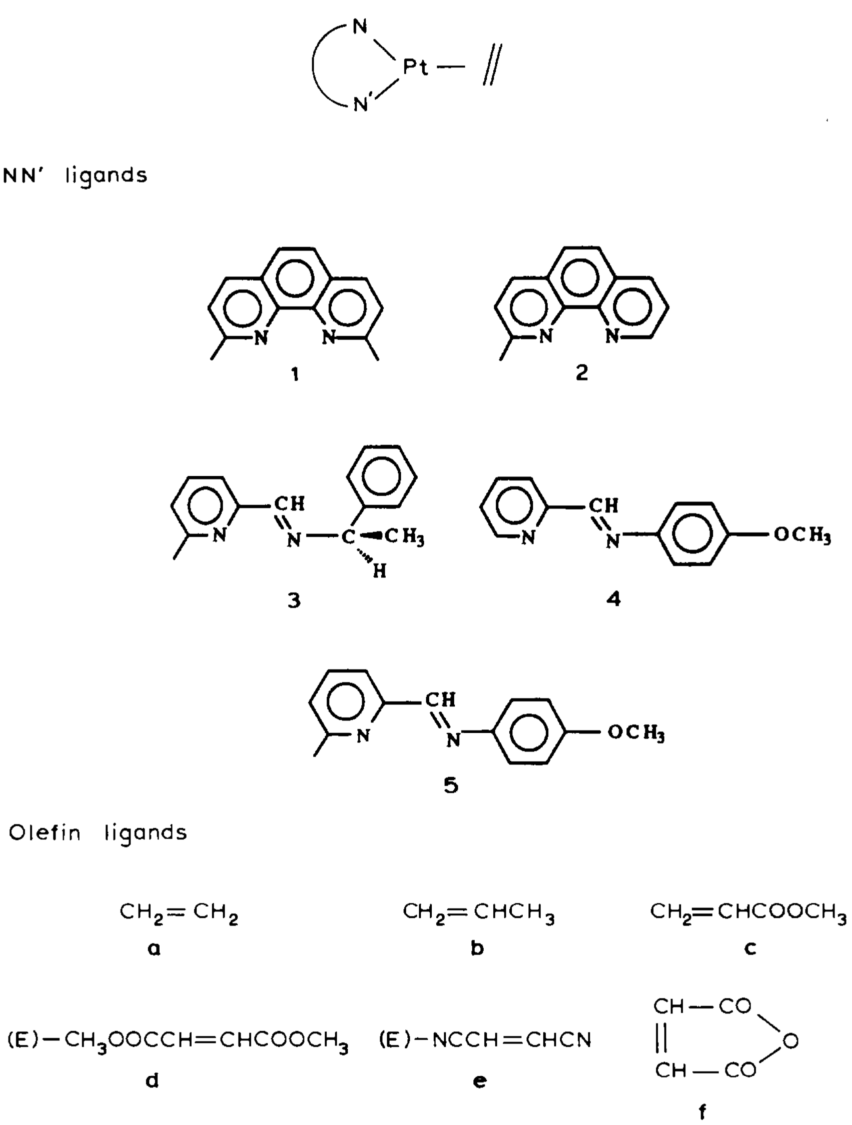
* A few of the previously described oxidative addition reactions lead to formation of five-coordinate derivatives of group 10 M(II) ions from three-coordinate species. One example was reported by H. Murnakata and T. Saito (Inorg. Synth., 17 (1977) 88). However, the process we describe appears to be the only one having wide applicability.

* A reference number with an asterisk indicates a note in the list of references.



Scheme 1. Olefin and bidendate ligands used in the three-coordinate compounds.

reaction mixture as precipitates that give satisfactory analysis, but attempts to recrystallize resulted in extensive decomposition. These complexes also react with halogenated solvents such as methylene chloride or chloroform by oxidative addition and represent one of the rare examples of activation of the C–Cl bond of methylene chloride by nucleophilic coordination compounds under mild conditions [12]. A propene complex (**1b**) was also possibly obtained: its formation was implied by the isolation of the product formed by oxidative addition of CH_3I.

A general feature of the ^1H NMR spectra reported in Table 1 is the high-field shift of the =CH protons relative to those for the free olefins. The same behaviour was observed for several olefin complexes of metals in low oxidation states, and its

Table 1

Microanalytical and ^{1}H NMR data (δ (ppm), J(Hz) for the three-coordinate species $[Pt(\overline{N\ N'})(olefin)]$ [a]

Entry	Anal. found (calcd.) (%)			Resonances [b]		
	C	H	N	N–CMe	=CH	other selected signals
1a	44.3 (44.55)	3.8 (3.74)	6.3 (6.49)	3.33	2.20 (87) (s, 4H)	
1c	44.1 (44.17)	3.8 (3.71)	5.8 (5.72)	3.18, 3.20	2.23 [c] (m, 1H) 2.45 [c] (m, 1H) 2H [d]	3.55 (s, OMe)
1d	43.8 (43.79)	3.6 (3.68)	5.3 (5.11)	3.18	3.75 (87) (s, 2H)	3.62 (s, OMe)
2a	43.0 (43.17)	3.4 (3.38)	6.9 (6.71)	3.28	2.12 (42) (s, 4H)	9.75 (d, 2-H)
2d	42.8 (42.78)	3.5 (3.40)	5.3 (5.24)	3.18	3.87 [c] ([e], 2H)	9.55 (m, 2-H) 3.68 (s, OMe), 3.64 (s, OMe)
3d	44.7 (44.76)	4.4 (4.29)	5.0 (4.97)	3.02	3.73 [c] ([e], 2H)	8.94 (54) (s, N=CH) 5.47 (q, N–CH) 3.59 (s, OMe), 3.42 (s, OMe) 1.96 (d, Me)
3d	(as above, diastereomer, 50% abundance)			3.04	2H [f]	8.78 (54), (s, N=CH) 5.42 (q, N–CH) 3.63 (s, OMe), 3.59 (s, OMe) 2.00 (d, Me)
3e	45.8 (45.87)	3.7 (3.65)	11.6 (11.26)	3.04	2.78 (84) (d, 1H) 2.50 (93) (d, 1H)	8.98 (56) (s, N=CH) 5.48 (q, N–CH) 1.98 (d, Me)
3e	(as above, diastereomer, 30% abundance)			3.04	2.74 (84) (d, 1H) 2.16 (93) (d, 1H)	9.12 (56) (s, N=CH) 5.30 (q, N–CH) 2.03 (d, Me)
3f	44.3 (44.27)	3.6 (3.52)	5.4 (5.43)	2.95	3.55 (83) (d, 1H) 3.27 (78) (d, 1H)	9.13 (59) (s, N=CH) 5.25 (q, N–CH) 1.89 (d, Me)
3f	(as above, isomer, 40% abundance)			2.96	3.66 (83) (d, 1H) 3.46 (88) (d, 1H)	8.96 (59) (s, N=CH) 5.43 (q, N–CH) 1.89 (d, Me)
4d	41.3 (41.38)	3.7 (3.66)	5.3 (5.08)		2H [d]	9.29 (55) (s, N=CH) 8.95 (30) (d, 2-H) 3.85 (s, OMe), 3.65 (s, OMe) 3.59 (s, OMe)
5d	42.5 (42.48)	3.9 (3.92)	5.1 (4.95)	2.93	3.75 [c] ([e], 2H)	9.27 (50) (s, N=CH) 3.86 (s, OMe), 3.63 (s, OMe) 3.45 (s, OMe)

[a] 200 or 270 MHz; in $CDCl_3$. Abbreviations: s, singlet; d, doublet; , t, triplet; q, quartet; m, multiplet. [b] The aromatic protons of the phenantroline rings are in the range: 8.60–8.31 (2H), 7.85–7.70 (2H), 7.80–7.70 (2H). [c] ^2J(Pt–H) not evaluable. [d] Overlapped by other signals. [e] AB quartet. [f] Signals partially or totally overlapped by those of the former isomer.

has been associated with both the extent of π-back-bonding and the distortion of the ligand [13]. Since in our case the high-field shift is moderately higher for olefins bearing electron-withdrawing substituents than for ethylene its association with π-back-bonding seems reasonable.

When the unsaturated ligand in the three-coordinate species has a symmetry lower than C_{2v} two stereoisomers are expected to be formed by coordination of the two prochiral faces of the olefin, and in **3d** and **3e**, where an additional chiral center is present, the presence of two diastereomeric pairs can be detected by ^{1}H NMR spectroscopy (see Table 1). Crystallization causes epimerization of one of them, and the other is thus obtained as the only product. Two isomers, in the approximate ratio 3/2, are also observed in solution in the case of complex **3c** owing to hindered rotation of the unsaturated ligand around the Pt–alkene bond.

The ethylene ligand in species **1a** can be readily displaced (in toluene suspension) by an olefin with electron-withdrawing groups, such as dimethylfumarate. In addition, dimethylfumarate can be displaced by other olefins bearing strongly electron-withdrawing substituents, such as fumarodinitrile or maleic anhydride. This behaviour provides an alternative route to the complexes listed in Table 1, as well as to similar species.

General features of the addition reactions

In previous papers [7,8] on five-coordinate olefin complexes of platinum(II) we noted the close relationship between the stability and the steric features of the $\widehat{N\ N'}$ ligands. A less marked but still substantial influence of the olefin properties was observed. The chelating and olefin ligands in the three-coordinate species with which this paper is concerned are such that most of them undergo oxidative addition to give isolable five-coordinate products. On the other hand, the product obtained by addition of CH_3I to **4d**, in which the $\widehat{N\ N'}$ ligand provides weak steric hindrance "in-plane" is the four-coordinate [Pt($\widehat{N\ N'}$)MeI] complex.

The yield of the five-coordinate product was particularly high with $\widehat{N\ N'}$ = **1**. In this case, the presence of the chelating ligand involves the "embracing" of the metal in the coordination plane by the two methyl groups protruding toward the opposite ligand. We noted previously [7] that this feature gives rise to a significantly larger constraint in the main plane for square planar than for *tbp* geometry, thus stabilizing the higher coordination number. Thus, a particularly suitable substrate, which has been used as the precursor in many of the oxidative addition experiments is **1d**, an orange micro-crystalline product storable in the air. The electrophilic reagents used in the additions were halogens and alkyl halides.

As noted above, most of the reactions were performed with **1d**. In this case the order of reactivity of the methyl halides was MeI > MeBr ≫ MeCl. Addition of MeI to **1d** was complete in a few minutes when an equimolar amount of the iodide was added in chloroform solution at room temperature, whereas reaction of the same complex with MeBr required several hours and an excess of the bromide for completion. No appreciable reaction was observed with MeCl at room temperature, and only small amounts, if any, of the expected five-coordinate were present in the mixture of compounds obtained at high temperature (60 °C). Higher alkyl halides reacted more slowly. The oxidative addition of CH_3CH_2I to **1d** required use of an excess (5 : 1) of the halide for completion at room temperature within 12 hrs. No reaction was detected with CH_3CH_2Br or CH_3CH_2Cl under these conditions. Branched haloalkyls of the type $(CH_3)_3CCH_2X$ did not react. Stable five-coordinate complexes were obtained by oxidative addition of $PhCH_2I$ and $PhCH_2Br$; both of these gave high yields of the product, a moderate excess of $PhCH_2Br$ being required.

Oxidative addition of a secondary halide, i.e. $PhCH(CH_3)Br$, to **1d** occurred in good yields. The addition was slower than that of the two benzyl halides, and a large excess was necessary to achieve high conversion at room temperature.

The reactions of the three-coordinate complexes with halogens (Cl_2, Br_2, I_2) in solutions of $CHCl_3$ give the corresponding dihalo five-coordinate complexes. The reaction is very fast and no marked differences were detected at room temperature. The halogen must be in a strictly stoichiometric amount, since of an excess of the reagent results in further reaction, probably another oxidative addition, to give a platinum(IV) derivative. No attempt was made to characterize the latter products. Additions involving other complexes containing olefin ligands with electron-withdrawing substituents gave similar results.

When the metal precursor was an ethylene derivative (i.e. **1a** or **2a**) a complication arose, since the two complexes are very poorly soluble except in chloroform or methylene chloride, and these solvents react readily with the two complexes to give dichloromethyl and chloromethyl derivatives, respectively. Even so products formed from the most reactive electrophilic reagents can be obtained by reaction in these two chlorine-containing solvents. When the ethylene ligand had an electron-donor substituent, i.e. in the case of the highly reactive propene complex, the reaction with MeI gave the expected product in high yield. Furthermore, the product of addition of iodobenzene to **1a** was obtained in the absence of a solvent. No reaction was observed between **1d** and phenyl halides.

The assignment of the geometry and of the coordination number to the five-coordinate products was made by ^1H NMR spectroscopy, as previously described for similar complexes obtained by other procedures [7,8]. Conductivity measurements were made for all the new complexes in order to rule out the formation of ionic species.

Previous reports on oxidative-addition reaction on d^{10} Pd and Pt derivatives indicated that at least three types of mechanism (S_{N2}, radical chain, and non-chain) are possible and their relative importance depends on the nature of the two reacting species. No definite general conclusion could be reached in most of the cases studied [2]. At present we offer some preliminary observations relevant to the mechanism:
(i) The reactivity order for the alkyl halides is (as in other cases) Me > primary > secondary > tertiary and MeI > MeBr ≫ MeCl.
(ii) The product formed by addition of optically pure $BrCH(Me)COOC_2H_5$ to **1a** is optically inactive, indicating racemization at the chiral carbon.
(iii) Previous observations [3,14] led to the conclusion that two-coordinate species can play a significant role as intermediates the additions to three-coordinate precursors [3,14]. In our case such an intermediate would most likely be $[\mathrm{Pt}(\overset{\frown}{\mathrm{N\ N'}})]$. We note: (1) the absence of significant amounts of $[\mathrm{Pt}(\overset{\frown}{\mathrm{N\ N'}})]$ and free olefin was indicated by the ^1H NMR spectra of type I complexes in solution; (2) the ^1H NMR spectra similarly indicated the absence of significant amounts of $\mathrm{Pt}(\overset{\frown}{\mathrm{N\ N'}})\mathrm{XY}$ in the I + XY reaction systems; (3) the olefin uptake from the latter species is slower than the addition of XY to $\mathrm{Pt}(\overset{\frown}{\mathrm{N\ N'}})$(olefin). It thus appears that $\mathrm{Pt}(\overset{\frown}{\mathrm{N\ N'}})$ species are not involved in a dominant addition pathway.
(iv) It is noteworthy that the reactivity of the precursor complex is strictly related to its nucleophilicity. Thus, the ethylene and propene complexes are much more reactive than type I derivatives of olefins with electron-withdrawing substituents.

Table 2

^{1}H NMR spectral data (δ (ppm), J (Hz)) for the five-coordinate products $[\mathrm{Pt}(\widehat{N\,N'})(A)(B)(\mathrm{olefin})]$ [a]

Sub-strate	Electrophile A–B	Resonances [b]			
		Pt–HC_x	N–CMe	=CH (olefinic)	other signals [b]
1a	CH_3–I	0.05(62) (s, 3H)	3.28	2.26(59) (d, 2H) [e] 3.29(75) (d, 2H) [e]	
1a	CH_3CH_2–Br	0.73(73) (q, 2H)	3.33	3.14(86) (d, 2H) [e] 2.20(73) (d, 2H) [e]	−0.06(49) (t, Me)
1a	Ph–I		3.60	3.64(88) (d, 2H) [e] 2.62(68) (d, 2H) [e]	6.80–6.50 (m, 5H)
1a	$CH_3CH(COOEt)$ –Br	1.66(83) (q, 1H)	3.33, 3.41	2H [g] 2.42 [f] (m, 1H) 2.85 [f] (m, 1H)	OCH_2 [g] 0.81 (t, OCH_2*Me*) 0.32 (48) (d, PtCH*Me*)
1a	CH_2Cl–Cl	3.09(59) (s, 2H)	3.33	3.21(86) (d, 2H) [e] 2.50 (69) (d, 2H) [e]	
(**1b**) [h]	CH_3–I	0.04(67) (s, 3H)	3.30, 3.35	2H [g] 2.41(77) (d, 1H)	1.80 (63) (d, Me)
1d	CH_3–I	0.41(65) (s, 3H)	3.32, 3.30	5.09 (93) (d, 1H) 4.03(75) (d, 1H)	3.64 (s, OMe), 3.59 (s, OMe)
1d	$CH_3CH(Ph)$–Br	1H [g]	3.43, 3.27	5.30(91) (d, 1H) 4.26(74) (d, 1H)	6.80–6.20 (m, 5H) 3.86 (s, OMe), 3.78 (s,OMe) 0.82 (37) (d, Me)
1d	CH_3–Br	0.39(66) (s, 3H)	3.74, 3.69	5.06(90) (d, 1H) 4.20(75) (d, 1H)	3.74 (s, OMe), 3.69 (s, OMe)
1d	CH_3CH_2–I	1.37(85) ([i], 2H)	3.36	5.19(93) (d, 1H) 4.07(66) (d, 1H)	3.71 (s, OMe), 3.68 (s, OMe) −0.25 (40) (t, Me)
1d	Cl–Cl		3.70	5.53(80) (s, 2H)	3.80 (s, OMe)
1d	Br–Br		3.63	5.52(80) (s, 2H)	3.73 (s, OMe)
1d	I–I		3.59	5.46(84) (s, 2H)	3.74 (s, OMe)
1d	$PhCH_2$–I	2.90(80) ([i], 2H)	3.40, 3.38	5.31(91) (d, 1H) 4.21(74) (d, 1H)	6.40 (t, 1H), 6.08 (t, 2H) 5.73 (d, 2H), 3.79 (s, OMe) 3.76 (s, OMe)
1d	$PhCH_2$–Br	2.80(84) ([i], 2H)	3.42, 3.41	5.20(91) (d, 1H) 4.30(72) (d, 1H)	6.39(t, 1H), 6.11 (t, 2H) 5.78 (d, 2H), 3.80 (s, OMe) 3.76 (s, OMe)
2a	CH_3–I	0.60(63) (s, 3H)	3.29	2.10-2.50 [f] (m, 2H) 3.15-3.50 [f] (m, 2H)	9.50 (d, 2-H)
2a	$CH_3CH(Ph)$–Br	2.62(70) (m, 1H)	2.90	3.33 [f] (m, 2H) 2.30 [f] (m, 2H)	9.60 (s, 2-H) 6.80–6.20 (m, 5H) 0.76 (48) (d, Me)
5d	CH_3–I	0.60(52) (s, 3H)	3.10	1H [g] 5.06(92) (d, 1H)	8.97 (45) (s, N=CH), 8.0–7.1 (m, 7H), 3.88 (s, Ph-OMe) 3.70 (s, OMe), 3.60 (s, OMe)

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[a] 270 or 200 MHz; in $CDCl_3$ solutions. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] In case of more than one isomer, the resonances of the major one are reported. [c] See Table 1. [d] The aromatic protons of the phenantroline rings are in the range: 8.35–8.10 (2H), 7.90–7.70 (2H), 7.70–7.35 (2H). [e] Pseudodoublets, actually constituting a AA′XX′ of more complex multiplet. [f] ^2J(Pt–H) not evaluable. [g] Overlapped by other signals. [h] The corresponding three-coordinate complex was not isolated, see text. [i] AB quartet.

Experimental

^{1}H NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively, with $CDCl_3$ as solvent and TMS or $CHCl_3$ as internal standard.

The platinum(0) complexes $[(COD)_2Pt]$ [15], [(COD)Pt(dimethylfumarate)] [16] and [(COD)Pt(maleic anhydride)] [16] (COD = 1,5-cyclooctadiene) were made by previously described procedures. Optically pure $BrCH(CH_3)COOC_2H_5$ was prepared by a published method [17]. Solvent and reagents were of AnalaR grade, and unless otherwise stated they were used without further purification. The complexes were prepared and stored in the air. Elemental analysis, and selected ^{1}H NMR spectroscopic data are given in Table 1 and 2.

*Synthesis of **1d**–**5d** and **3f***

To a stirred solution of [(COD)Pt(dimethylfumarate)] (0.225 g, 0.5 mmol) in the minimum amount (ca. 20 ml) of dry toluene was added 0.5 mmol of the appropriate $\widehat{N\,N'}$ ligand. After a few minutes separation of a precipitate began. After 4 h the mixture was concentrated under vacuum to about half its volume and the precipitate was filtered off and dried. The crude products (> 80% yield) were recrystallized from chloroform–diethyl ether to give the pure compounds **1d**–**5d**.

A similar procedure gave **3f** in 85% yield starting from [(COD)Pt(maleic anhydride)] and the $\widehat{N\,N'}$ ligand **3**.

*Synthesis of **1a** and **2a***

The synthesis and isolation were carried out under an ethylene atmosphere. A suspension of $[Pt(COD)_2]$ (0.20 g, 0.5 mmol) in 1 ml of dry toluene was saturated with ethylene at 0 °C. After 15 min, 104 mg of 2,9-dimethyl-1,10-phenanthroline (0.5 mmol) were added with stirring to the yellow solution containing the complex $[Pt(C_2H_4)_3]$ [18]. Separation of a red precipitate began. After one hour, the red product was collected and washed three times with 1 ml of dry diethyl ether (195 mg, 90% yield).

The same procedure gave **2a** in 78% yield.

*Synthesis of **1c***

A solution of methyl acrylate (50 mg, 0.06 mmol) in 2 ml of dry methanol was added to solid **1a** (0.21 g, 0.5 mmol) at room temperature. The red complex was converted into to an orange product, which was filtered off, washed with methanol, and dried (0.22 g, 90% yield).

*Synthesis of **3e***

To a solution of **3d** (0.22 g, 0.5 mmol) in 5 ml of chloroform at room temperature was added fumarodinitrile (40 mg, 0.5 mmol). After 15 min the volume of the mixture was reduced to ca. 1 ml. Crystallization of **3e** was achieved by adding diethyl ether. The product was filtered off and dried (0.21 g, 85% yield).

*Addition of X_2 to **1d** (X = Cl, Br, I)*

To a stirred solution of **1d** (0.200 g, 0.36 mmol) in 8 ml of chloroform was added an equimolar amount of the appropriate halogen. After 15 min the solution was filtered and evaporated to dryness under vacuum. The crude products were recrystallized from chloroform–diethyl ether to give the corresponding dihalo derivatives in 70–80% yield. Anal. (X = Cl) Found: C, 38.7; H, 3.2; N, 4.6. $C_{20}H_{20}Cl_2N_2O_4Pt$ calcd: C, 38.85; H, 3.26; N, 4.53%.

*Addition of RX to **1d** (X = Br, I; R = Me, Et, $PhCH_2$, Ph(Me)CH)*

To a stirred solution of **1d** (0.200 g, 0.36 mmol) in 8 ml of chloroform at room temperature was added a 3–10 molar excess of the appropriate alkyl halide. The mixture was stirred overnight and the solution then concentrated in vacuo and filtered. Yellow to dark-yellow precipitates were obtained by addition of diethyl ether to the filtrate (70–90% yield). Anal. (X = Br, R = Me) Found: C, 39.3; H, 3.7; N, 4.2. $C_{21}H_{23}BrN_2O_4Pt$ calcd: C, 39.26; H, 3.61; N, 4.36%.

*Addition of CH_2Cl_2 to **1a***

Dry methylene chloride (1 ml) was added with stirring to **1a** (0.050 g, 0.116 mmol) under an ethylene atmosphere at room temperature. After 30 min stirring the dark suspension was filtered and the residue was washed with 2 ml of methylene chloride. The solvent was removed in vacuo from the combined filtrates and the residue crystallized from methylene chloride–diethyl ether (70% yield). Anal. Found: C, 39.6; H, 3.5; N, 5.5. $PtC_{17}H_{18}Cl_2N_2$ clacd.: 39.55; H, 3.51; N, 5.43.

*Addition of CH_3I, CH_3CH_2Br, $CH_3CH(COOEt)Br$ to **1a** and **2a***

A solution of a 50% molar excess of the electrophilic reagent in 1 ml of dry methylene chloride was added to solid **1a** (or **2a**) at 0 °C under an ethylene atmosphere. After 20 min the mixture was diluted with n-hexane and a brown solid was filtered off, washed with n-hexane, and dissolved in methylene chloride. The solution was filtered through Florisil, and n-hexane added to give the crystalline product (70–80% yield). Anal. (X = Br, R = Et, **1a**) Found: C, 40.0; H, 3.8; N, 5.2. $C_{18}H_{21}BrN_2$ Pt calcd.: C, 40.01; H, 3.92; N, 5.18%.

*Addition of iodobenzene to **1a***

Iodobenzene (1 ml) was added to solid **1a** (100 mg, 0.23 mmol) under an ethylene atmosphere and the suspension was stirred 20 h at room temperature. Diethyl ether was added and the brown residue was filtered off and washed with 4 × 1 ml portions of diethyl ether. No recrystallization was attempted.

*Addition of CH_3I to **1b***

Propene was bubbled through on suspension of 100 mg (0.25 mmol) di[$Pt(COD)_2$] in dry toluene (2ml) at 0 °C. To the resulting yellow solution were added 52 mg (0.25 mmol) of 2,9-dimethyl-1,10-phenanthroline to give a red solution. A large excess of CH_3I (20 μl) was added from a syringe to give a yellow precipitate. Recrystallization from methylene chloride–diethyl ether gave the crystalline product in 70% yield. Anal. Found: C, 36.9; H, 3.7; N, 4.8. $C_{18}H_{21}N_2IPt$ calcd.: C, 36.81; H, 3.60; N, 4.77%.

*Addition of CH_3I to **4d** and **5d***

To a solution of **4d** or **5d** (0.36 mmol) in 8 ml of chloroform at room temperature was added an equimolar amount of CH_3I. After 30 min the mixture was concentrated, and addition of diethyl ether gave the precipitate of the products (85% yield). Oxidative addition of CH_3I to **4d** afforded the four-coordinate complex [PtMeI($\widehat{N\,N'}$)] (see text): Anal. Found: C, 30.5; H, 2.7; N, 5.0. $C_{14}H_{15}IN_2OPt$ calcd: C, 30.61; H, 2.75; N, 5.10%. ^1H NMR ($CDCl_3$): δ 10.0 (m, 1H, 2-H-py); 9.20 (s, 1H, N=CH, ^2J(Pt–H) = 94 Hz); 8.2–6.8 (m, 7H, aromatic and pyridine protons); 3.87 (s, 3H, OMe); 1.20 (s, 3H, PtMe, ^2J(Pt–H) = 75 Hz).

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