Four- *versus* Five-co-ordination in Palladium(II) and Platinum(II) Complexes containing 2,9-Dimethyl-1,10-phenanthroline (dmphen). Crystal Structures of [PtCl$_2$(dmphen)] and [Pt(η^2-C$_2$H$_4$)Cl$_2$(dmphen)]†

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The four-co-ordinate complexes with 2,9-dimethyl-1,10-phenanthroline [MX$_2$(dmphen)] (M = Pt, X$_2$ = Cl$_2$ **1**, ClBr **2**, Br$_2$ **3**, or I$_2$ **4**; M = Pd, X$_2$ = Cl$_2$ **5**, ClBr **6**, Br$_2$ **7** or I$_2$ **8**) have been prepared for the first time. The crystal structure of [PtCl$_2$(dmphen)] **1**, has been determined by X-ray diffraction methods. The complex has a square-planar geometry around the metal and the steric interaction between the methyl groups of dmphen and the *cis* chlorine ligands causes a narrowing of the Cl–Pt–Cl angle [85.8(1)°], a displacement of the two chlorine atoms from the N–Pt–N plane [0.286(4) and 0.372(4) Å respectively], a bending of the phenanthroline (*ca.* 17°), and a rotation of the overall ligand plane with respect to the platinum co-ordination plane (*ca.* 28°). All interligand steric constraints are released in the five-co-ordinate complexes obtained from the four-co-ordinate species by direct uptake of olefins, [M(η^2-olefin)X$_2$(dmphen)] (olefin = ethylene, **a**; propene, **b**; but-1-ene, **c**; *cis*-but-2-ene, **d**; *trans*-but-2-ene, **e**; or styrene, **f**). The structure of [Pt(η^2-C$_2$H$_4$)Cl$_2$(dmphen)] **1a**, has been determined by X-ray diffraction methods. The complex has a trigonal-bipyramidal geometry around the Pt atom; the phenanthroline ligand and the olefinic carbons occupy the equatorial plane while the two chlorine atoms are in axial positions. Bond distances and angles are similar to those found in other five-co-ordinate complexes of platinum(II). The rate of uptake of olefin by the four-co-ordinate complexes, the equilibrium constant (K_f) of the formation reaction [MX$_2$(dmphen)] + olefin $\rightleftharpoons$ [M(η^2-olefin)X$_2$(dmphen)], and the activation energy for olefin rotation in the five-co-ordinate complexes have been measured for different olefins and halogen ions. The uptake, in chloroform, takes place in a one-step process and the reaction rate increases by a factor of 10^4 going from the chloro **1** to the iodo **4** complex. The equilibrium constant for the formation reaction decreases by a factor of 10^3 going from ethylene to *trans*-but-2-ene and increases by a factor of 10^2 going from the chloro **1** to the iodo **4** species. The activation energy for olefin rotation (ethylene and propene) (*ca.* 20.5 kcal mol^{-1}) is higher than any reported value for platinum complexes and does not appear to depend upon the nature of the halogen atoms.

In recent years a number of chelating nitrogen ligands, when combined with a π-acceptor ligand like an olefin or an acetylene, have been found to stabilize five-co-ordination in platinum(II) species,[1–5] *e.g.* [Pt(η^2-olefin)(Me){HB(pz)$_3$}] (pz = pyrazol-1-yl),[2] [Pt(η^2-olefin)Cl(Me)(L–L)] and [Pt(η^2-olefin)X$_2$(L–L)] [X = halogen, L–L = neutral bidentate ligand such as a bis(hydrazone), a diamine, or a diimine].[3–5]

Several attempts have been made to correlate the steric and electronic properties of the co-ordinated ligands with the stability of the five-co-ordinate species. Concerning bidentate N-donor ligands, in a recent study dealing with the absolute configuration of the co-ordinated amine nitrogens in four- and five-co-ordinate complexes of platinum(II) {[PtCl$_2$(L–L)] and [Pt(η^2-olefin)Cl$_2$(L–L)]} (L–L = *N,N'*-disubstituted ethylenediamine), we concluded that in both cases the ligand minimizes the steric hindrance inside the co-ordination sphere by directing the least bulky group towards the contiguous chlorine ligands.[6] The halogen atoms, however, are coplanar with the nitrogen chelate in the square-planar four-co-ordinate complexes, orthogonal to it in the trigonal-bipyramidal five-co-ordinate species. Therefore the use of a planar bidentate ligand sterically hindered at both co-ordinating ends, such as 2,9-dimethyl-1,10-phenanthroline (dmphen), would greatly favour five- over four-co-ordination.

We have succeeded in preparing a series of complexes of formula [MX$_2$(dmphen)] (M = Pt or Pd; X = Cl, Br or I) which react reversibly with olefins to give the corresponding five-co-ordinate species. The effects of the metal, of the halide ions, and of the substituents at the olefin ligand upon (*i*) the rate of uptake of olefin by the four-co-ordinate complexes, (*ii*) the stability of the five- *versus* four-co-ordinate species, and (*iii*) the olefin rotation in the five-co-ordinate complexes have been investigated.

Results and Discussion

Synthesis of the Complexes.—2,9-Dimethyl-1,10-phenanthroline was reported to react with K$_2$[PtCl$_4$] in ethyl acetate to

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† Dichloro(2,9-dimethyl-1,10-phenanthroline-κ$^2N,N'$)platinum(II) and dichloro(2,9-dimethyl-1,10-phenanthroline-κ$^2N,N'$)(η^2-ethylene)platinum(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: cal = 4.184 J, atm = 101 325 Pa.

form a complex which, judged from elemental analysis, was considered to be polynuclear and to have the formula $[\mathrm{Pt_3Cl_6(dmphen)_4}]$.[7] Four-co-ordinate complexes of platinum(II),[8] palladium(II)[9] and gold(III)[10] containing a singly bonded dmphen in association with other ligands such as halide ions and phosphines have also been reported. Since the second nitrogen atom of the phenanthroline comes near to an axial position, these complexes could also be described as pseudo-five-co-ordinate species. Finally the preparation of [PdCl(Me)(dmphen)][11] and the X-ray structure of five-co-ordinate $[\mathrm{Pd}\{\eta^2\text{-}\overline{\mathrm{C({=}O)CH{=}CHC({=}O)O}}\}\mathrm{Cl_2(dmphen)}]$[11] and four-co-ordinate $[\mathrm{Pd(NO_2)_2(dmphen)}]$,[12] which do not show unusual structural features, have been reported.

Contrary to what has been generally observed with other bidentate N-donor ligands, dmphen does not react with $[\mathrm{PtCl_2(dmso)_2}]$ (dmso = dimethyl sulphoxide) in methanol at room temperature, to give dmso substitution and formation of $[\mathrm{PtCl_2(dmphen)}]$ **1**; prolonged reaction leads to formation of the dimeric species $[\{\mathrm{PtCl_2(dmso)}\}_2]$. Compound **1** can be obtained as the major product if the reaction between dmphen and $[\mathrm{PtCl_2(dmso)_2}]$ is performed in ethanol at 80 °C for 1 d; it is partially soluble in ethanol, can be chromatographed on silica gel, and crystallized from chloroform–diethyl ether.

The bromo and iodo derivatives, $[\mathrm{PtBr_2(dmphen)}]$ **3** and $[\mathrm{PtI_2(dmphen)}]$ **4**, were obtained from the chloro complex by metathesis. It is worth noting that the use of a small excess of bromide ion leads to substitution of only one chloride and formation of the mixed-halide complex [PtBr(Cl)(dmphen)] **2**. Its solubility characteristics are such that it precipitates pure from a solution of the chloro complex and $\mathrm{NBu_4Br}$.

The palladium complex $[\mathrm{PdCl_2(dmphen)}]$ **5** was readily prepared from $[\mathrm{PdCl_2(NCPh)_2}]$ and dmphen, the reaction being complete within a few minutes. The complexes [PdBr(Cl)(dmphen)] **6**, $[\mathrm{PdBr_2(dmphen)}]$ **7** and $[\mathrm{PdI_2(dmphen)}]$ **8** were obtained by metathesis.

The ^{1}H NMR data for the four-co-ordinate complexes are given in Table 1. In the mixed ClBr species the two halves of the co-ordinated dmphen ligand are not equivalent and give separate sets of signals. In the case of palladium, on increasing the temperature the signals coalesce to a single set in accord with a fast site exchange of the Cl and Br ligands, a kind of fluxionality often observed in palladium(II) chemistry.[13,14]

In chloroform solution, at room temperature and atmospheric pressure, complexes **1**–**8** react with olefins (ethylene, **a**; propene, **b**; but-1-ene, **c**; *cis*-but-2-ene, **d**; *trans*-but-2-ene, **e**; or styrene, **f**) to give 1:1 adducts, NMR data for which are collected in Table 2. Comparison of the chemical shifts and ^{195}Pt coupling constants of the ligand protons, in the four- and five-co-ordinate species, gives an insight into the bonding situations in the two different types of complexes. The ^4J(PtH) and ^5J(PtH) of the aromatic protons and the ^4J(PtH) of the methyl protons of dmphen are, respectively, 16, 4 and 7 Hz in the four-co-ordinate complexes, and 3, 0 and 7 Hz in the five-co-ordinate species. Hence the coupling with platinum of the ring protons, which is transmitted through bonds, is drastically reduced on going from four- to five-co-ordination and this is in full agreement with a parallel weakening (and lengthening) of the Pt–N bonds. On the contrary, the coupling with platinum of the methyl protons is left unchanged, indicating that (*i*) it results mainly from a through-space interaction and (*ii*) such an interaction is of the same magnitude in the four- and five-co-ordinate complexes.

The resonances of the olefinic protons show their characteristic large upfield shift (*ca.* 2–3 ppm) and coupling constant with platinum (*ca.* 70 Hz). These data are indicative of a rather strong platinum–olefin bond which has been generally attributed to a substantial π-back donation from platinum to the olefin.

Table 1 Proton chemical shifts (δ, downfield from $\mathrm{SiMe_4}$)[a] for square-planar complexes $[\mathrm{MX_2(dmphen)}]$[b] and the free ligand

Compd.	Me(2,9)	H(3,8)	H(4,7)	H(5,6)
dmphen	2.93	7.47 (d, 8)	8.11 (d, 8)	7.70
1	3.25 [7]	7.56 (d, 8) [16]	8.35 (d, 8) [4]	7.81
2	3.23 [7] 3.27 [7]	7.55 (d, 8) [16]	8.31 (d, 8) [4] 8.35 (d, 8) [4]	7.80
3	3.25 [7]	7.56 (d, 8) [16]	8.34 (d, 8) [4]	7.80
4	3.25 [7]	7.57 (d, 8) [16]	8.34 (d, 8) [4]	7.80
5	3.25	7.53 (d, 8)	8.31 (d, 8)	7.83
6	3.24 3.26	7.53 (d, 8)	8.28 (d, 8) 8.29 (d, 8)	7.81
7	3.27	7.55 (d, 8)	8.28 (d, 8)	7.81

[a] Values of J(H–H) (in parentheses) and J(Pt–H) (in square brackets) in Hz are given when assignable; solvent $\mathrm{CDCl_3}$. [b] M = Pt, $\mathrm{X_2 = Cl_2}$ **1**, ClBr **2**, $\mathrm{Br_2}$ **3** or $\mathrm{I_2}$ **4**. M = Pd, $\mathrm{X_2 = Cl_2}$ **5**, ClBr **6**, $\mathrm{Br_2}$ **7** or $\mathrm{I_2}$ **8**. The low solubility in chloroform of compound **8** did not allow the detection of the NMR spectrum.

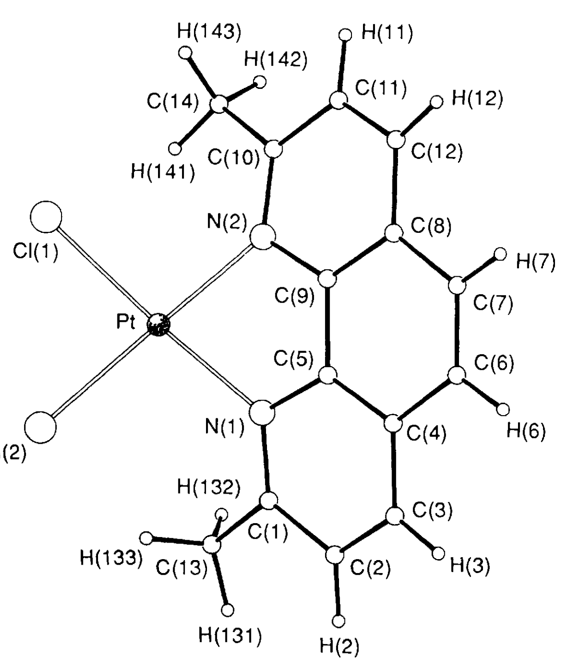

Fig. 1 View of the molecular structure of the complex $[\mathrm{PtCl_2(dmphen)}]$ **1** together with the atomic numbering scheme

Crystal Structures of $[\mathrm{PtCl_2(dmphen)}]$ **1** *and* $[\mathrm{Pt(\eta^2\text{-}C_2H_4)Cl_2(dmphen)}]$ **1a**.—The solid-state structures of $[\mathrm{PtCl_2(dmphen)}]$ **1** and $[\mathrm{Pt(\eta^2\text{-}C_2H_4)Cl_2(dmphen)}]$ **1a** have been determined in order to compare the structural features of the bidentate dimethyl-substituted phen ligand in the four-co-ordinate square-planar and in the five-co-ordinate trigonal-bipyramidal arrangements.

A view of the structure of **1** is given in Fig. 1, and relevant bond distances and angles are reported in Table 3. The platinum atom exhibits the expected square-planar co-ordination with two *cis* positions occupied by the nitrogen atoms of dmphen and the other two by chlorine atoms. The bond distances in the co-ordination sphere of Pt are normal and comparable to those found in other four-co-ordinate complexes of platinum(II).[6] Severe distortions are found in the co-ordination geometry and in the phenanthroline ligand (Fig. 2) which can be attributed to constraints inside the chelate ring [N(1)–Pt–N(2) bite angle of 79.8(4)°] and to interligand steric tensions. The close contacts between each chlorine atom and the contiguous methyl group [Cl(1)···C(14) 3.18(2) and Cl(2)···C(13) 3.22(2) Å] determine: (*i*) a narrowing of the Cl(1)–Pt–Cl(2) angle [85.8(1)° compared to a theoretical value of 90°], (*ii*) a displacement of the Cl atoms on the opposite side

Table 2 Proton chemical shifts (δ, downfield from $SiMe_4$) for five-co-ordinate complexes $[M(\eta^2\text{-olefin})X_2(\text{dmphen})]$[a]

			dmphen[b]			
Complex		Olefin[b,c]	Me(2,9)	H(3,8)	H(4,7)	H(5,6)
1a		3.67 [70]	3.49 [7]	7.80 (d, 8) [3]	8.32 (d, 8)	7.85
2a		3.68 (m) [70][d]	3.48 [7]	7.79 (d, 8) [3]	8.31 (d, 8)	7.85
		3.78 (m) [70][d]				
3a		3.80 [70]	3.47 [7]	7.79 (d, 8) [3]	8.30 (d, 8)	7.85
4a		4.20 [71]	3.44 [7]	7.79 (d, 8) [3]	8.25 (d, 8)	7.85
1b	CH_3	1.34 (d, 6) [44]	3.47 [7]	7.78 (d, 8)	8.30 (d, 8)	7.84
	$=CH_2$	3.74 (m) [68]	3.56 [7]	7.80 (d, 8)	8.31 (d, 8)	
	=CH	4.29 (m) [70]				
1c	CH_3	1.21 (t, 7)	3.47 [7]	7.77 (d, 8)	8.30 (d, 8)	7.84
	CH_2	2.02 (m)	3.55 [7]	7.80 (d, 8)	8.31 (d, 8)	
	$=CH_2$	3.70 (m) [70]				
	=CH	4.23 (m) [70]				
1d	CH_3	1.29 (d, 5) [40]	3.55 [7]	7.77 (d, 8)	8.28 (d, 8)	7.81
	=CH	4.35 (m) [82]				
1e	CH_3	1.32 (d, 6) [40]	3.55 [7]	7.79 (d, 8)	8.29 (d, 8)	7.83
	=CH	4.27 (m) [72]				
1f	$=CH_2$	3.84 (m) [70]	3.33 [7]	7.70 (d, 8)	8.26 (d, 8)	7.82
		4.48 (m) [60]	3.54 [7]	7.75 (d, 8)	8.31 (d, 8)	
	=CH	5.52 (m) [65]				
	Ph	7.70 (m) {3}				
		7.75 (m) {2}				
5a		4.95	3.56	7.74 (d, 8)	8.28 (d, 8)	7.80
6a		4.96	3.55	7.74 (d, 8)	8.27 (d, 8)	7.80
6a[e]		4.86[d]	3.53	7.76 (d, 8)	8.31 (d, 8)	7.83
		5.00[d]				
7a		4.98	3.53	7.74 (d, 8)	8.26 (d, 8)	7.80
8a		5.15	3.45	7.73 (d, 8)	8.24 (d, 8)	7.81
5b	CH_3[f]	1.84 (d, 8)	3.61	7.73 (d, 8)	8.26 (d, 8)	7.79
5b[e]	CH_3[f]	1.80 (d, 8)	3.52	7.76 (d, 8)	8.30 (d, 8)	7.82
			3.67	7.79 (d, 8)	8.33 (d, 8)	
7b	CH_3[f]	1.98 (d, 8)	3.57	7.73 (d, 8)	8.25 (d, 8)	7.79
7b[e]	CH_3[f]	1.98 (d, 8)	3.47	7.75 (d, 8)	8.27 (d, 8)	7.82
			3.63	7.78 (d, 8)	8.30 (d, 8)	7.83

[a] Olefin = ethylene, **a**; propene, **b**; but-1-ene, **c**; *cis*-but-2-ene, **d**; *trans*-but-2-ene, **e**; or styrene, **f**. *T* 20 °C, solvent $CDCl_3$. [b] Values of *J*(H–H) (in parentheses) and *J*(Pt–H) (in square brackets) in Hz are given when assignable. [c] Integral values are given in braces. [d] Centres of two close symmetrical multiplets belonging to an AA′BB′ system. [e] *T* −40 °C. [f] Signals of other protons of co-ordinated olefins are obscured by those of excess of free olefin.

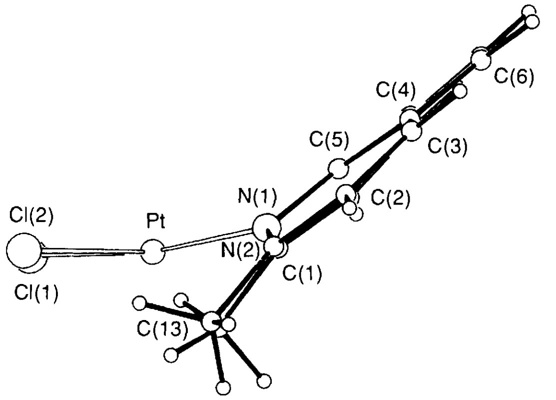

Fig. 2 Projection of the structure of complex **1** along the N(1)–N(2) vector showing the bending of the phenanthroline ligand and its rotation with respect to the platinum co-ordination plane

of the methyl groups with respect to the N(1)–Pt–N(2) plane [by 0.286(4) and 0.372(4) Å respectively] with consequent pyramidal distortion of the square-planar geometry [the Pt atom is out the mean plane through Cl(1), Cl(2), N(1) and N(2) by 0.159(1) Å], (*iii*) a bending of the phen ligand which adopts a butterfly conformation [the mean planes through the N(1)–C(1)–C(2)–C(3)–C(4)–C(5) and N(2)–C(10)–C(11)–C(12)–C(8)–C(9) rings make a dihedral angle of 16.6(4)° with respect to each other], and finally (*iv*) a remarkable rotation of the ligand plane around the N(1)–N(2) direction so that the chelating moiety [N(1)–C(5)–C(9)–N(2)] forms with the co-ordination plane [N(1)–Pt–N(2)] a dihedral angle of 27.5(5)°.

A somewhat similar distortion in the co-ordination geometry was observed in the complex $[PtCl_2(\text{dben})]$ (dben = *N*,*N*′-di-t-butylethylenediamine) in which there was a close contact between the t-butyl substituents at the nitrogen atoms and the *cis* chlorine ligands; the degree of distortion, however, was far from being comparable with that observed in the present case.[6] On the other hand, in the complex $[PtCl(Me)\{NC_5H_3\text{-}(CH{=}NCHMePh\text{-}2)(Me\text{-}6)\}]$, in which the steric bulk of the bidentate ligand is similar to that of a phen ligand having only one methyl substituent adjacent to one nitrogen atom, the ligand is coplanar with the co-ordination plane indicating that it can be accommodated in the co-ordination plane without creating close interligand contacts.[11]

A view of the structure of complex **1a** together with the atomic numbering scheme is given in Fig. 3, and relevant bond distances and angles are given in Table 4. In the complex, having a crystallographically imposed C_2 and an approximate C_{2v} symmetry, the Pt atom exhibits a trigonal-bipyramidal co-ordination with the axial positions occupied by the two Cl atoms [Cl–Pt–Cl′ 179.4(1)°]. The equatorial sites are occupied by the nitrogen atoms of the bidentate phen ligand and by the carbon atoms of ethylene. If the aromatic system is taken as a reference for the equatorial plane, small deviations from this plane are only observed for the methyl carbons of the bidentate ligand [0.06(1) Å] and for the C(8) atoms of ethylene [0.03(1) Å].

Table 3 Selected bond distances (Å) and angles (°) in complex **1**

Pt–Cl(1)	2.301(3)	Pt–N(1)	2.045(8)
Pt–Cl(2)	2.313(3)	Pt–N(2)	2.046(12)
N(1)–C(1)	1.35(2)	N(2)–C(10)	1.34(2)
C(1)–C(2)	1.43(2)	C(10)–C(11)	1.38(2)
C(2)–C(3)	1.37(2)	C(11)–C(12)	1.38(2)
C(3)–C(4)	1.39(2)	C(8)–C(12)	1.40(2)
C(4)–C(5)	1.37(2)	C(8)–C(9)	1.39(2)
C(5)–N(1)	1.38(2)	C(9)–N(2)	1.37(2)
C(4)–C(6)	1.44(2)	C(7)–C(8)	1.45(2)
C(5)–C(9)	1.43(2)	C(6)–C(7)	1.34(2)
C(1)–C(13)	1.48(2)	C(10)–C(14)	1.48(2)
Cl(1)–Pt–Cl(2)	85.8(1)	Cl(1)–Pt–N(2)	95.4(3)
N(1)–Pt–N(2)	79.8(4)	Cl(2)–Pt–N(1)	97.8(3)
Pt–N(1)–C(1)	130.8(8)	Pt–N(2)–C(10)	132.6(9)
Pt–N(1)–C(5)	110.1(7)	Pt–N(2)–C(9)	109.0(9)
C(1)–N(1)–C(5)	118(1)	C(9)–N(2)–C(10)	118(1)
N(1)–C(1)–C(13)	122(1)	N(2)–C(10)–C(14)	120(1)
N(1)–C(1)–C(2)	120(1)	N(2)–C(10)–C(11)	119(1)
C(2)–C(1)–C(13)	117(1)	C(11)–C(10)–C(14)	119(1)
C(1)–C(2)–C(3)	120(1)	C(10)–C(11)–C(12)	122(1)
C(2)–C(3)–C(4)	119(1)	C(11)–C(12)–C(8)	119(1)
C(3)–C(4)–C(5)	119(1)	C(12)–C(8)–C(9)	116(1)
C(3)–C(4)–C(6)	124(1)	C(12)–C(8)–C(7)	125(1)
C(5)–C(4)–C(6)	117(1)	C(9)–C(8)–C(7)	119(1)
C(4)–C(5)–N(1)	123(1)	C(8)–C(9)–N(2)	124(1)
C(9)–C(5)–N(1)	114(1)	C(5)–C(9)–N(2)	117(1)
C(4)–C(5)–C(9)	122(1)	C(8)–C(9)–C(5)	119(1)
C(4)–C(6)–C(7)	122(1)	C(8)–C(7)–C(6)	120(1)

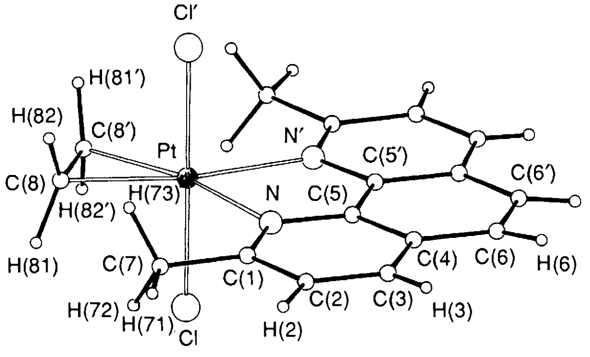

Fig. 3 View of the molecular structure of the complex [Pt(η^2-C_2H_4)Cl_2(dmphen)] **1a** together with the atomic numbering scheme

The most marked differences between complexes **1a** and **1** are concerned with the dmphen ligand. In **1a** this ligand is nearly planar and the carbon atoms of the methyl groups do not suffer particularly short contacts [the shortest non-bonding distance being C(7) ··· Pt 3.388(8) Å]. On the contrary in **1** the dmphen ligand is bent and the methyl groups interact strongly with the *cis*-chlorine atoms causing a 28° rotation of the ligand plane with respect to the metal co-ordination plane. In spite of the absence of steric constraints inside the co-ordination sphere, the Pt–N bonds in **1a** [2.236(5) Å] are much longer than those in **1** [2.045(8) and 2.046(12) Å] and consequently the N–Pt–N bite angle is smaller in **1a** [74.5(2)°] than in **1** [79.8(4)°]. Comparable lengthening of Pt–N bonds in five- with respect to four-co-ordinate species has also been observed in complexes with substituted ethylenediamine ligands.[6]

The Pt–Cl bond lengths [2.311(3) Å] in **1a** are comparable to those found in **1** [2.301(3) and 2.313(3) Å], and this appears to be a common feature for four- and five-co-ordinate complexes of the type investigated here. The Pt–C bond lengths in **1a** [2.083(7) Å] are comparable to those found in other five-co-ordinate complexes of platinum(II) {*e.g.* 2.05(2)–2.08(2) Å in [Pt(η^2-C_2H_4)Cl_2(*N,N′*-R_2en)]},[6] but are at the lower limit of those found in four-co-ordinate ethylene complexes of platinum(II) {*e.g.* 2.128(3) Å in K[Pt(C_2H_4)Cl_3],[15] 2.184(5) Å in [Pt(C_2H_4)Cl(tmen)]ClO_4 (tmen = $Me_2NCH_2CH_2NMe_2$)[16] and 2.16(2) Å in [$PtCl_2$(trans-MeCH=CHMe)(Bu^{t}N=CHCH=NBu^t)][4c]}.

Therefore the lengthening of the bond distances in five- as compared to four-co-ordinate species only concerns the bidentate nitrogen ligand which occupies two equatorial sites of the trigonal bipyramid. This lengthening is observed also in the present case (in which severe interligand steric repulsions are present in the four- but not in the five-co-ordinate complex) and should be explained on the basis of a greater electron density at the platinum atom and a less favourable bite of the chelate ring.

Rate of the Olefin Addition and Equilibrium Constant of the Formation Reaction.—The uptake of the olefin by the four-co-ordinate species can be monitored by ^1H NMR spectroscopy (the free and co-ordinated olefins give separate signals in all cases). By integration of the NMR signals, values of the reaction rate and of the equilibrium constant can be obtained.

The reaction of compounds **1**, **3** and **4** with styrene to give the corresponding five-co-ordinate complex, in chloroform at 20 °C and in the presence of excess of olefin, has been investigated. It takes place in one step and the rate is first order in the substrate and olefin concentrations. The rate constant increases by a factor of $> 10^2$ on going from the chloro to the bromo and from the bromo to the iodo complex (Table 5). This gives a clear indication that the reactivity towards olefin addition is determined by the destabilization of the four-co-ordinate ground state caused by the steric interactions between the methyl groups of dmphen and the halogen ligands of increasing size. It is also to be noted that the addition of free halide ion to the reaction medium does not influence the reaction rate, indicating that no dissociation of a halide ion from the four-co-ordinate ground state takes place.

A great effect of the steric bulk of the olefin and of the halogen ligands, upon the thermodynamic stability of the five-co-ordinate complexes, has also been observed. Equilibrium constants for reaction (1) are reported in Table 6. As the

$$[MX_2(\text{dmphen})] + \text{olefin} \rightleftharpoons [M(\eta^2\text{-olefin})X_2(\text{dmphen})] \quad (1)$$

steric bulk at both ends of the olefin is increased, the stability of the complex decreases; for instance the formation constant in the case of *trans*-but-2-ene is *ca.* 500 times smaller than in the case of ethylene. Also remarkable is the different stability of the five-co-ordinate complexes with *cis*- and *trans*-but-2-ene. A possible explanation for the latter observation could be that in the five-co-ordinate species the *cis*-but-2-ene ligand, having both substituents on one side of the equatorial plane, can alleviate interligand contacts by a slight rotation of the olefin around the double-bond axis. On the contrary, the *trans*-but-2-ene ligand, having the methyl substituents on both sides of the equatorial plane, can reduce interligand contacts only by bending back of the methyl groups.

The dependence of the equilibrium constants upon the nature of the halogen atoms has been investigated with reference to the uptake of *trans*-but-2-ene from compounds **1**–**4**. The formation constant increases by a factor of 10 on going from the chloro to the bromo complex and by a factor of 10^2 on going from the bromo to the iodo species. Once again, as observed for the rate of addition of olefins, the trend might reflect a decreased stability of the four-co-ordinate substrates (as the size of the halogen atoms increases) rather than an increased stability of the five-co-ordinate addition products.

The formation constants in the case of palladium are always smaller than in the case of platinum, indicating that five-

Table 4 Selected bond distances (Å) and angles (°) in complex **1a** *

Pt–Cl	2.311(3)	Pt–N	2.236(5)
Pt–C(8)	2.083(7)	C(8)–C(8′)	1.41(1)
N–C(1)	1.32(1)	N–C(5)	1.37(1)
C(1)–C(2)	1.42(1)	C(5)–C(5′)	1.43(1)
C(2)–C(3)	1.36(1)	C(4)–C(6)	1.42(1)
C(3)–C(4)	1.41(1)	C(6)–C(6′)	1.36(1)
C(4)–C(5)	1.40(1)	C(1)–C(7)	1.49(1)
Cl–Pt–Cl′	179.4(1)	N–Pt–N′	74.5(2)
Cl–Pt–N	89.7(2)	Cl–Pt–N′	90.9(2)
Cl–Pt–C(8)	90.2(2)	Cl–Pt–C(8′)	89.2(2)
N–Pt–C(8)	122.9(3)	C(8)–Pt–C(8′)	39.7(3)
Pt–N–C(1)	125.9(5)	C(3)–C(4)–C(5)	116.9(7)
Pt–N–C(5)	115.0(4)	C(3)–C(4)–C(6)	122.9(7)
C(1)–N–C(5)	119.1(6)	C(5)–C(4)–C(6)	120.2(8)
N–C(1)–C(2)	121.1(7)	N–C(5)–C(4)	123.0(6)
N–C(1)–C(7)	118.7(7)	N–C(5)–C(5′)	117.7(6)
C(2)–C(1)–C(7)	120.2(7)	C(4)–C(5)–C(5′)	119.3(6)
C(1)–C(2)–C(3)	120.0(8)	C(4)–C(6)–C(6′)	120.5(7)
C(2)–C(3)–C(4)	119.9(7)		

* The primed atoms are related to the unprimed ones by the transformation $-x, y, \frac{1}{2} - z$.

Table 5 Kinetic constants (k/dm^3 mol^{-1} s^{-1}) derived from values of rate constants (k_{obs}/s^{-1} = k[olefin]) measured for the reaction [PtX$_2$(dmphen)] + CH$_2$=CHPh ⟶ [Pt(η^2-PhCH=CH$_2$)X$_2$(dmphen)], performed in chloroform at 20 °C

Complex	k*
1	$1.5(3) \times 10^{-5}$
3	$6.1(3) \times 10^{-3}$
4	$6.9(3) \times 10^{-1}$

* The number in parentheses refers to the error in the last digit.

Table 6 Values of K_f/dm^3 mol^{-1} for the reaction [MX$_2$(dmphen)] + olefin ⇌ [M(η^2-olefin)X$_2$(dmphen)], calculated from ^{1}H NMR data in CDCl$_3$ at 25 °C

Complex	Olefin	K_f*
1	Ethylene	8.3×10^2
	Propene	3.3×10^2
	But-1-ene	1.1×10^2
	cis-But-2-ene	1.1×10
	Styrene	5.5
	trans-But-2-ene	1.7
3	*trans*-But-2-ene	1.5×10
4	*trans*-But-2-ene	4.6×10^2
5	Ethylene	4.5×10
	Propene	9.1×10^{-1}
7	Propene	4.2

* Estimated error within ±5%.

co-ordination is less favoured in the case of palladium with respect to platinum. In both cases, however, the dependence of K_f upon the steric bulk of the olefin and of the halogen ligands is similar.

Olefin Rotation.—Several studies have dealt with olefin rotation in four-co-ordinate platinum(II) complexes (the olefin perpendicular to the square-planar co-ordination plane),[17] in three-co-ordinate platinum(0) species (the olefin coplanar with the trigonal co-ordination plane),[18] and finally in five-co-ordinate platinum(II) complexes (the olefin lying in the equatorial plane of a trigonal bipyramid).[12] It was concluded that the $\Delta G^\ddagger$ values fall in the same range for the three different types of platinum complexes (10–16 kcal mol^{-1}) and also for many other five-co-ordinate species {*e.g.* [Fe(CO)$_4$(η^2-olefin)] (10–16 kcal mol^{-1})[19] and [RhX$_2$(N≡CR)$_2$(η^2-olefin)] (10–18 kcal mol^{-1})[20]}.

Table 7 Values of $\Delta G^\ddagger$ for olefin rotation in five-co-ordinate [M(η^2-propene)X$_2$(dmphen)] complexes[a]

Complex	$\Delta G^{\ddagger b}$/kcal mol^{-1}
1b	20.6
3b	20.8
4b	20.5
5b	14.1
7b	13.6

[a] Data obtained from the coalescence temperature (T_c) of the ^{1}H NMR signals of the two methyls of dmphen. The spectra were recorded in CDCl$_3$ **5b** and **7b** and in [^{2}H$_8$]toluene (sealed tube) **1b**, **3b** and **4b**. Some dissociation of the five-co-ordinate species into free olefin and four-co-ordinate complex occurred. [b] Estimated error of each value ±0.2 kcal mol^{-1}.

The ethylene protons in the complex [Pt(η^2-C$_2$H$_4$)Br(Cl)(dmphen)] (having two different halogen atoms in axial positions) give rise to an AA′BB′ multiplet which is consistent with the olefin lying in the equatorial plane and being in restricted rotation about the platinum-olefin bond. This resonance pattern remained unchanged up to 105 °C where only a slight broadening of the olefin resonances was observed. This allowed us to establish a low energy limit for $\Delta G^\ddagger$ of 20 kcal mol^{-1} which is higher than any other value reported, up to now, for complexes of this type. The $\Delta G^\ddagger$ values for olefin rotation in a series of propene complexes are given in Table 7. Spectral changes as a function of temperature for compounds **3b** and **7b** are given in Fig. 4.

For the platinum complexes the $\Delta G^\ddagger$ values are always well above 20 kcal mol^{-1} and do not change significantly on going from the dichloro to the dibromo, and to the diiodo complexes. Also in the case of palladium complexes the $\Delta G^\ddagger$ values, for olefin rotation, appear to be independent of whether Br or Cl is present at the axial positions and, on average, the values are about 6–7 kcal mol^{-1} lower than those found for the platinum species.

Hoffmann and co-workers[19] note that the important factor determining the barrier to olefin rotation is the degree of bending back of the groups connected to the C=C moiety of the olefin which is a measure of the extent of the electron charge back donation from the metal to the olefin. The bending back of the olefin substituents is generally larger in five- than it is in four-co-ordinate species (*e.g.* the bending of the phenyl substituent in the styrene complexes, as defined by Nyburg *et al.*,[21] is 27° in five-co-ordinate [PtCl$_2$(η^2-PhCH=CH$_2$)(Bu^{t}N=CHCH=NBu^t)][12] and 16.5–18.5° in four-co-ordinate [PtCl$_2$(η^2-PhCH=CH$_2$)(NC$_5$H$_4$X)] species (X = Me or Cl).[21] Similarly the C(1)–C(2)–C(3)–C(4) torsion angle of *trans*-but-2-ene is 50(2)° in five-co-ordinate [PtCl$_2$(η^2-*trans*-MeCH=CHMe)(Me$_2$N–N=CMeCMe=N–NMe$_2$)][4d] and 27(1)° in four-co-ordinate [{PtCl$_2$(η^2-*trans*-MeCH=CHMe)}$_2$(Bu^{t}N=CHCH=NBu^t)][4c]).

Our structural data do not allow an accurate estimate of the bending back of the olefin protons which, however, was found to be 58(10)°, much bigger than the value of 32° found in four-co-ordinate [Pt(η^2-C$_2$H$_4$)Cl$_3$]$^-$ and [Pt(η^2-C$_2$H$_4$)Cl(tmen)]$^+$.[15,16] Therefore we are inclined to emphasize electronic over steric factors in order to explain the exceedingly high values of $\Delta G^\ddagger$ found in the present case. That steric factors (mostly the interaction between the axial halogen ligands and the olefin when it passes through the upright position) are not so important in the present case is also shown by the small changes of $\Delta G^\ddagger$ values observed whether Cl, Br or I is present in the axial sites.

The values of $\Delta G^\ddagger$ are smaller in the case of palladium than in the case of platinum and might reflect a less favourable bonding

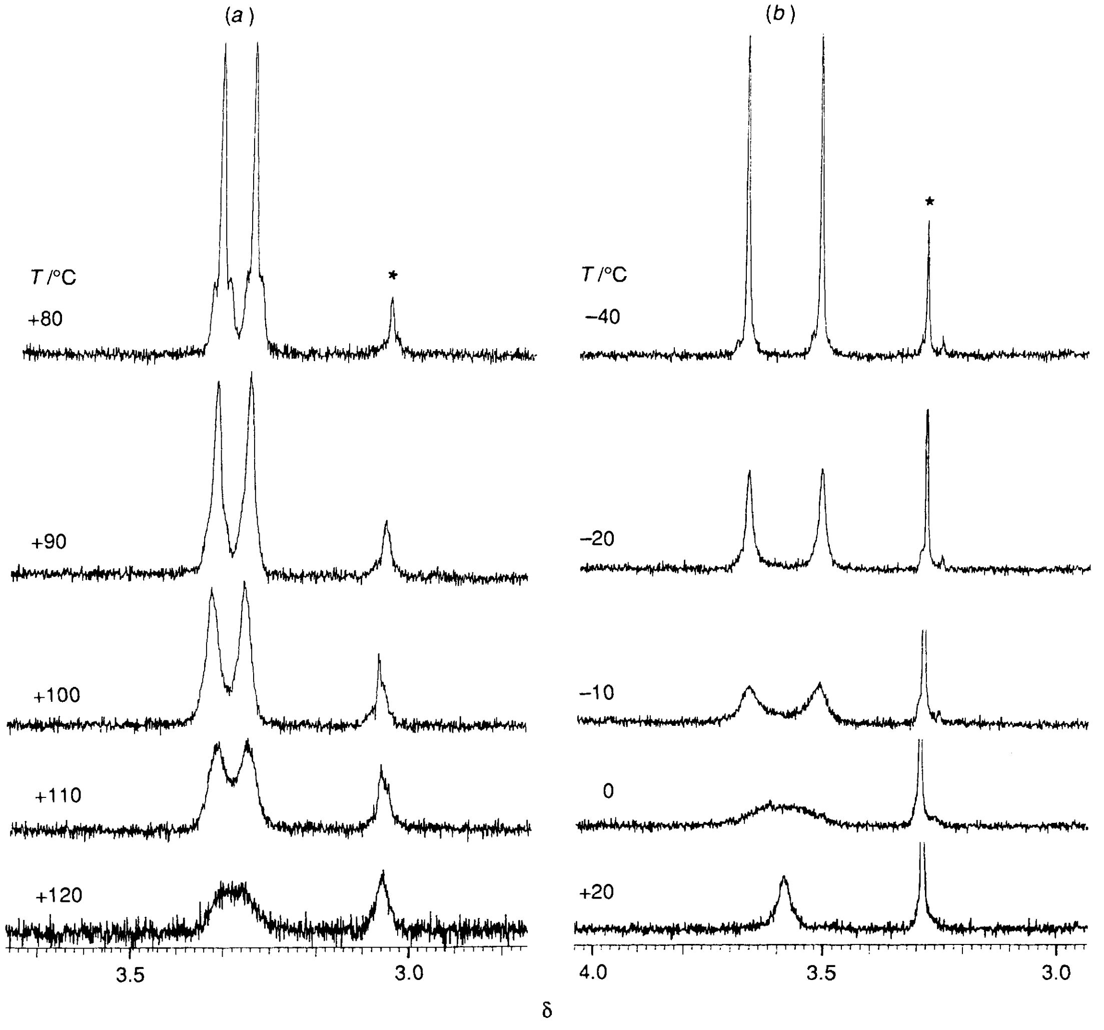

Fig. 4 Changes in Me(2,9) resonances as a function of temperature for compounds **3b** (solvent [$^2H_8$]toluene) (*a*) and **7b** (solvent $CDCl_3$) (*b*). The asterisks mark the resonances of compounds **3** and **7**

situation which is also shown by the smaller values of the formation constants (Table 6).

Conclusion

On the basis of the above results it is possible to explain why compounds **1**–**8**, containing dmphen, react directly with olefins to give the corresponding addition products in a reversible process. Concerning the composition at equilibrium, the structural data of complexes **1** and **1a** have shown that the interligand steric interactions are relevant in the square-planar species but negligible in the trigonal-bipyramidal complex. Therefore the relief of the interligand contacts, which takes place on rearranging the molecular geometry from a square plane to a trigonal bipyramid, results in a greater thermodynamic stability of the five- *versus* four-co-ordinate species.

Concerning the reversibility of the addition–dissociation reaction, this cannot be explained on the basis of a reaction pathway in which the transition states have a square-pyramidal geometry with either the entering or the leaving group in the axial position and the other ligands (comprising the L–L chelate) in the equatorial plane. Such square-pyramidal transition states would be destabilized by the dmphen ligand having bulky substituents on both ends. A different, low-energy, path for the olefin uptake by compounds **1**–**8** must be operating. The same reaction pathway might also apply to the complexes [MCl(Me)(L–L)] (M = Pd or Pt) which also take up olefin under normal conditions and which contain a metal-bonded methyl group exerting a great *trans*-labilizing effect.[11] The latter compounds will be considered first. The X-ray structure of one of them, [$PtCl(Me)\{NC_5H_3(CH{=}NCHMePh\text{-}2)(Me\text{-}6)\}$], has shown that the two Pt–N bonds are not equivalent, that *trans* to the methyl being some 0.22 Å longer than the other.[11] We propose that such a weak bond could easily be broken so providing a three-co-ordinate T-shaped intermediate species which could first isomerize to the one having the Me and Cl ligands in *trans* position and then add the olefin. A re-entering of the dissociated end of the L–L bidentate ligand into the co-ordination sphere would lead to the final five-co-ordinate complex. A similar mechanism could also apply to compounds **1**–**8**. The great interligand steric interactions could be released by displacement of one end of the bidentate ligand and rotation of the ligand plane in the upright position (in a fashion similar to that observed in the X-ray structure of other complexes of this ligand with Pt^{II}, Pd^{II} and Au^{III}).[8–10] An isomerization of the three-co-ordinate T-shaped intermediate which brings the two halogen ligands *trans* to each other, followed by co-ordination of one olefin molecule and resetting of the phen molecule (so that the interaction with the metal can be equally shared by the two nitrogens), would give the final five-co-ordinate complex. This mechanism would fully account for the observed dependence of the rate constants for olefin addition upon the different sizes of the halogen ligands.

Finally, concerning the barrier to olefin rotation in the five-co-ordinate species, this does not change whether Cl, Br or I is present in the axial sites, indicating that electronic factors (that is electron charge back donation from the metal to the olefin) are more important than steric factors.

Experimental

Starting Materials.—Commercial reagent-grade chemicals, dmphen, ethylene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene and styrene (Aldrich), were used without further purification. The complexes $[PtCl_2(dmso)_2]$,[22] $[PdCl_2(PhCN)_2]$,[23] $K[Pt(\eta^2-C_2H_4)Cl_3]$ (Zeise's salt)[24] and $K[PtCl_3(\eta^2-PhCH{=}CH_2)]$[12] were prepared by the reported procedures.

Preparation of Four-co-ordinate Complexes.—$[PtCl_2(dmphen)]$ **1**. A suspension of $[PtCl_2(dmso)_2]$ (315 mg, 0.75 mmol) in ethanol (80 cm^3) was treated, with stirring, with the stoichiometric amount of dmphen and the reaction mixture refluxed at 80 °C for 1 d. After evaporation of the solvent under vacuum, the crude reddish product was dissolved in CH_2Cl_2 and chromatographed on an open column of silica gel using CH_2Cl_2 as eluent. The collected yellow fraction was evaporated to dryness and the lemon-yellow solid washed several times with diethyl ether and dried in the air. The yield of the isolated product was above 80% (Found: C, 34.9; H, 2.5; Cl, 14.7; N, 5.7. Calc. for $C_{14}H_{12}Cl_2N_2Pt$: C, 35.5; H, 2.5; Cl, 14.9; N, 5.9%).

$[PtBr(Cl)(dmphen)]$ **2**, $[PtBr_2(dmphen)]$ **3** *and* $[PtI_2(dmphen)$ **4**. An excess of tetrabutylammonium bromide or iodide was added, with stirring, to a solution of $[PtCl_2(dmphen)]$ (50 mg, 0.1 mmol) in $CHCl_3$ (15 cm^3). The yellow-green solution turned to orange in the case of bromide and to red in the case of iodide ion. The solvent was then removed under vacuum and the solid residue treated with methanol (20 cm^3) to give microcrystalline needles of $[PtBr_2(dmphen)]$ **3** (orange) and $[PtI_2(dmphen)]$ **4** (red). The reaction leads to the formation of **4** even when only a stoichiometric amount of iodide ion is added to the solution of the chloro complex. On the other hand the formation of **3** requires a ratio of bromide ion to chloro complex of *ca*. 200:1. If the molar ratio is smaller (20:1) a deep yellow solid of $[PtBr(Cl)(dmphen)]$ **2** is obtained. Compound **2** is not stable in solution and leads to an equilibrium mixture of **1**–**3**; for this reason by reaction of **2** with ethylene an equilibrium mixture of **1a**–**3a** is obtained (Found: C, 31.8; H, 2.3; Br, 15.2; Cl, 6.7; N, 5.2. Calc. for $C_{14}H_{12}BrClN_2Pt$ **2**: C, 32.4; H, 2.3; Br, 15.4; Cl, 6.8; N, 5.4. Found: C, 30.0; H, 2.1; Br, 28.2; N, 5.0. Calc. for $C_{14}H_{12}Br_2N_2Pt$ **3**: C, 29.9; H, 2.1; Br, 28.4; N, 5.0. Found: C, 26.0; H, 1.9; I, 38.6; N, 4.3. Calc. for $C_{14}H_{12}I_2N_2Pt$ **4**: C, 25.5; H, 1.8; I, 38.8; N, 4.2%).

$[PdCl_2(dmphen)]$ **5**. A solution of $[PdCl_2(PhCN)_2]$ (115 mg, 0.3 mmol) in $CHCl_3$ (50 cm^3) was treated with dmphen (80 mg, 0.4 mmol) and the reaction mixture left to stir for 2 h. Addition of diethyl ether to the filtered solution caused the precipitation of an orange solid, which was collected, washed with diethyl ether and dried in the air. Yield 80% (Found: C, 43.5; H, 3.2; Cl, 18.2; N, 7.2. Calc. for $C_{14}H_{12}Cl_2N_2Pd$: C, 43.6; H, 3.1; Cl, 18.4; N, 7.3%).

$[PdBr_2(dmphen)]$ **7**. Twice the stoichiometric amount of tetrabutylammonium bromide (168 mg, 0.52 mmol) was added, with stirring, to a solution of $[PdCl_2(dmphen)]$ **5** (50 mg, 0.13 mmol) in $CHCl_3$ (15 cm^3), and immediately the colour of the solution turned from orange to purple. The solvent was removed under vacuum and the residue triturated with methanol (20 cm^3) to give a purple microcrystalline solid which was washed with methanol and dried in the air. Yield 80% (Found: C, 35.5; H, 2.5; Br, 33.5; N, 5.8. Calc. for $C_{14}H_{12}Br_2N_2Pd$: C, 35.4; H, 2.5; Br, 33.7; N, 5.9%).

$[PdI_2(dmphen)]$ **8**. Complex **5** (50 mg, 0.13 mmol) was dissolved in $CHCl_3$ (15 cm^3) and treated with twice the stoichiometric amount of tetrabutylammonium iodide (96 mg, 0.26 mmol) with stirring. Immediately the solution turned black and a black solid separated. This was collected, washed with $CHCl_3$, and dried in the air. Yield 80% (Found: C, 29.4; H, 2.1; I, 44.5; N, 4.8. Calc. for $C_{14}H_{12}I_2N_2Pd$: C, 29.5; H, 2.1; I, 44.8; N, 4.9%). The use of an excess of iodide ion leads to the formation of $[NBu_4]_2[Pd_2I_6]$ as a by-product.

Preparation of Five-co-ordinate Complexes.—The square-planar complexes **1**–**8** react directly with olefins to give the corresponding addition products. The general procedure for the preparation of the chloro compounds **1a**–**1f** is given below, the yields of the isolated products and the microanalysis data being given in Table 8.

Complex **1** (100 mg) was dissolved in $CHCl_3$ (70 cm^3) and placed in a Schlenk tube (400 cm^3) fitted with a screw lid. The air was removed and the tube connected to a rubber balloon (2 dm^3) containing the gaseous olefin. After stirring at room temperature for the time required (from 0.5 d in the case of ethylene to 5 d in the case of *trans*-but-2-ene) the reaction solution was filtered and chromatographed on an open column of silica gel using CH_2Cl_2–diethyl ether (1:1, v/v) as eluent. The first yellow fraction was collected and the solvent evaporated under vacuum at room temperature. Under these conditions the formation of the five-co-ordinate species is quantitative only in the case of ethylene and nearly quantitative in the case of propene and but-1-ene. In the case of *cis*- and *trans*-but-2-ene a pressure of *ca*. 8 atm of olefin was used in order to increase the yield of the five-co-ordinate species. However, even under these conditions the yield with *trans*-but-2-ene (evaluated by ^1H NMR spectroscopy of the crude product) did not exceed 50%. In the case of styrene a pure sample of the five-co-ordinate species was obtained by reaction of the styrene analogue of Zeise's salt with dmphen. In the case of 2-methylpropene no formation of five-co-ordinate complex was detected even under pressure of olefin (8 atm).

The reaction with olefins of the bromo and iodo complexes **3** and **4** was much faster than that of the chloro species **1** and the equilibrium was shifted towards the formation of the five-co-ordinate species. Compounds **3a** and **4a** were prepared in the following way. Either **3** or **4** (30 mg) was dissolved in $CHCl_3$ (10 cm^3) and placed in a Schlenk tube, then the air was removed and the tube connected to a rubber balloon (2 dm^3) containing C_2H_4. Immediately the colour of the solution turned from orange to light yellow in the case of the bromo, from red to orange in the case of the iodo complex. Addition of pentane to the solution caused the precipitation of either $[Pt(\eta^2-C_2H_4)Br_2(dmphen)]$ **3a** or $[Pt(\eta^2-C_2H_4)I_2(dmphen)]$ **4a**. The solid was collected, washed with pentane, and dried in the air. Yield 90% (Found: C, 32.7; H, 2.7; Br, 26.7; N, 4.6. Calc. for $C_{16}H_{16}Br_2N_2Pt$ **3a**: C, 32.5; H, 2.7; Br, 27.0; N, 4.7. Found: C, 27.5; H, 2.2; I, 37.0; N, 3.9. Calc. for $C_{16}H_{16}I_2N_2Pt$ **4a**: C, 28.0; H, 2.3; I, 37.2; N, 4.1%).

The palladium complexes **5**–**8** also react with olefins (ethylene and propene) to give the corresponding five-co-ordinate species. These, however, were not isolated since, in the absence of excess of free olefin, the five-co-ordinate species readily reverts to the starting four-co-ordinate complex. They were characterized in solution by ^1H NMR spectroscopy (Table 2).

Rate of Uptake of Styrene.—The uptake of styrene by compounds **1**, **3** and **4** was monitored by ^1H NMR and UV/VIS spectroscopy. The complexes were dissolved in chloroform and treated with an excess of styrene (molar ratio from 1:10 to 1:500). Changes in band intensity with time were plotted in a semilogarithmic diagram to give the observed rate constants. Under the experimental conditions used the reaction was complete in the case of **3** and **4**, at equilibrium in the case of **1**. The experimental data were treated accordingly.

Equilibrium constants. Values of the equilibrium constants ($K_f/dm^3\ mol^{-1}$) for the reaction of the four-co-ordinate complex with olefin to give the five-co-ordinate species were obtained from ^1H NMR data. A known amount of complex (3–6 mg) was dissolved in $CDCl_3$ (1 cm^3), containing a known amount of olefin, and placed in an NMR tube which was sealed. Spectra were recorded from time to time until no further

Table 8 Yields and microanalytical data (%) for [Pt(η^2-olefin)Cl_2(dmphen)] complexes[a]

Complex	Olefin	Analysis C	H	Cl	N	Yield
1a	Ethylene	38.5 (38.3)	3.0 (3.2)	13.9 (14.1)	5.5 (5.6)	95
1b	Propene	39.6 (39.5)	3.4 (3.5)	13.5 (13.7)	5.5 (5.4)	90
1c	But-1-ene	41.0 (40.8)	3.9 (3.8)	13.2 (13.4)	5.2 (5.3)	80
1d	*cis*-But-2-ene	41.1 (40.8)	4.0 (3.8)	13.1 (13.4)	5.1 (5.3)	50
1e	*trans*-But-2-ene	41.0 (40.8)	4.0 (3.8)	13.0 (13.4)	5.0 (5.3)	20
1f	Styrene[b]	45.5 (45.7)	3.3 (3.5)	12.0 (12.3)	4.8 (4.8)	85

[a] Calculated values are given in parentheses. Yields are for isolated products. [b] Obtained from K[$PtCl_3$(η^2-PhCH=CH_2)] and dmphen.

Table 9 Experimental data for the X-ray diffraction studies*

	1	**1a**
Formula	$C_{14}H_{12}Cl_2N_2Pt$	$C_{16}H_{16}Cl_2N_2Pt$
M	474.26	502.31
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
a/Å	16.175(4)	14.960(4)
b/Å	16.377(6)	11.149(4)
c/Å	10.364(3)	10.281(2)
β/°		108.75(2)
U/Å^3	2745(1)	1623.8(8)
Z	8	4
D_c/g cm^{-3}	2.295	2.055
F(000)	1776	952
Crystal dimensions/mm	0.07 × 0.16 × 0.38	0.15 × 0.23 × 0.34
μ/cm^{-1}	107.07	90.58
Scan speed/° min^{-1}	3–14	3–12
Reflections measured	h,k,l	$\pm h,k,l$
Unique total data	3017	1876
Unique observed data [$I > 2\sigma(I)$]	1274	1496
R	0.0319	0.0380
R'	0.0440	0.0474

* Details in common: graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å); Philips PW 1100 diffractometer; scan type ω–2θ; scan width (θ – 0.6) – (θ + 0.6 + 0.346 tan θ); 2θ range 6–54°; one standard reflection every 50.

Table 10 Fractional atomic coordinates (× 10^5 for platinum, × 10^4 for all other atoms) with esds in parentheses for the non-hydrogen atoms of complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	20 842(3)	12 268(3)	6 371(5)
Cl(1)	3 489(2)	1 019(3)	529(3)
Cl(2)	2 185(2)	748(2)	2 731(3)
N(1)	823(5)	1 277(7)	529(9)
N(2)	1 937(7)	1 456(7)	–1 290(12)
C(1)	249(9)	1 350(9)	1 462(14)
C(2)	–586(8)	1 105(10)	1 223(14)
C(3)	–814(8)	846(9)	22(16)
C(4)	–234(9)	848(8)	–972(13)
C(5)	564(8)	1 069(7)	–693(13)
C(6)	–420(10)	642(9)	–2 295(14)
C(7)	143(10)	708(9)	–3 234(16)
C(8)	965(10)	1 019(8)	–2 952(16)
C(9)	1 178(9)	1 172(8)	–1 672(12)
C(10)	2 452(8)	1 733(9)	–2 198(15)
C(11)	2 274(11)	1 603(10)	–3 488(17)
C(12)	1 558(11)	1 219(10)	–3 880(14)
C(13)	441(10)	1 701(11)	2 740(14)
C(14)	3 191(9)	2 216(10)	–1 842(14)

Table 11 Fractional atomic coordinates (× 10^5 for platinum, × 10^4 for all other atoms) with esds in parentheses for the non-hydrogen atoms of complex **1a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	0	33 610(3)	25 000
Cl	1 190(1)	3 372(2)	1 520(2)
N	–642(4)	1 765(5)	1 223(6)
C(1)	–1 257(5)	1 793(6)	–34(8)
C(2)	–1 621(6)	722(7)	–748(8)
C(3)	–1 337(6)	–362(7)	–143(10)
C(4)	–670(6)	–416(6)	1 187(9)
C(5)	–346(5)	677(5)	1 830(7)
C(6)	–323(8)	–1 513(6)	1 863(11)
C(7)	–1 556(6)	2 976(7)	–696(9)
C(8)	–351(7)	5 119(6)	1 847(8)

change was observed. The concentrations of the species at equilibrium were evaluated by integration of the NMR signals and used to calculate the equilibrium constants. On some occasions the K_f values were also measured by following the reverse reaction, that is dissociation of olefin from the five-co-ordinate species dissolved in chloroform and sealed in the NMR tube.

Calculation of $\Delta G^\ddagger$. Values of the free energy of activation for olefin rotation in the five-co-ordinate species were calculated by using the expression $\Delta G^\ddagger_{T_c} = -RT \ln[\pi(\Delta\nu)h/2^{\frac{1}{2}}kT]$, where $\Delta\nu$ represents the chemical shift difference ($\Delta\delta$/Hz) of the coalescing peaks in the absence of exchange, T_c represents the coalescence temperature, and R, k and h have their normal thermodynamic significance.[25]

Physical Measurements.—The NMR studies were performed on Varian EM 390 and XL 200 spectrometers. UV/VIS spectra were recorded on a Varian 2002 double-beam spectrophotometer.

X-Ray Data Collections, Structure Determinations and Refinements for Complexes **1** *and* **1a**.—Single crystals of complexes **1** and **1a** were obtained by crystallization from $CHCl_3$–Et_2O; those of **1** were thin and their reflections rather weak. The crystallographic data are summarized in Table 9. Unit-cell parameters were determined from the θ values of 30 carefully centred reflections, having 9 < θ < 16 for **1** and 10 < θ < 17° for **1a**. Data were collected at room temperature, the individual profiles having been analysed following Lehmann and Larsen.[26] Intensities were corrected for Lorentz and polarization effects and a semiempirical correction for absorption was applied (maximum and minimum values for the transmission factors were 1.427 and 1.000 for **1**, 1.437 and 1.000 for **1a**).[27] Only the observed reflections were used in the structure solution and refinement.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of complex **1** were placed at their geometrically calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms; the hydrogen atoms of **1a**, except those of the methyl groups, were clearly located in the final Fourier difference map and refined isotropically. The final cycles of refinement were carried out on the basis of 175 (**1**) and 119 (**1a**) variables; after the last cycles, no parameters shifted by more than 0.47 (**1**) and 0.86 (**1a**) estimated standard deviation (esd). The biggest remaining peaks (close to the Pt atoms) in the final difference maps were equivalent to about 2.13 (**1**) and 1.89 (**1a**) e Å^{-3}. In the final cycles of refinement a weighting scheme $w = K/\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K values were 0.127 and 1.000 and the g values 0.0101 and 0.0045 for **1** and **1a** respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 28. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio Bologna) and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR Parma using the SHELX 76 and SHELXS 86 systems of crystallographic computer programs.[29] The final atomic coordinates for the non-hydrogen atoms are given in Tables 10 for **1** and 11 for **1a**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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