

Reactions of Stable $[\text{PtCl}_2(\eta^2\text{-olefin})(\alpha\text{-di-imine})]$ Complexes. Retention of the Five-co-ordinate Structure upon Halogen Exchange and Ligand Substitution with Olefins, α -Di-imines, and N,N' -Disubstituted 1,2-Diaminoethanes

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The axial halogen atoms as well as the equatorial $\eta^2\text{-C}_2\text{H}_4$ and $\sigma,\sigma\text{-}N,N'$ chelate-bonded R-N=CH-CH=N-R or $\text{R-N(H)CH}_2\text{CH}_2\text{N(H)-R}$ ligands (L-L) in five-co-ordinate $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\sigma,\sigma\text{-}N,N'\text{-L-L})]$ can be replaced with retention of the trigonal-bipyramidal structure. Halogen exchange is initiated by formation of an ionic intermediate $[\text{PtCl}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]\text{Cl}$. The reversible exchange of the equatorial ligands with olefins, α -di-imines, or 1,2-diamine ligands is proposed to proceed *via* five-co-ordinate intermediates. The selectivity observed in these exchange reactions is explained on the basis of the difference in steric constraints of the various olefins and bidentate ligands used.

EXCHANGE of the N -donor ligand (L) and olefin in $[\text{PtX(Y)}(\eta^2\text{-olefin})\text{L}]$ complexes has been demonstrated to proceed *via* the five-co-ordinate transition states $[\text{PtX(Y)}(\eta^2\text{-olefin})\text{L(L')}]$ ($\text{L}' = N'$ -donor ligand or olefin).^{1,2} The five-co-ordinate transition state is reached either by association with the N' -donor ligand or solvent molecules. These exchange mechanisms have not only been experimentally studied, but theoretical studies have recently been reported also.^{1,2} Owing to the transient character of these five-co-ordinate intermediates, aspects such as ligand exchange and intramolecular rearrangements *via* concerted mechanisms (Berry pseudo-rotation or Turnstile processes) which influence the products formed are difficult to investigate.

Recently, a large series of stable five-co-ordinate $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L-L})]$ ($\text{L-L} =$ bidentate donor ligand) complexes were reported in the literature³⁻⁷ which makes the gathering of important information possible. It was seen that in these complexes where L-L was an α -di-imine (R-N=CHCH=N-R), $\text{R-N(H)CH}_2\text{CH}_2\text{N(H)-R}$, or the 2,6-disubstituted pyridine $\text{R'NC}_5\text{H}_3\text{CH=NR}$ the various ligands show a strong site preference in the trigonal-bipyramidal array. The electronegative X atoms reside in the axial positions, while the neutral ligands are in the equatorial plane. For these complexes, no experimental evidence for the occurrence of stereoisomerization processes could be obtained.^{4,5,7} However, we did observe dynamic behaviour in the RN=CHCH=NR and $\text{RN(H)CH}_2\text{CH}_2\text{N(H)R}$ complexes, as evidenced by multinuclear n.m.r. spectra, involving pure olefin rotation. The ΔG values (13–15 kcal *) for the barrier to olefin rotation were in the range found for four-co-ordinate platinum-olefin species.⁴ It was concluded that bending back of the axial atoms in the direction of the bidentate ligand, when the olefin passed the upright conformation, was an important factor. The kinetic stability of these five-co-ordinate species with respect to platinum-olefin bond dissociation to give four-co-

ordinate $[\text{PtX}_2(\text{L-L})]$ complexes depends mainly on steric factors. For example introduction of a methyl group in the 6-position of $\text{R'NC}_5\text{H}_3\text{CH=NR}$ (*i.e.* $\text{R}' = \text{Me}$) enhanced the solution stability considerably. This was tentatively explained by the fact that in four-co-ordinate $[\text{PtCl}_2(\text{R'NC}_5\text{H}_3\text{CH=NR})]$ complexes all the ligands reside in one plane which necessarily brings one of the atoms close to the 6- R' substituent.⁵

In this paper we describe studies concerning intermolecular exchange processes of the five-co-ordinate platinum-olefin complexes with olefins, uni- and bidentate N -donor ligands, and sodium halides which occur with retention of the five-co-ordinate geometry.⁸

EXPERIMENTAL

α -Di-imines (RNCHCHNR), N,N' -substituted 1,2-diaminoethanes $[\text{RN(H)CH}_2\text{CH}_2\text{N(H)R}]$, and 6- R' -pyridine-2-carbaldimines ($\text{R'NC}_5\text{H}_3\text{CH=NR}$) were prepared by methods described elsewhere.⁹ Five-co-ordinate $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L-L})]$ complexes [$\text{L-L} = \text{RNCHCHNR}$, $\text{RN(H)CH}_2\text{CH}_2\text{N(H)R}$, $\text{R'NC}_5\text{H}_3\text{CH=NR}$, 2,2'-bipyridyl (bipy), or 2,11-dimethylphenanthroline (dmphen)] were obtained from the reaction of Zeise's salt $\{\text{K}[\text{PtCl}_3(\eta^2\text{-olefin})]\}$ with L-L .⁴⁻⁶ Solvents were purified and distilled before use; all exchange reactions were carried out in a nitrogen atmosphere.

Exchange Reactions.—The complexes obtained from these experiments were characterized by comparison of their spectroscopic data (¹H, ¹³C n.m.r., and i.r.) with those of authentic samples.^{4,5}

Exchange of σ -N-bonded L and σ,σ - N,N' -bonded L-L donor ligands in $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)\text{L}]$. The preparation of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)\{\text{Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t\}]$ from $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ (1) described here is representative. The compound $\text{Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t$ (2 mmol) was added to a stirred solution of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ (1) (1 mmol) in dichloromethane (10 cm³). The solution was stirred for 10 min, evaporated to dryness, and the residue washed with pentane (4×10 cm³) to remove $\text{Bu}^t\text{NCHCHNBu}^t$ as well as the excess of $\text{Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t$. Yellow microcrystalline $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)\{\text{Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t\}]$ was isolated in 75% yield. When $\text{R'NC}_5\text{H}_3\text{CH=NR}$, bipy, or dmphen were used, the reaction mixture was cooled to -20°C directly after mixing

* Throughout this paper: 1 cal = 4.184 J; 1 atm = 101 325 Pa.

the reactants in order to minimize decomposition according to $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})] \rightarrow [\text{PtCl}_2(\text{L-L})] + \text{C}_2\text{H}_4$.

Halogen exchange. $[\text{PtI}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})][\text{L-L}=\text{Bu}^t\text{NCHCHNBU}^t, \text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et, or Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t]$ from $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$. The complex $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ (1 mmol) was added to a stirred solution of NaI (6 mmol) in acetone (10 cm³). The reaction mixture was stirred for 24 h, after which NaCl was filtered off. The filtrate was evaporated to dryness and the residue extracted with benzene (3 × 30 cm³). Concentration of the benzene extract resulted in orange-red crystals of $[\text{PtI}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$. The yield after recrystallization from a hexane-benzene mixture was 40–60%.

Halogen-halogen exchange between $[\text{PtX}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ (X = Cl or Br; R = Bu^t or CMe₂Et). The complex $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ (0.2 mmol) and $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ (0.2 mmol) were dissolved in oxygen-free CDCl₃ (0.5 cm³) and then sealed in a n.m.r. tube. For the exchange reaction monitored by ¹H and ¹³C n.m.r. spectrometry for 3 weeks see Results section.

Exchange of ethylene in $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ (1). The preparation of $[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})(\text{Bu}^t\text{NCHCHNBU}^t)]$ from $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ described here is representative.

Methyl acrylate (4 mmol) was added to a stirred solution of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ (1 mmol) in dichloromethane (10 cm³). The solution was stirred for 24 h and then concentrated below 25 °C. The residue was washed

with pentane (4 × 10 cm³) to remove excess of methyl acrylate and dried *in vacuo*. Yield 80% {Found: C, 31.85; H, 5.10; N, 5.35; O, 5.70. Calc. for $[\text{PtCl}_2\{\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me}\}(\text{Bu}^t\text{NCHCHNBU}^t)]$: C, 32.3; H, 5.05; N, 5.40; O, 6.15%. Found: C, 31.75; H, 4.95; N, 4.65. Calc. for $[\text{PtCl}_2\{\eta^2\text{-C}_2\text{H}_2(\text{CO}_2\text{Me})_2\}(\text{Bu}^t\text{NCHCHNBU}^t)]$: C, 33.25; H, 4.90; N, 4.85%}.

Separation of a 1:1 cis-trans mixture of $(\text{MeO}_2\text{C})\text{CH}=\text{CH}(\text{CO}_2\text{Me})$ by means of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ (1). A solution of dimethyl maleate (*cis* 0.5 mmol) and dimethyl fumarate (*trans* 0.5 mmol) was added to a solution of (1) (2.0 mmol) in dichloromethane (10 cm³) which was stirred for 48 h and then concentrated to 2 cm³. Addition of pentane (10–15 cm³, –20 °C) resulted in the precipitation of a mixture of (1) and $[\text{PtCl}_2\{\eta^2\text{-MeO}_2\text{C}(\text{CH})_2\text{CO}_2\text{Me}\}(\text{Bu}^t\text{NCHCHNBU}^t)]$ which was filtered off and washed with pentane (3 × 5 cm³). From the filtrate, dimethyl fumarate could be isolated. For the isolation of free dimethyl maleate from $[\text{PtCl}_2\{\eta^2\text{-MeO}_2\text{C}(\text{CH})_2\text{CO}_2\text{Me}\}(\text{Bu}^t\text{NCHCHNBU}^t)]$ see below.

$[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ (1) from $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{Bu}^t\text{NCHCHNBU}^t)]$ (olefin = methyl acrylate or dimethyl maleate). A solution of $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{Bu}^t\text{NCHCHNBU}^t)]$ (0.2 mmol) in CDCl₃ was kept under a C₂H₄ atmosphere (50 atm) in an autoclave for 6 h. The solution was degassed and N₂ bubbled through the reaction mixture. Nuclear magnetic resonance spectra were recorded directly after this work-up procedure and showed exclusively the

TABLE I

Proton n.m.r. data for $[\text{PtX}_2(\eta^2\text{-olefin})(\text{RNCHCHNR})]$ and $[\text{PtX}_2(\eta^2\text{-olefin})\{\text{RN(H)CH}_2\text{CH}_2\text{N(H)R}\}]$ complexes ^a

Complex	CH ₃	CH ₂	HC=N	HC=O CH ₃ -C=O	HC=	Method of preparation ^b
$[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ ^c (1)	1.66(s, br)		8.63(s, br) [36]		3.50(s) [70]	A
$[\text{PtClBr}(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ ^c	1.66(s, br)		8.63(s, br) [36]		3.57(s) [70]	B
$[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$ ^c	1.66(s, br)		8.63(s, br) [36]		3.63(s) [70]	A, B
$[\text{PtI}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.77(s)		8.93(s) [38]		3.68(s) [72]	B
$[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$ ^d	0.83(t), 1.57(s, br)	1.98(q)	8.48(s, br) [36]		3.45(s) [69]	A
$[\text{PtClBr}(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$ ^d	0.83(t), 1.57(s, br)	1.98(q)	8.48(s, br) [36]		3.52(s) [70]	B
$[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$ ^d	0.83(t), 1.57(s, br)	1.98(q)	8.48(s, br) [36]		3.60(s) [69]	A, B
$[\text{PtI}_2(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$	0.93(t), 1.68(s)	2.05(q)	8.47(s) [37]		3.88(s) [72]	B
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.63(s)		8.70(s) [40]	3.68(s)	3.43(d) [70], 3.98(d) [64], 4.75(dd) [84]	B
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$	0.87(t), 1.60(s), 1.64(s)	2.02(q)	8.63(s) [40]	3.67(s)	3.38(d), 3.93(d), 4.67(dd)	B
$[\text{PtCl}_2\{\eta^2\text{-cis-C}_2\text{H}_2(\text{CO}_2\text{Me})_2\}(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.67(s)		8.73(s) [42]	3.70(s)	4.50(s) [77]	B
$[\text{PtCl}_2\{\eta^2\text{-cis-C}_2\text{H}_2(\text{CO}_2\text{Me})_2\}(\text{Bu}^t\text{N(H)CH}_2\text{CH}_2\text{N(H)Bu}^t)]$	1.46(s)		3.05(s) [15] ^e	3.71(s)	4.21(s) [75]	B
$[\text{PtCl}_2\{\eta^2\text{-OCCH=CHC(O)O}\}(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.67(s)		9.08(s) [50]		4.57(s) [74]	B
$[\text{PtCl}_2\{\eta^2\text{-OCCH=CHC(O)O}\}(\text{EtMe}_2\text{CNCHCHNCMe}_2\text{Et})]$	0.87(t), 1.66(s)		9.27(s) [50]		4.65(s) [76]	B
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCHO})(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.67(s, br)		8.70(s, br) [41]	9.73(s)	3.68(d), 4.25(d)	B
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})\{\text{EtMe}_2\text{CN(H)CH}_2\text{CH}_2\text{N(H)CMe}_2\text{Et}\}]$	0.93(t), 1.37(s), 1.42(s), 1.58(s)	1.80(q)	3.00(s, br) [16] ^e	3.68(s)	3.33(d) [68], 3.98(d), 4.67(dd)	B
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHPh})(\text{Bu}^t\text{NCHCHNBU}^t)]$			8.57(s) [38]		3.84(d) [70], 4.51(d) [62], 5.78(dd) [82]	A, B
$[\text{PtCl}_2(\eta^2\text{-cis-C}_2\text{H}_2\text{Me}_2)(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.60(s)		8.80(s) [41]		5.22(m) [72]	A, B
$[\text{PtCl}_2(\eta^2\text{-trans-C}_2\text{H}_2\text{Me}_2)(\text{Bu}^t\text{NCHCHNBU}^t)]$	1.52(s)		8.66(s) [41]		5.3(m) [62]	A, B

^a δ In p.p.m., values of ⁿJ(¹⁹⁵Pt–¹H) in Hz are given in square brackets; q = quartet. ^b Route A: directly from $[\text{PtX}_3(\eta^2\text{-C}_2\text{H}_4)]$ or $[\text{PtX}_3(\eta^2\text{-olefin})]$; B by ligand exchange, see also the Scheme. ^{c, d} Spectra obtained of a 1:1 mixture of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ and $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ with R = Bu^t (c) or R = CMe₂Et (d). ^e H₂C–N–.

characteristic resonance patterns of (1) and the free olefin, see Table 1.

Physical Measurements.—Hydrogen-1 n.m.r. spectra were recorded on a Varian T-60 or XL-100 (Fourier-transform) spectrometer with SiMe₄ as internal standard; ¹³C n.m.r. spectra were obtained on a Varian CFT-20 with SiMe₄ as internal standard. Infrared spectra were measured on a Beckman 4250 spectrophotometer.

RESULTS

Exchange of σ -N- and σ,σ -N,N'-bonded Ligands.—The general route for the preparation of *trans*-[PtX₂(η^2 -olefin)L] complexes comprises the reaction of Zeise's salt or Zeise's dimer with the appropriate ligand L. When L is bidentate [e.g. RNCHCHNR, RN(H)CH₂CH₂N(H)R, R'NC₅H₃CH=NR, bipy, or dmphen] this route affords the five-co-ordinate complex [PtCl₂(η^2 -C₂H₄)(L-L)] containing the olefin and the bidentate ligand in the equatorial plane of a trigonal-bipyramidal array.

In the course of our study we found new alternative routes for the preparation of five-co-ordinate platinum-olefin complexes. First, the reaction of four-co-ordinate *trans*-[PtCl₂(η^2 -C₂H₄)(NC₅H₂Me₃-2,4,6)] with one of the σ,σ -N,N' ligands in a 1:1—1:3 molar ratio resulted in formation of [PtCl₂(η^2 -C₂H₄)(L-L)] in almost quantitative yields. Secondly, the reaction starting from five-co-ordinate (1) with RNCHCHNR, RN(H)CH₂CH₂N(H)R, R'NC₅H₃CH=NR, bipy, and dmphen likewise resulted in quantitative formation of the five-co-ordinate complexes [PtCl₂(η^2 -C₂H₄)(L-L)].

These substitution reactions were carried out in dichloromethane, acetone, or toluene using a 1:1—1:3 platinum-ligand molar ratio. The five-co-ordinate complexes formed

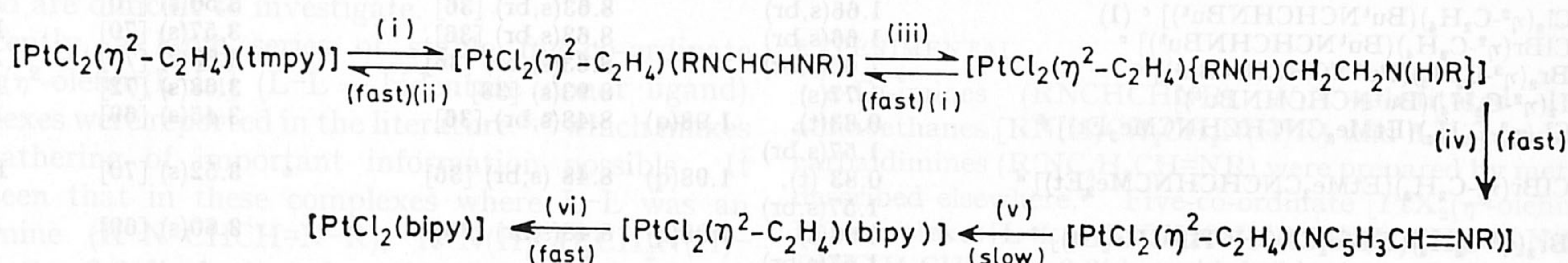
reactions could readily be followed by n.m.r. spectroscopy. This is illustrated by two examples.

The substitution reaction of [PtCl₂(η^2 -C₂H₄)(tmpy)] with Bu^tNCHCHNBu^t (3:4 molar ratio) in CDCl₃ at -40 °C followed by ¹H n.m.r. revealed a concomitant disappearance of [PtCl₂(η^2 -C₂H₄)(tmpy)] and free Bu^tNCHCHNBu^t ligand, and appearance of the five-co-ordinate complex (1) and accompanying exchanged tmpy ligand. The resonance patterns belonging to each of the components of the equilibrium mixture remained sharp while chemical-shift and coupling data [ⁿJ(¹⁹⁵Pt-¹H)] were similar to the data obtained for the pure compounds. This indicates that intermolecular exchange between the species is slow on the n.m.r. time scale, but that equilibrium is attained rapidly on the laboratory time scale.

The ¹³C n.m.r. spectra of a 1:1 molar mixture of (1) and EtMe₂CNCHCHNCMe₂Et in CDCl₃ (34 °C) showed four sharp resonance patterns corresponding to the respective components of the equilibrium mixture {i.e. Bu^tNCHCHNBu^t, EtMe₂CNCHCHNCMe₂Et, (1), and [PtCl₂(η^2 -C₂H₄)(EtMe₂CNCHCHNCMe₂Et)]}.

While MeNC₅H₃CH=NR and bipy are neither substituted by RNCHCHNR nor RN(H)CH₂CH₂N(H)R, MeNC₅H₃CH=NR is irreversibly substituted by bipy. This was concluded from the reaction of [PtCl₂(η^2 -C₂H₄)(MeNC₅H₃CH=NR)], which is stable in solution for several days, with bipy followed by ¹H n.m.r. spectroscopy. Slow formation of free MeNC₅H₃CH=NCMe₂Et, as well as unco-ordinated C₂H₄, pointed to the occurrence of the reaction sequence given in the Scheme.

One of the reaction products [PtCl₂(η^2 -C₂H₄)(bipy)], which is unstable in solution, has been studied in detail by Natile and co-workers.¹⁰ In our reaction a mixture of the red and yellow forms¹¹ of the [PtCl₂(bipy)] complex was obtained.



SCHEME (i) RNCHCHNR; (ii) 2,4,6-trimethylpyridine (tmpy); (iii) RN(H)CH₂CH₂N(H)R; (iv) NC₅H₃CH=NR, -RN(H)CH₂CH₂N(H)R; (v) bipy, -NC₅H₃CH=NR; (vi) -C₂H₄

were characterized by comparison of their ¹H and ¹³C n.m.r. and i.r. spectra with those of authentic samples obtained *via* the Zeise's salt route. Clear advantages of the two alternative methods over this latter route are the excellent solubilities of the four- and five-co-ordinate starting materials, absence of KCl or H₂O in the reaction mixture, and the easy removal of the soluble and volatile 2,4,6-trimethylpyridine or Bu^tNCHCHNBu^t from the final mixtures. The reactions, which were virtually instantaneous at 25 °C (slow at -50 °C), were reversible when the L-L ligand in the five-co-ordinate complexes was RNCHCHNR or RN(H)CH₂CH₂N(H)R.

Addition of excess of either unidentate 2,4,6-trimethylpyridine (tmpy) or bidentate R'NCHCHNR' or R'N(H)CH₂CH₂N(H)R' to a solution of [PtCl₂(η^2 -C₂H₄)(L-L)] afforded a quantitative substitution of the σ,σ -N,N'-bonded ligand. For L-L = R'NC₅H₃CH=NR or bipy no substitution was observed even when a large excess of tmpy, R'NCHCHNR', or R'N(H)CH₂CH₂N(H)R' was used. These substitution

Exchange of the Halogen Atoms.—The 1:6 molar ratio reactions of [PtCl₂(η^2 -C₂H₄)(L-L)] [L-L = RNCHCHNR or RN(H)CH₂CH₂N(H)R] with NaI in acetone afforded ultimately (24 h) orange-red [PtI₂(η^2 -C₂H₄)(L-L)]. The displacement of the Cl atoms by I was established by the observation of the characteristic Pt-X absorptions in the i.r. spectra of the compounds and the chemical-shift position of the ethylene resonance in the ¹H n.m.r. spectrum [ν (Pt-I) 172 cm⁻¹, δ (CH₂=CH₂) 3.68 p.p.m., ²J(¹⁹⁵Pt-¹H) 72 Hz], see also Table 1.

The reaction with NaBr is considerably slower and requires repeated removal of the NaCl-NaBr precipitate followed by addition of fresh NaBr. A better route for obtaining [PtBr₂(η^2 -C₂H₄)(L-L)] appeared to be the reaction of K[PtBr₃(η^2 -C₂H₄)] with L-L {[PtBr₂(η^2 -C₂H₄)(Bu^tNCHCHNBu^t)], ν (Pt-Br) 256 cm⁻¹}.

In order to exclude the possibility that these halogen-exchange reactions occur *via* intermediate formation of Na[PtX₃(η^2 -C₂H₄)] the 1:1 reaction of [PtCl₂(η^2 -C₂H₄)-

TABLE 2

Carbon-13 n.m.r. data for $[\text{PtX}_2(\eta^2\text{-olefin})(\text{Bu}^t\text{NCHCHNBu}^t)]$ complexes ^a

Complex	CH ₃	C-N	C=N	C=C	O=CCH ₃	C=O
$[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ ^b (1)	30.45	64.31 (24)	156.69	37.98 (297)		
$[\text{PtClBr}(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ ^b	30.87	64.31 (24)	157.14	36.78 (286)		
$[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ ^b	31.27	64.31 (24)	157.59	35.46 (295)		
$[\text{PtI}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$	32.17	65.05 (24)	162.14	33.92 (294)		
$[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})(\text{Bu}^t\text{NCHCHNBu}^t)]$ -16 °C	29.43,	64.71,	156.89,	33.68 (289),	50.97	171.38
	30.35	65.17 (24)	158.28	38.54 (317)		
	39.29	64.95 (24)	157.68	34.64 (290),	50.50	171.21
			39.40 (321)			
$[\text{PtCl}_2(\eta^2\text{-cis-C}_2\text{H}_2(\text{CO}_2\text{Me})_2)(\text{Bu}^t\text{NCHCHNBu}^t)]$	29.94	65.87	158.43	37.55 (340)	51.32	168.71

^a δ In p.p.m. values of $^nJ(^{195}\text{Pt}-^{13}\text{C})$ are given in parentheses, recorded as CDCl_3 solutions. ^b Spectra obtained of a 1 : 1 mixture of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ and $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ in CDCl_3 after 15 d.

(RNCHCHNR) with $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ ($\text{R} = \text{Bu}^t$ or CMe_2Et) in CDCl_3 was followed by ^1H and ^{13}C n.m.r. spectroscopy. (The various halogen complexes have distinctly different resonance patterns, see Tables 1 and 2.)

In addition to the pattern of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ and $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$, a new set of resonances was observed which was assigned to the mixed complex $[\text{PtClBr}(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$, see Figure 1.

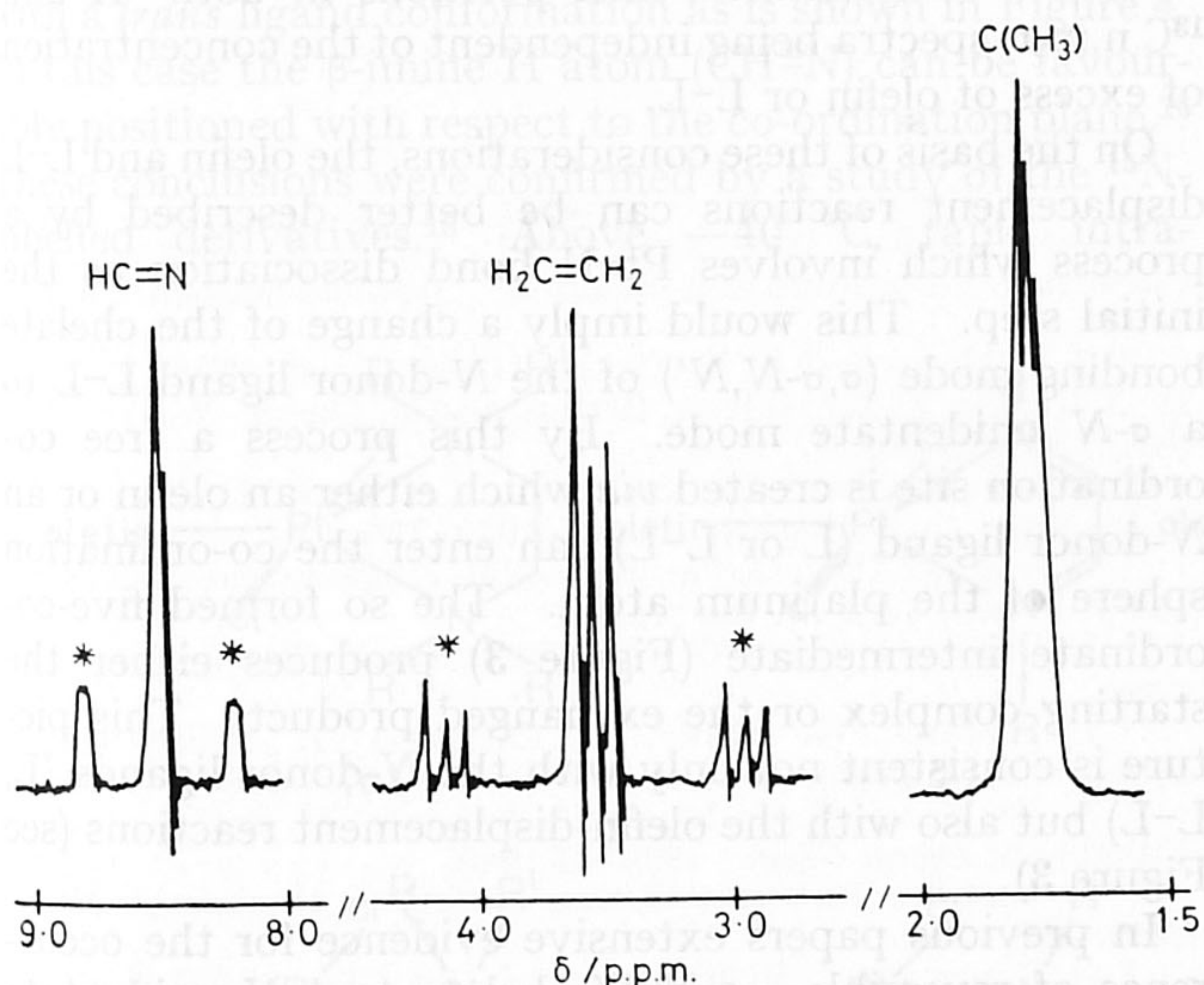


FIGURE 1 Proton n.m.r. spectrum of a mixture of $[\text{PtX}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ ($\text{X} = \text{Cl}$ or Br) in CDCl_3 after standing for 15 d. Besides $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ and $[\text{PtBr}_2(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$, the mixed-halide product $[\text{PtClBr}(\eta^2\text{-C}_2\text{H}_4)(\text{Bu}^t\text{NCHCHNBu}^t)]$ is also present in solution. $^nJ(^{195}\text{Pt}-^1\text{H})$ is indicated by asterisks

Olefin Exchange.—The number of $[\text{PtX}_2(\eta^2\text{-olefin})\text{L}]$ and $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L}-\text{L})]$ complexes which are directly available from the reaction of olefin analogues of Zeise's salt with $\text{L}-\text{L}$ is restricted because only a few stable $\text{K}[\text{PtX}_3(\eta^2\text{-olefin})]$ complexes are available. The last species have to be prepared (i) via the exchange of C_2H_4 in Zeise's salt by the respective olefin or (ii) via a reaction of olefin with $\text{K}_2[\text{PtCl}_4]$ (catalyzed by $\text{SnCl}_2 \cdot n\text{H}_2\text{O}$): $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)] + \text{olefin} \rightarrow \text{K}[\text{PtCl}_3(\eta^2\text{-olefin})] + \text{C}_2\text{H}_4$.

During our study we found that direct substitution of the ethylene by olefin in five-co-ordinate $[\text{PtX}_2(\eta^2\text{-ethylene})(\text{L}-\text{L})]$ was also possible. In Table 1 it has been indicated by which routes the compounds are accessible. These results show that this direct olefin exchange depends on the nature of the olefin and the chelating coligand. In general, exchange was observed only with RNCHCHNR and $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}$ as a coligand and with certain mono-

(styrene, methyl acrylate, or acrylaldehyde) or di-substituted (*cis*- and *trans*-but-2-ene, dimethyl maleate, or maleic anhydride) olefins.

Reaction of (1) with stilbene, dimethyl fumarate, crotonaldehyde, or $\text{CH}_2=\text{C}(\text{Me})\text{CHO}$ was not observed. In these cases the starting material could be recovered almost quantitatively after reaction periods of up to 170 h. Likewise, the $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{MeNC}_5\text{H}_3\text{CH}=\text{NCMe}_2\text{Et})]$ complex appeared to be unreactive with respect to exchange with, for example, methyl acrylate or maleic anhydride.

The study of the olefin-ethylene exchange in bipy complexes was hampered by solution instability.

The $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{L}-\text{L})]$ complexes were characterized by ^1H and ^{13}C n.m.r. and i.r. spectroscopy (see Tables 1 and 2) using the assignment criteria emerging from our detailed structural investigation of five-co-ordinated ethylene, butene, and styrene complexes $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L}-\text{L})]$ [$\text{L}-\text{L} = \text{RNCHCHNR}$, $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}$, or $\text{R}'\text{NC}_5\text{H}_3\text{CH}=\text{NR}$].^{4,5} In several cases the complexes were compared with samples of the complexes obtained *via* other routes. The styrene complexes, for example, were also prepared starting from $\text{K}[\text{PtCl}_3(\eta^2\text{-styrene})]$. It appeared that the new complexes (olefin = methyl acrylate, maleic anhydride, dimethyl maleate, and acrylaldehyde) also have a trigonal-bipyramidal structure indicating that substitution of olefins takes place with retention of configuration.

DISCUSSION

The present results show that the $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L}-\text{L})]$ $[\text{RNCHCHNR}$ or $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}]$ complexes can undergo ligand-displacement reactions of all three types of ligands with retention of the special arrangement of the ligands in the trigonal-bipyramidal array. Exchange of C_2H_4 in $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RR}'\text{NCH}_2\text{CH}_2\text{NRR}')]$ [$\text{R} = \text{CH}_3$, $\text{R}' = (\text{R})\text{-CH}(\text{CH}_3)\text{C}_6\text{H}_5$] was already established, using labelled $^{14}\text{C}_2\text{H}_4$, by Panunzi¹² and co-workers.⁷ The mechanism of these displacement reactions has to account for the following general observations. The rate of ligand displacement, which is in all cases slow on the n.m.r. time scale, follows the order halide < olefin < *N*-donor ligands, while the reactions strongly depend on the nature of the bidentate *N*-donor ligand. Whereas with RNCHCHNR and $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}$ the displacement is a reversible process, exchange of these *N*-donor ligands with bipy or pyridinecarbaldimines appeared to be irreversible. Finally, the occurrence of ligand displacement *via* an associative process as the first step seems unlikely because this would require rehybridization

of the platinum(II) orbitals in order to allow increase of the co-ordination number around the platinum centre from five (18-electron) $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L-L})]$ to six (20 electron) in $[\text{PtX}_2(\eta^2\text{-olefin})(\text{L-L})\text{L}']$.

Halogen-Halogen Exchange.—An important aspect of the halogen-halogen exchange reaction of $[\text{PtX}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ is the observation that no *trans*-to-*cis* isomerization occurs. This can be explained on the basis of the strong site preference of the *N*-donor ligand for equatorial sites in the trigonal-bipyramidal array. As a consequence, the olefin will reside in the equatorial plane because of the mutual stabilizing effect of these ligands with the platinum centre (*cf.* the M-olefin bonding scheme of Dewar, and Chatt and Duncanson).^{4,13,14}

It is known that, in the presence of excess of NaX, $[\text{PtX}_3(\eta^2\text{-C}_2\text{H}_4)]^-$ undergoes fast halide exchange.¹ In principle, formation of a $[\text{PtX}_3(\eta^2\text{-C}_2\text{H}_4)]^-$ species from $[\text{PtX}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ by displacement of the ligand L-L is possible. Subsequent association of L-L with concomitant Pt-X bond cleavage could explain the halogen exchange observed for $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ and $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)\{\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}\}]$ with NaBr or NaI. This process requires complete loss of L-L. Moreover, the $[\text{PtX}_3(\eta^2\text{-C}_2\text{H}_4)]^-$ intermediate could not explain the scrambling of halogens in the reaction of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{RNCHCHNR})]$ with its bromo-analogue. Therefore we prefer to describe this exchange reaction by initial Pt-X bond dissociation leading to cationic $[\text{PtX}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]\text{X}$ intermediates.

Recently Maresca *et al.*¹⁰ found in their study of the solvent-dependent decomposition of $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ [L-L = *N,N,N',N'*-tetramethylethylenediamine (tmen) or bipy] complexes that stable intermediates $[\text{PtCl}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]\text{X}$ were formed. Complexes of this type were stabilized with suitable counter ions (ClO_4^-) and the structure of $[\text{PtCl}(\eta^2\text{-C}_2\text{H}_4)(\text{tmen})][\text{ClO}_4^-]$ was determined by X-ray methods¹⁵ (see Figure 2).

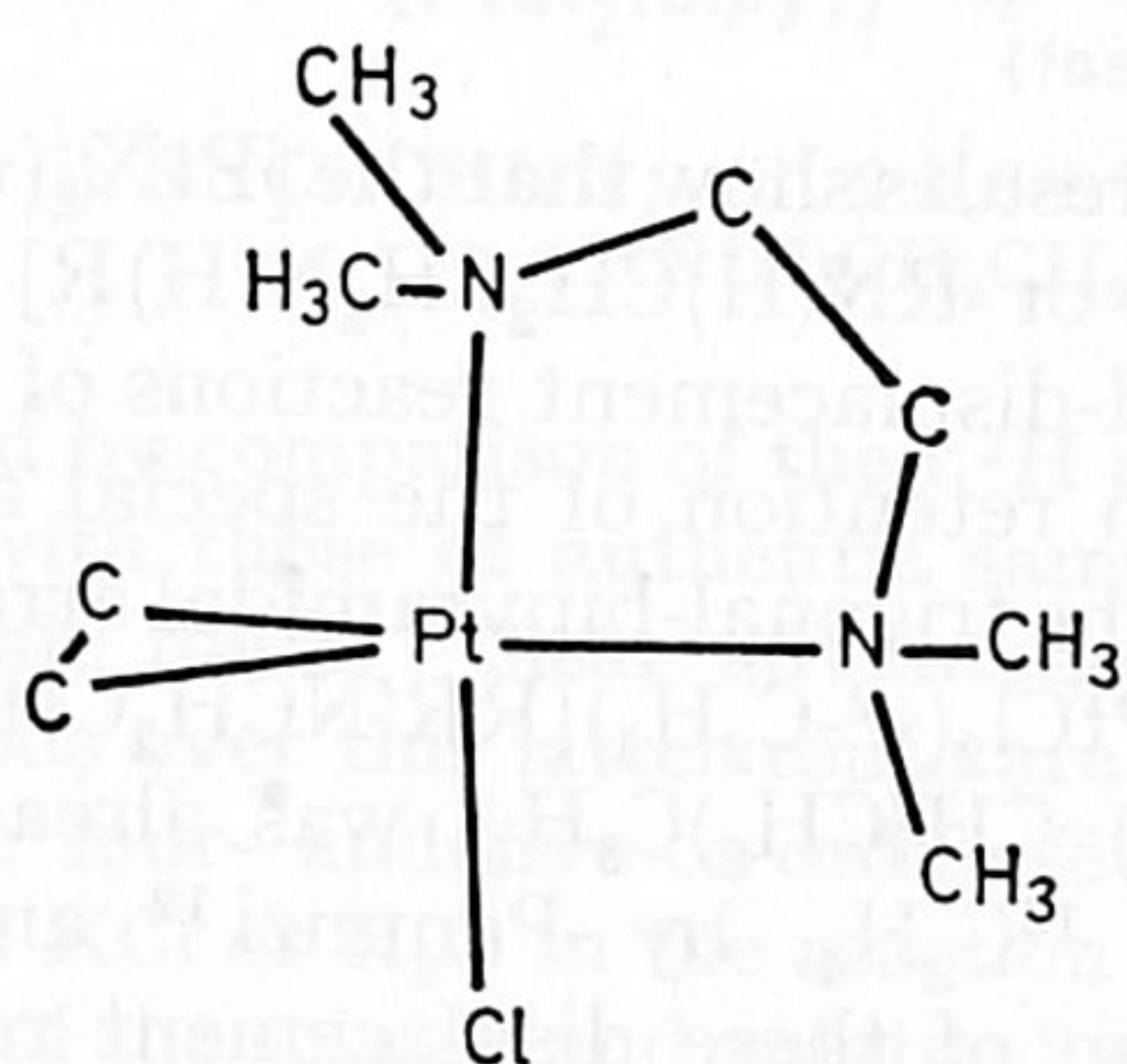


FIGURE 2 Crystal structure of $[\text{PtCl}(\eta^2\text{-C}_2\text{H}_4)(\text{tmen})][\text{ClO}_4^-]$ (ref. 15)

However, our attempts to prepare stable $[\text{PtX}(\eta^2\text{-olefin})(\text{RNCHCHNR})]\text{X}$ complexes by treating (1) with $\text{Na}[\text{BF}_4]$, $\text{Tl}[\text{PF}_6]$, or $[\text{NH}_4][\text{PF}_6]$ failed, although we did observe decomposition (Pt- $\eta^2\text{-C}_2\text{H}_4$ bond dissociation). With silver salts ($\text{Ag}[\text{NO}_3]$, $\text{Ag}[\text{BF}_4]$, or $\text{Ag}[\text{O}_3\text{SCF}_3]$) by contrast, rapid $\text{Bu}^t\text{NCHCHNBu}^t$ transfer from (1) to Ag^+ did occur.

On the basis of the results of Maresca *et al.*,^{10,15} a plausible route for the halogen-halogen exchange would

be formation of a $[\text{PtX}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]^+$ cation which can then interact with neutral $[\text{PtX}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ *via* one of the axial halogen ligands. This would result in formation of a binuclear cationic intermediate $[(\text{L-L})(\eta^2\text{-C}_2\text{H}_4)\text{ClPt-Cl-PtBr}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]^+$ which can dissociate to produce either the starting species or the exchanged products. In this proposed mechanism the *N*-donor ligand remains $\sigma,\sigma\text{-N,N'}$ -chelate bonded during the whole displacement reaction. Likewise, olefin dissociation is not possible since in separate experiments we found that this leads irreversibly to *cis*- $[\text{PtCl}_2(\text{L-L})]$ complexes.

Olefin and N-Donor Ligand Displacement.—Since both the olefin- and the ligand-displacement reactions are much faster than the halogen-exchange reactions it seems unlikely that these displacements proceed *via* a cationic intermediate $[\text{PtCl}(\eta^2\text{-olefin})(\text{L-L})]^+$. Furthermore, we have shown that the platinum-olefin bonds in the five-coordinate $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{L-L})]$ [L-L = RNCHCHNR , $\text{R}'\text{NC}_5\text{H}_3\text{CH}=\text{NR}$, or $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}$] complexes are inert on the n.m.r. time scale with the coupling constants and chemical-shift positions in both ^1H and ^{13}C n.m.r. spectra being independent of the concentration of excess of olefin or L-L.

On the basis of these considerations, the olefin and L-L displacement reactions can be better described by a process which involves Pt-N bond dissociation as the initial step. This would imply a change of the chelate bonding mode ($\sigma,\sigma\text{-N,N'}$) of the *N*-donor ligand L-L to a $\sigma\text{-N}$ unidentate mode. By this process a free co-ordination site is created *via* which either an olefin or an *N*-donor ligand (L or L-L) can enter the co-ordination sphere of the platinum atom. The so formed five-coordinate intermediate (Figure 3) produces either the starting complex or the exchanged product. This picture is consistent not only with the *N*-donor ligands (L, L-L) but also with the olefin-displacement reactions (see Figure 3).

In previous papers extensive evidence for the occurrence of reversible $\sigma,\sigma\text{-N,N'}$ chelate to $\sigma\text{-N}$ unidentate processes in square-planar $[\text{PtX}_{2-n}(\text{PR}_3)_{1+n}(\text{L-L})]\text{X}_n$ ($n = 0$ or 1) complexes has been put forward.¹⁶⁻¹⁹ In these intramolecular rearrangements the bidentate *N*-donor ligand changes its point of attachment to the Pt atom (head-to-tail rearrangement) *via* five-coordinate intermediates. The kinetics of this fluxional behaviour depend strongly on the stereochemistry of the *N*-donor ligands. A common feature of these ligands shown in Figure 4 is that in the *syn* conformation the electron pairs on the nitrogen atoms are suitably positioned for $\sigma,\sigma\text{-N,N'}$ chelation. A difference, however, is the flexibility of the skeleton for rotation around the central C-C bond in the unidentate co-ordination mode and the steric consequences of such a rotation with respect to possible interaction of the metal atom with the substituents connected to the β -imine C atom. Considering the series shown in Figure 4, it is obvious that the tendency towards unidentate Pt-N interaction will increase on going from bipy to $\text{RN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{R}$. This is indeed the case. For example, Dixon¹⁷ studied $[\text{PtCl}$ -

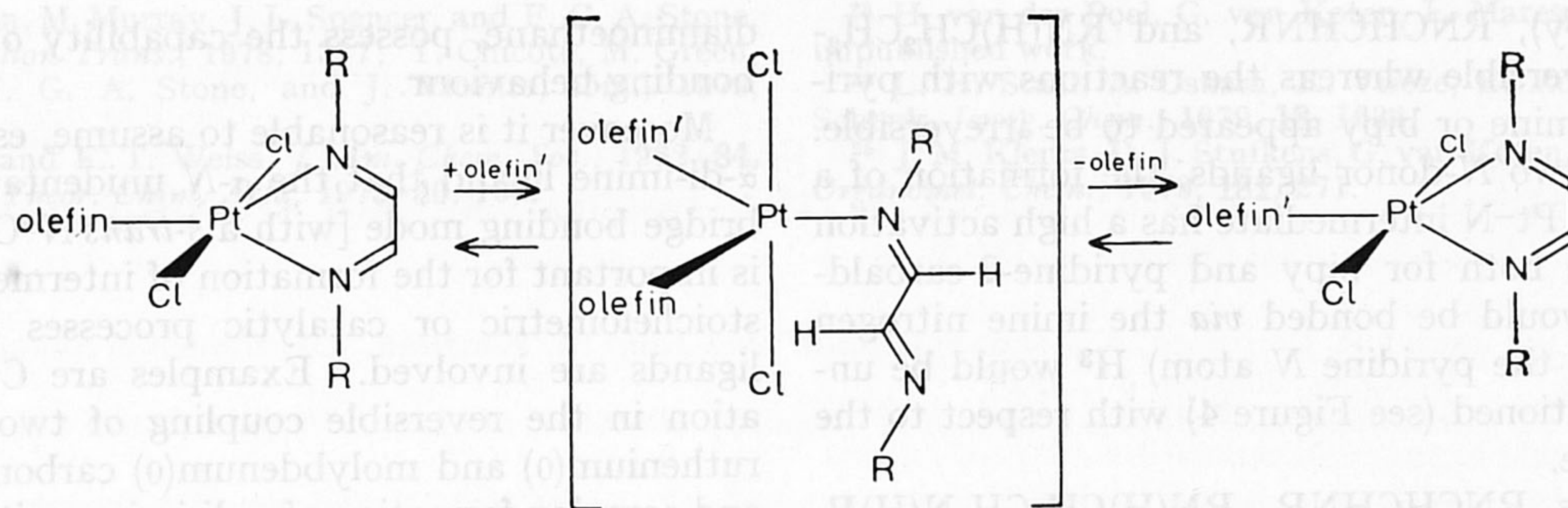


FIGURE 3 Mechanism proposed for olefin exchange in $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{L-L})]$ complexes. Initial Pt-N bond dissociation provides a four-co-ordinate species (not shown) which has a free co-ordination site for the incoming olefin. Similar intermediates are proposed for the bidentate N -donor ligand exchange when olefin is replaced by $\text{L-L}'$ for the incoming ligand and olefin is replaced by RNCHCHNR as leaving group

$(\text{PR}_3)_2(\text{L-L})\text{X}$ ($\text{L} = \text{bipy}$ or phen) complexes and found that the slow exchange limit was not reached at -80°C . However, ^1H and ^{13}C n.m.r. studies of $[\text{PtCl}_2(\text{PR}_3)(\text{RNCHCHNR})]$ having the less sterically hindered ligand (see above) revealed that in the slow-exchange limit (*ca.* -40°C) the RNCHCHNR ligand is unidentate with a *trans* ligand conformation as is shown in Figure 4. In this case the β -imine H atom ($\text{CH}=\text{N}$) can be favourably positioned with respect to the co-ordination plane.¹⁶ These conclusions were confirmed by a study of the ^{15}N -labelled derivatives.¹⁸ Above -40°C , rapid intra-

molecular N,N' site exchange took place. It should be mentioned that in these complexes a phosphine ligand acts as coligand instead of an olefinic ligand.

Maresca *et al.*¹⁹ showed that $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)\{\text{R}^1\text{R}^2\text{N}(\text{CH}_2)_n\text{NR}^1\text{R}^2\}]$ complexes for $n = 3$ exist only at low temperature in the five-co-ordinate form; at higher temperature they have to be formulated as four-co-ordinate platinum compounds with unidentate $\text{R}^1\text{R}^2\text{N}(\text{CH}_2)_3\text{NR}^1\text{R}^2$.

These results provide an explanation for the observation that displacement of L-L in $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$

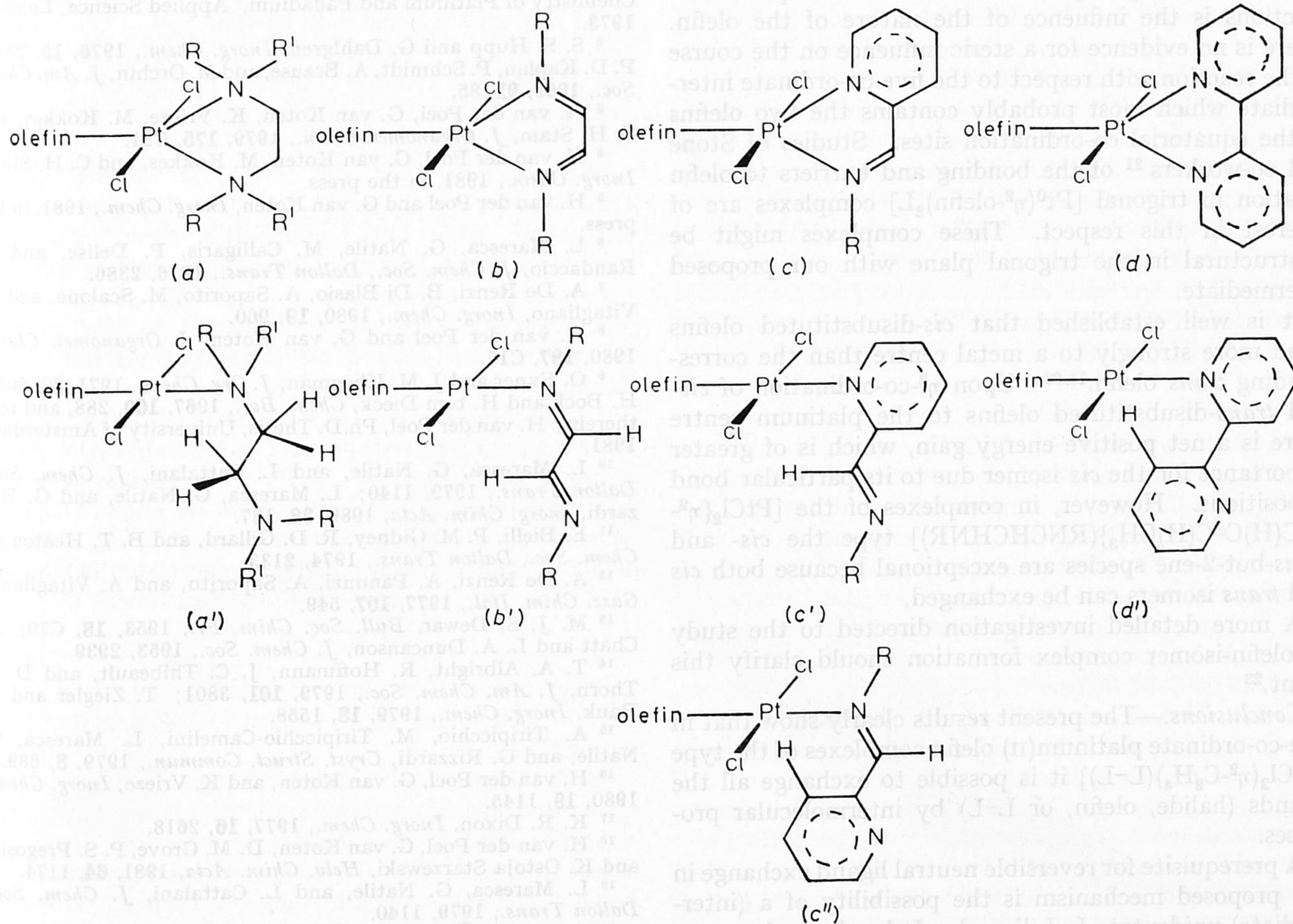


FIGURE 4 Comparison of the $\sigma, \sigma\text{-}N, N'$ -chelating [(a)–(d)] and $\sigma\text{-}N$ unidentate [(a')–(d'), (c'')] bonding mode of several bidentate N -donor ligands. Structure (c') is unfavourable since the pyridine N -donor atom is a much poorer electron-releasing atom than the alkyl imine N atom

by pyridine (py), RNCHCHNR, and RN(H)CH₂CH₂-N(H)R was reversible whereas the reactions with pyridine-2-carbaldimine or bipy appeared to be irreversible. For the latter two *N*-donor ligands, the formation of a σ -*N* unidentate Pt-N intermediate has a high activation barrier because both for bipy and pyridine-2-carbaldimine (which would be bonded *via* the imine nitrogen rather than *via* the pyridine *N* atom) H³ would be unfavourably positioned (see Figure 4) with respect to the platinum centre.

In the series RNCHCHNR, RN(H)CH₂CH₂N(H)R, and py the tendency towards four-co-ordination increases and for the py ligand it has been shown that only under special conditions (below -30 °C with excess of py) could a five-co-ordinate species, in low concentration, be observed by n.m.r.²⁰

In the olefin-displacement reactions of [PtCl₂(η^2 -C₂H₄)(L-L)] it was only for L-L = RNCHCHNR or RN(H)CH₂CH₂N(H)R that we observed (reversible) olefin displacement. The proposed displacement of one *N* co-ordination site of the L-L ligand by the second olefin ligand is analogous to the mechanisms proposed for olefin exchange in square-planar platinum-olefin complexes. In the latter case it is always the non-olefinic ligand which is the 'leaving' group.^{1,2}

An interesting aspect of these olefin-displacement reactions is the influence of the nature of the olefin. There is no evidence for a steric influence on the course of the reaction with respect to the five-co-ordinate intermediate which most probably contains the two olefins in the equatorial co-ordination sites. Studies of Stone and co-workers²¹ of the bonding and barriers to olefin rotation in trigonal [Pt⁰(η^2 -olefin)₂L] complexes are of interest in this respect. These complexes might be isostructural in the trigonal plane with our proposed intermediate.

It is well established that *cis*-disubstituted olefins bond more strongly to a metal centre than the corresponding *trans* olefin.^{1b,22} Upon η^2 -co-ordination of *cis*- and *trans*-disubstituted olefins to the platinum centre there is a net positive energy gain, which is of greater importance for the *cis* isomer due to its particular bond oppositions. However, in complexes of the [PtCl₂{ η^2 -H₃C(H)C=C(H)CH₃}(RNCHCHNR)] type the *cis*- and *trans*-but-2-ene species are exceptional because both *cis* and *trans* isomers can be exchanged.

A more detailed investigation directed to the study of olefin-isomer complex formation should clarify this point.²³

Conclusions.—The present results clearly show that in five-co-ordinate platinum(II) olefin complexes of the type [PtCl₂(η^2 -C₂H₄)(L-L)] it is possible to exchange all the ligands (halide, olefin, or L-L) by intermolecular processes.

A prerequisite for reversible neutral ligand exchange in the proposed mechanism is the possibility of a (intermediate) unidentate L-L ligand. It has been shown on both stereochemical and electronic grounds that the α -di-imine ligand and its hydrogenated analogue, 1,2-

diaminoethane, possess the capability of such versatile bonding behaviour.

Moreover it is reasonable to assume, especially for the α -di-imine ligand that the σ -*N* unidentate or σ -*N*, σ -*N'* bridge bonding mode [with a *s-trans* N=C-C=N skeleton] is important for the formation of intermediates in either stoichiometric or catalytic processes in which such ligands are involved. Examples are C-C bond formation in the reversible coupling of two α -di-imines in ruthenium(0) and molybdenum(0) carbonyl chemistry²⁴ and complex formation of α -di-imines with alkyl aluminium (AlR₃) which occurs with concomitant -C=N- bond reduction and alkyl transfer.²⁵

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Comparison with $\epsilon_{\text{P}}(\text{H})$ n.m.r. spectra obtained from the initial stages of reaction ² indicate that the red species can be assigned either as $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_2]$ or $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_3]$. However, spectroscopic metric determination of the overall formation constant of this species indicates that the latter assignment must be preferred. Solutions in which the ratio $\text{Fe}^{2+}:\text{P}(\text{OMe})_2$ is 2:1, 1:1 or 1:2 are yellow but their electronic spectra contain the two bands described above in addition to a broad asymmetric band with a maximum at 11 300 cm^{-1} . Typical of high-spin Fe^{2+} the former is a new band which does not produce consistent values for the formation constant but consistent values are obtained if a 1:2 complex is assumed, the latter value being $(1.0 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$. We conclude that the formation of $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_2]$ is very rapid and that this species is not detectable using our stopped-flow equipment. The implication that the transition from high- to low-spin Fe^{2+} occurs with the formation of $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_2]$ is supported by n.m.r. spectra assigned to this species. The n.m.r. spectra of a 2:1 complexation ratio is also suggestive that it has a d^6 configuration. This is the definitive assignment.

In the presence of a large excess of $\text{P}(\text{OMe})_2$, the red species is the red species, $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_3]$. The pseudo-first-order rate constants for the concentration of $\text{P}(\text{OMe})_2$ (Figure 1) which can be written in an expression of the form (1). Constants k_1 and k_2 were determined by least-squares analysis of the reciprocal of equation (1) to be $4.17 \pm 0.20 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $4.04 \pm 0.18 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

Both dissociative and interchange mechanisms can give rise to rate laws of this type,⁸ and it is not clear that the limiting rate behaviour observed could also result from a medium effect, since the composition of the solvent changes over the range examined. However, such a marked effect, and change in order, is considered unlikely.

Stopped-flow Studies—Addition of an excess of $\text{P}(\text{OMe})_2$ to a colourless solution of $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_2]$ in MeCN at room temperature results in the formation of a red soluble species. Its formation is too rapid to be followed by electronic spectroscopy using conventional methods, but it is conveniently within the stopped-flow range. The electronic spectrum of the red species, obtained by point-by-point determination over the range 17 000–33 000 cm^{-1} , $\text{Fe}^{2+}:\text{P}(\text{OMe})_2 = 1:3$ (100 concentration), consists of two bands with maxima at 23 000 and 29 000 cm^{-1} , $\epsilon = 320$ and 270 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. This spectrum is essentially identical to the 'initial' spectrum of the reaction, and was obtained by conventional means,² and is independent of the ratio $\text{Fe}^{2+}:\text{P}(\text{OMe})_2$ over the range 1:30–1:500. By analogy with the spectra of $[\text{Fe}(\text{NCMe})_4(\text{P}(\text{OMe})_2)_2]$ (rel. λ_{max} 23 000 cm^{-1} , $\epsilon = 320$) (rel. λ_{max} 29 000 cm^{-1} , $\epsilon = 270$) the red species has a ground state derived from a d^6 configuration.