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PREPARATION AND CHARACTERIZATION OF CHELATING MONOOLEFIN-ANILINE LIGANDS AND THEIR PLATINUM(II) COMPLEXES

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Summary

A number of new chelating monoolefin-aniline ligands have been prepared and treated with platinum(II). ^1H NMR spectra of the ligands and their platinum(II) complexes have been recorded in order to investigate the bonding between the platinum and the olefin group. This has shown that all the olefins except *o*-vinyl-*N,N*-diphenylaniline bond to the platinum through both the olefin and the amine group to give complexes similar to those formed by the chelating monoolefin-phosphines and -arsines.

Reaction of the complex $\text{Pt}(\text{IMN})\text{Cl}_2$ with a series of anionic ligands *L* gave complexes of the type $\text{Pt}(\text{IMN})\text{CIL}$. Comparison of the ^{195}Pt – ^1H (olefin) coupling constants enabled a *trans*-influence series to be determined for this type of complex.

Introduction

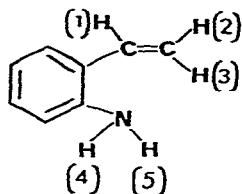
In a preliminary communication we reported the ^1H NMR spectral data for the ligands *o*-vinylaniline (VHN), *o*-vinyl-*N,N*-dimethylaniline (VMN), *o*-isopropenylaniline (IHN) and *o*-isopropenyl-*N,N*-dimethylaniline (IMN) and their platinum(II) complexes [1]. VMN [2] and IMN [3,4] have since been used for studying the coordination of several other ligands to platinum(II). We now report the details of the preparation and characterization of these ligands and complexes as well as a number of new chelating monoolefin-aniline ligands and their platinum(II) complexes.

The aniline ligands are the Group V analogues of the monoolefin-phosphines and -arsines which have received considerable attention with respect to the reactivity of the coordinated olefin [5].

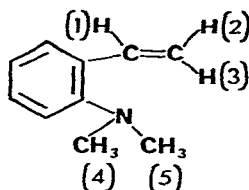
Experimental

Preparation of ligands

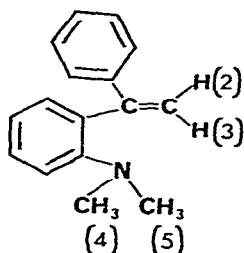
o-Vinylaniline (VHN). *o*-Nitrocinnamic acid (31.3 g, 0.16 mol) was prepared by reaction of *o*-nitrobenzaldehyde (30.2 g, 0.2 mol) with malonic acid (20.8 g, 0.2 mol) in pyridine [6]. The nitrocinnamic acid (30.0 g, 0.15 mol) was decarboxylated by the method of Wiley and Smith [7] to produce *o*-nitrostyrene (2.4 g, 0.016 mol). Reduction of the nitro group with tin and hydrochloric acid [8] and vacuum distillation of the crude product yielded *o*-vinylaniline (1.3 g, 0.011 mol) as a pale yellow oil, b.p. (25 mmHg) = 98–100° C. Anal. Found: C, 81.06; H, 7.63; N, 11.40. Calcd. for C_8H_7N : C, 80.63; H, 7.61; N, 11.76%.



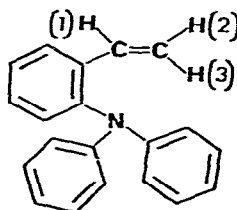
I, VHN

o-Vinylaniline

II, VMN

o-Vinyl-*N,N*-dimethylaniline

III, PVMN

o-(1-Phenylvinyl)-*N,N*-dimethylaniline

IV, VPN

o-Vinyl-*N,N*-diphenylaniline

o-Vinyl-*N,N*-dimethylaniline (VMN). *o*-Vinyl-*N,N*-dimethylaniline was prepared from indoline by the method of Booth, King and Parrick [9]. Anal. Found: C, 81.22; H, 8.93; N, 9.79. Calcd. for $C_{10}H_{15}N$: C, 81.58; H, 8.90; N, 9.52%.

o-Vinyl-*N,N*-diphenylaniline (VPN). *N,N*-Diphenylanthranilic acid was prepared [10] by refluxing a mixture of *N*-phenylanthranilic acid (50.0 g, 0.23 mol), potassium carbonate (55.0 g, 0.45 mol), iodobenzene (82.0 g, 0.52 mol), copper powder (2 g) and copper oxide (2 g) in nitrobenzene (150 ml) for four hours. After steam distillation to remove the nitrobenzene and any iodobenzene the purple mixture was boiled with activated charcoal and filtered. The filtrate was then acidified with dilute hydrochloric acid (3 *M*). The green-yellow precipitate

of *N,N*-diphenylanthranilic acid (43.5 g, 0.15 mol, 63.8%) was collected, washed with water, and dried.

A solution of the acid (41.0 g, 0.14 mol) in dry tetrahydrofuran (400 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (90 g, 0.24 mol) in dry tetrahydrofuran (200 ml). The mixture was refluxed for three hours, and the excess lithium aluminium hydride was then decomposed by slow addition of water. The resulting alkaline mixture was neutralized with sulphuric acid (6 *M*) and extracted with ether (3 × 300 ml). The combined ether extracts were dried (Na_2SO_4) and the solvent removed to produce crude *N,N*-diphenyl-*o*-aminobenzyl alcohol as a brown-green oil which solidified on standing. Recrystallization from petroleum spirit yielded a pale brown solid, m.p. 72–74°C (30.5 g, 0.11 mol, 79%). The NMR spectrum (CDCl_3) showed signals due to: Ar—H (m, δ = 6.72–7.62 ppm 14 protons); Ar—CH₂— (s, δ = 4.40 ppm, 2 protons); O—H (s, δ = 2.18 ppm, 1 proton). Anal. Found: C 82.82; H, 6.09; N, 5.05. Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}$: C, 82.88; H, 6.23; N, 5.09%.

A mixture of chromium trioxide (60 g, 0.6 mol) in pyridine (400 ml) was cooled and stirred and a solution of *N,N*-diphenyl-*o*-aminobenzyl alcohol (32.0 g, 0.12 mol) in pyridine (100 ml) added slowly. Stirring was continued for 2 hours, followed by the addition of methanol (200 ml). The mixture was then allowed to stand at room temperature for 2 hours after which sodium hydroxide solution (125 g/400 ml) was added and the precipitated chromium hydroxide collected by filtration. The solution was extracted with ether (4 × 200 ml) and the combined ether extracts dried (Na_2SO_4). Removal of the solvent yielded a yellow-brown oil. This was chromatographed on alumina with an eluant of petroleum spirit/ether (95/5). Bright yellow crystals of *N,N*-diphenyl-*o*-aminobenzaldehyde separated from the solution on standing (20.5 g, 0.075 mol, 65%). M.p. = 74–75°C. The NMR spectrum showed signals due to: Ar—H (m, δ = 6.77 → 8.05 ppm, 14 protons); —CHO (s, δ = 10.30 ppm, 1 proton). Anal. Found: C, 83.68; H, 5.58; N, 5.06. Calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}$: C, 83.49; H, 5.53; N, 5.13%.

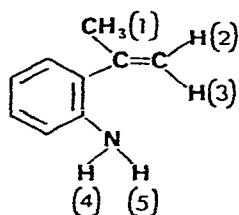
o-Vinyl-*N,N*-diphenylaniline (VPN) was prepared in the following manner [11]. Magnesium turnings (3.2 g, 0.13 mol) and a crystal of iodine were placed in a flask containing dry tetrahydrofuran (50 ml) under nitrogen, and a solution of *N,N*-diphenyl-*o*-aminobenzaldehyde (10.8 g, 0.04 mol) and diiodomethane (120 g, 0.045 mol) in tetrahydrofuran (80 ml) was slowly added with stirring. The mixture was refluxed for two hours, then cooled and added to ice. Sulphuric acid (100 ml, 1.5 *M*) was added and the solution extracted with ether (3 × 200 ml). The combined extracts were washed with sodium bisulphite solution (10%, 100 ml) followed by water (2 × 100 ml), and then dried (Na_2SO_4). Removal of the solvent and chromatography on alumina (petroleum spirit eluant) yielded a colourless solution, from which colourless crystals of *o*-vinyl-*N,N*-diphenylaniline deposited on standing: Yield = 1.5 g, 5.5 mmol, 13.8%, M.p. = 87.5–89.0°C. Anal. Found: C, 88.62; H, 6.36; N, 5.05. Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}$: C, 88.52; H, 6.32; N, 5.16%.

o-(1-Phenylvinyl)-*N,N*-dimethylaniline (PVMN). *o*-Aminobenzophenone was methylated by the method of Gilman and Banner [12] to yield, *N,N*-dimethyl-*o*-aminobenzophenone.

Methylmagnesium iodide was prepared by adding a solution of methyl iodide

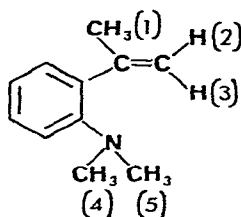
(9.6 g, 0.069 mol) in dry ether (100 ml) slowly, with stirring, to magnesium turnings (1.35 g, 0.056 mol) in dry ether (150 ml). To the stirred mixture was added a solution of *N,N*-dimethyl-*o*-aminobenzophenone (8.0 g, 0.036 mol) in ether (100 ml). The mixture was refluxed for two hours and then stirred at room temperature overnight. Hydrochloric acid (3 *M*, 100 ml) was added slowly and the solution neutralized with ammonia (3 *M*). The neutralized solution was then extracted with ether (3 × 100 ml) and the combined ether extracts washed with sodium bisulphite (10%, 100 ml), water (100 ml), and brine (100 ml) and then dried (Na_2SO_4). Removal of the solvent yielded a brown oil which solidified on standing. Chromatography of the oil on alumina with petroleum spirit/ether (90%) eluant gave a brown solution which deposited pale brown crystals of *N,N*-dimethyl-*o*-amino-(1-phenyl-1-methyl)benzyl alcohol on standing. Yield 6.1 g, 0.026 mol, 72.2%, M.p. = 54–56°C. The NMR spectrum showed signals due to: Ar-*H* (m, δ = 7.08–7.65 ppm, 9 protons); N- CH_3 (s, broad, δ = 2.32, 6 protons); C- CH_3 (s, δ = 1.95 ppm, 3 protons); O-*H* (s, δ = 8.98 ppm, 1 proton). Anal. Found: C, 79.30; H, 7.92; N, 5.58. Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}$: C, 79.63; H, 7.94; N, 5.81%.

The broad peak at δ = 2.32 ppm for the protons of the dimethylamino group implied hindered rotation of the methyl groups about the nitrogen. Variable temperature NMR spectroscopy showed that this was indeed the case.



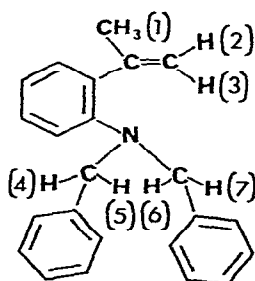
V, IHN

o-Isopropenylaniline



VI, IMN

o-Isopropenyl-*N,N*-dimethylaniline



VII, IBN

o-Isopropenyl-*N,N*-dibenzylaniline

o-(1-Phenylvinyl)-*N,N*-dimethylaniline was prepared from the alcohol by dehydration with phosphorus pentoxide [13]. *N,N*-Dimethyl-*o*-amino(1-phenyl-1-methyl)benzyl alcohol (6.0 g, 0.025 mol) was dissolved in dry benzene (100 ml) and phosphorus pentoxide (15 g) added. The mixture was stirred vigorously and refluxed for six hours and then cooled. Water was added slowly to decompose any unchanged phosphorus pentoxide. The solution was then made strongly alkaline with ammonia (15 *M*) and extracted with ether (4 × 100 ml), and the combined ether extracts were dried (Na_2SO_4). Removal of the solvent yielded a brown oil which was purified by chromatography on alumina with petroleum spirit as eluant. *o*-(1-Phenylvinyl)-*N,N*-dimethylaniline (PVMN) was obtained as a pale yellow oil. Yield = 4.7 g, 0.021 mol, 84%. This oil could not be distilled as it decomposed on heating for extended periods, even at reduced pressure. Anal. Found: C, 85.34; N, 7.59; N, 6.02. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}$: C, 86.05; N, 7.68; N, 6.72%.

o-Isopropenylaniline (IHN). *o*-Isopropenylaniline was prepared as a pale yellow oil from methylanthranilate by the method of Atkinson and Simpson [13]. Anal. Found: C, 81.20; H, 8.42; N, 10.42. Calculated for $\text{C}_9\text{H}_{11}\text{N}$: C, 81.16; H, 8.33; N, 10.52%.

o-Isopropenyl-*N,N*-dimethylaniline (IMN). Methylation [14] of the amino group of *o*-isopropenylaniline gave *o*-isopropenyl-*N,N*-dimethylaniline, a colourless oil which distilled at 96–98°C (25 mmHg). Anal. Found: C, 81.99; H, 9.27; N, 8.94. Calcd. for $\text{C}_{11}\text{H}_{15}\text{N}$: C, 81.93; H, 9.38; N, 8.69%.

o-Isopropenyl-*N,N*-dibenzylaniline (IBN)

A mixture of *o*-isopropenylaniline (1.6 g, 0.012 mol), benzyl bromide (5.5 g, 0.032 mol) and sodium acetate (3.0 g, 0.037 mol) was stirred vigorously at 120–130°C for four hours [15] then cooled, and hydrochloric acid (10 *M*, 60 ml) added. The resulting solution was allowed to stand overnight, during which time an off-white precipitate formed. This was filtered off, washed with dilute hydrochloric acid (3 *M*, 2 × 20 ml) and suspended in water. The suspension was made strongly alkaline with sodium hydroxide pellets and extracted with chloroform (3 × 50 ml). The combined chloroform extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to yield a viscous brown oil. This was purified by chromatography on alumina using petroleum spirit eluant to give *o*-isopropenyl-*N,N*-dibenzylaniline as a pale oil. Yield 2.2 g, 0.007 mol, 58.3%. Anal. Found: C, 88.35; H, 7.76; N, 4.13. Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}$: C, 88.13; H, 7.40; N, 4.47%.

Preparation of the platinum(II) complexes PtLX_2 ($X = \text{Cl}, \text{Br}$)

Preparation from PtCl_2 or PrBr_2 . A typical example of the preparation of the platinum(II) complexes of chelating monoolefin-aniline ligands, L, from the metal dihalide is given by the preparation of dichloro(*o*-isopropenyl-*N,N*-dimethylaniline)platinum(II) based on the method of Bennett et al. [16].

To a stirred suspension of platinum(II) chloride (1.10 g, 4.1 mmol) in refluxing chloroform (30 ml) was added a solution of *o*-isopropenyl-*N,N*-dimethylaniline (0.72 g, 4.5 mmol) in chloroform (20 ml). The mixture was refluxed for two hours, then filtered hot through a pad of Kieselguhr. The clear yellow filtrate was concentrated to approximately 10 ml and an equal volume of metha-

nol added. This solution was placed in the freezer (-20°C) overnight during which time a pale yellow microcrystalline solid formed. This was filtered off, washed with methanol, and air dried. The yield of Pt(IMN)Cl_2 was 0.80 g. A further crop of crystals (0.15 g) was collected by partial evaporation of the filtrate. Total yield = 0.95 g, 2.2 mmol, 53.6%.

The compounds given in Table 1 were prepared in a similar manner in each case as pale yellow microcrystals.

Preparation from Zeise's salt. The preparation of Pt(VMN)Cl_2 , dichloro(*o*-vinyl-*N,N*-dimethylaniline)platinum(II), from Zeise's salt has been described in a previous publication [2]. The yields of the complexes prepared by this method were generally higher than those obtained from PtCl_2 .

Preparation of the platinum(II) complexes Pt(IMN)ClL (where $L = \text{Cl}^-$, Br^- , I^- , NNN^- , SCN^-)

These complexes were prepared by the reaction of Pt(IMN)Cl_2 , in acetone, with the sodium salt of the appropriate ligand L. The preparation of Pt(IMN)ClI is described as a typical example.

Dichloro(*o*-isopropenyl-*N,N*-dimethylaniline)platinum(II) (0.21 g, 0.5 mmol) was dissolved in acetone (25 ml). Solid sodium iodide (0.5 g, 34 mmol) was added and the mixture stirred for 30 minutes. The acetone was then removed at room temperature under reduced pressure, and chloroform (35 ml) was added to yield a golden yellow solution and a precipitate of sodium chloride. Filtration through Kieselguhr gave a clear yellow solution, which was evaporated under reduced pressure to 10 ml, treated with an equal volume of methanol, and placed in the freezer overnight. The deep yellow microcrystals which separated on standing were filtered off, washed with methanol and air-dried. Yield of $\text{Pt(IMN)ClI} = 0.2$ g, 0.4 mmol, 80.0%. M.p. = 209°C (d).

The compounds given in Table 3 were prepared in a similar manner. The analytical data for these complexes are contained in Table 4.

The ^1H NMR spectra of the ligands and the platinum(II) complexes were recorded on a Varian HA100, 100 MHz spectrometer using $\text{DMF-}d_7$ solution with TMS as internal standard. Melting points were measured in air on a Reichert hot-stage melting point apparatus with microscope, and are corrected.

TABLE 1
YIELDS AND MELTING POINTS OF THE MONOOLEFIN-ANILINE PLATINUM COMPLEXES

Compound	Yield (%)	Melting point ($^{\circ}\text{C}$)
Pt(VHN)Cl_2	26	210–214(d)
Pt(VMN)Cl_2	44	206–209(d)
Pt(VMN)Br_2	52	208(d)
Pt(PVMN)Cl_2	42	158–162(d)
Pt(IHN)Cl_2	32	213–217(d)
Pt(IMN)Cl_2	54	227(d)
Pt(IMN)Br_2	62	231(d)
Pt(IBN)Cl_2	67	235–239(d)
Pt(IBN)Br_2	69	254–258(d)

d = decomposition. Analytical data for these compounds are given in Table 2.

TABLE 2

ANALYTICAL DATA FOR MONOOLEFIN-ANILINE COMPLEXES OF PLATINUM(II), PtLX₂

L	X	Analysis. Found (Calcd.) (%)			
		C	H	N	X
VHN	Cl	25.33 (24.95)	2.51 (2.35)	3.79 (3.64)	18.4 (18.4)
VMN	Cl	29.04 (29.07)	3.23 (3.17)	3.36 (3.39)	17.4 (17.2)
VMN	Br	23.97 (23.92)	2.63 (2.61)	2.77 (2.79)	31.7 (31.8)
PVMN	Cl	39.55 (39.27)	3.51 (3.50)	2.80 (2.86)	14.9 (14.5)
IHN	Cl	27.16 (27.08)	2.71 (2.78)	3.52 (3.51)	17.9 (17.8)
IMN	Cl	30.99 (30.92)	3.44 (3.54)	3.21 (3.28)	16.9 (16.6)
IMN	Br	25.82 (25.60)	2.99 (2.93)	2.62 (2.71)	30.6 (31.0)
IBN	Cl	47.33 (47.67)	4.08 (4.00)	2.35 (2.42)	12.5 (12.2)
IBN	Br	41.29 (41.33)	3.49 (3.47)	1.97 (2.10)	23.6 (23.9)

TABLE 3

MELTING POINTS OF THE COMPOUNDS Pt(IMN)ClL

Compound	Melting point (°C)
Pt(IMN)ClBr	223(d)
Pt(IMN)Cl(SCN)	165–170(d)
Pt(IMN)Cl(NCO)	195(d)
Pt(IMN)Cl(N ₃)	198(d)

d = decomposition.

TABLE 4

ANALYTICAL DATA FOR THE COMPLEXES Pt(IMN)ClL (%)^a

L	C	H	N	Cl	Others
Cl ⁻	30.99 (30.92)	3.44 (3.54)	3.21 (3.28)	16.9 (16.6)	—
Br ⁻	28.39 (28.01)	3.22 (3.21)	3.12 (2.97)	7.4 (7.5)	Br, 16.6 (16.9)
I ⁻	25.37 (25.47)	2.99 (2.92)	2.96 (2.70)	7.1 (6.8)	I, 24.9 (24.5)
NCO ⁻	33.03 (33.22)	3.25 (2.46)	6.31 (6.46)	8.3 (8.2)	—
SCN ⁻	31.93 (32.04)	3.33 (3.36)	6.03 (6.23)	8.2 (7.9)	S, 7.4 (7.1)
N ₃ ⁻	30.80 (30.45)	3.66 (3.49)	13.08 (12.92)	8.1 (8.2)	—

^a Analysis found (calcd.).

Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, CSIRO, University of Melbourne.

Results and discussion

Ligands related to *o*-vinylaniline

The chemical shift and coupling constant data for the ligands VHN, VMN and PVMN and their platinum(II) complexes are given in Tables 5 to 7. Data for VPN are included although the platinum complex of this compound could not be made.

TABLE 5

PROTON CHEMICAL SHIFTS (δ) ^a FOR *o*-VINYLANILINE LIGANDS AND PLATINUM(II) COMPLEXES

Compound	H(1)	H(2)	H(3)	H(4)	H(5)
Styrene ^b	6.64	5.16	5.66	—	—
VHN	6.97	5.24	5.58	4.9 ^c	4.9 ^c
Pt(VHN)Cl ₂	5.73	4.91	4.30	3.5 ^d	7.7 ^d
VMN	7.05	5.24	5.72	2.65 ^e	2.65 ^e
Pt(VMN)Cl ₂	5.78	5.18	4.37	3.42	3.44
Pt(VMN)Br ₂	5.62	5.17	4.42	3.45	3.52
VPN	6.82	5.06	5.61	^f	^f
PVMN	^f	5.68	5.35	2.51 ^e	2.51 ^e
Pt(PVMN)Cl ₂	^f	5.75	4.37	3.55	3.63

^a Measured in ppm downfield from TMS as internal standard. Error = ± 0.01 ppm. ^b Included for comparison; ref. 17(a). ^c NH₂ protons; broad and equivalent in the uncomplexed ligand. ^d Each broad resonance integrates for slightly more than one proton. ^e N(CH₃)₂ protons; equivalent in the uncomplexed ligand. ^f Aromatic protons, not assignable.

TABLE 6

INTERPROTON COUPLING CONSTANTS (*J*) ^a FOR *o*-VINYLANILINE LIGANDS AND THEIR PLATINUM(II) COMPLEXES

Compound	<i>J</i> (1,2)	<i>J</i> (1,3)	<i>J</i> (2,3)
VHN	11.0	17.2	1.8
Pt(VHN)Cl ₂	7.8	12.7	0.8
VMN	11.1	17.6	1.8
Pt(VMN)Cl ₂	7.6	12.8	0.8
Pt(VMN)Br ₂	7.6	12.0	1.3
VPN	11.4	17.4	1.4
PVMN	^b	^b	1.6
Pt(PVMN)Cl ₂	^b	^b	<0.1

^a Measured in Hz. Error = ± 0.1 Hz. ^b Coupling between the aromatic protons in the '1' position and H(2) and H(3) could not be measured (if it existed).

TABLE 7

¹⁹⁵Pt—¹H COUPLING CONSTANTS (*J*) ^a FOR THE DIHALO-*o*-VINYLANILINEPLATINUM(II) COMPLEXES

Complex	<i>J</i> (Pt—1)	<i>J</i> (Pt—2)	<i>J</i> (Pt—3)	<i>J</i> (Pt—4)	<i>J</i> (Pt—5)
Pt(VHN)Cl ₂	58.0	67.3	68.5	^b	^b
Pt(VMN)Cl ₂	53.5	68.8	72.7	31.2	29.1
Pt(VMN)Br ₂	53.6	70.8	74.0	33.6	31.4
Pt(PVMN)Cl ₂	^c	69.7	75.9	32.0	29.6

^a Measured in Hz. Error = ± 0.2 Hz. ^b Not measurable: N—H protons. ^c Coupling between the platinum and the aromatic ring protons of the 1-phenyl group was not observed.

Two important features of the monoolefin-anilines, I–IV, should be mentioned:

(i) The parent ligand, *o*-vinylaniline (VHN), represents the first example of a chelating monoolefin-Group V ligand in which the Group V donor is unsubstituted.

(ii) The compound *o*-vinyl-*N,N*-diphenylaniline (VPN) does not coordinate to platinum(II) as do its phosphine and arsine analogues. This is presumably due to the presence of the three phenyl groups attached to the nitrogen. These prevent the nitrogen from binding to the platinum both by their size and by their delocalizing effect on the nitrogen lone pair (triphenylamine itself is known to have a very small dipole moment) [18].

Chemical shifts

The olefinic protons. For the *o*-vinylaniline series of ligands these have approximately the same ^1H chemical shift values as the corresponding protons of styrene [17a]. On coordination of the olefin there is an upfield shift of all the olefinic proton resonances. H(1) and H(3) show a large shift (1.2 to 1.4 ppm) while H(2) is moved only slightly (<0.5 ppm) from its position in the free ligand spectrum (Table 5).

Bonding between platinum(II) and the olefin moiety is usually represented by the Dewar-Chatt-Duncanson [19,20] model. This type of interaction weakens the carbon-carbon bond by withdrawal of π -electron density towards the metal with concomitant acceptance of metal electrons by the π^* orbitals of the olefin. This may be thought of as causing a change in hybridization from sp^2 towards sp^3 in the olefinic carbons which would account for the upfield shift of the olefinic protons. It does not explain the large difference in the shifts of H(2) and H(3).

It has been proposed that in the Group VIA metal carbonyls of *o*-vinyl-phenyldiphenylphosphine (VPP) this difference in coordination shift is due to a slight twisting of the olefin [21] so that the two protons are not equidistant from the metal, H(3) being closer than H(2). We believe that this situation may also apply to the *o*-vinylanilineplatinum(II) complexes. If this is so then H(1) should be twisted away from the metal (being *cis* to H(2)) and the large upfield shift of this proton on coordination can then only be explained by a change in its orientation with respect to the aromatic ring. In the uncomplexed ligand the olefin lies in the plane of this ring and therefore H(1) is in the deshielding region of the aromatic ring. Coordination of the olefin shifts the proton, H(1), out of this plane so that it moves into a region of shielding above the plane of the ring.

The amine protons. Coordination of the nitrogen atoms of the ligands *o*-vinyl-*N,N*-dimethylaniline (VMN) and *o*-(1-phenylvinyl)-*N,N*-dimethylaniline (PVMN) shifts the *N*-methyl protons downfield (H(4) and H(5), Table 5). This is the expected result of withdrawal of electron density from the nitrogen towards the metal with consequent deshielding of the $\text{N}(\text{CH}_3)_2$ protons.

The nitrogen atom in these complexes is four-coordinate and is part of the ring formed by the bidentate ligand and the metal. This brings about an environmental inequivalence in the methyl protons and therefore each methyl group has a separate resonance.

In the platinum complex of the parent ligand, *o*-vinylaniline (VHN), the separation of the N-H proton resonances is greater than that of the CH_3 protons in the *N*-methyl-substituted complexes. One moves slightly upfield ($\delta = 3.5$ ppm) from its position in the free ligand ($\delta = 4.9$ ppm) while a large downfield shift ($\delta = 7.8$ ppm) is observed for the other. Both resonances are broad

and each peak integrates to slightly more than one proton. This may be due to a trace of water in either the sample or the solvent.

Interproton coupling

The extent of nuclear spin-spin coupling between the olefinic protons decreases markedly on coordination (Table 6). A similar decrease in coupling has been noted by Bennett et al. [22] in platinum(II) complexes of *o*-vinylphenyldimethylarsine and appears to be due to the withdrawal of electron density from the carbon-carbon double bond by the platinum.

¹⁹⁵Platinum-proton coupling

Coupling between the platinum-195 nucleus and the olefinic and amine protons is evident in the ¹H NMR spectra of all the platinum(II) complexes (Table 7). The extent of this coupling indicates that both the olefin and the amine groups are strongly bound to the metal.

The data in Table 7 show that H(3) is more strongly coupled to the platinum than is H(2). The difference between these coupling constants suggests (as do the chemical shift data (Table 5) that the olefin is slightly twisted with respect to the metal, H(3) being closer to the metal than H(2). A similar effect has been observed in monoolefin complexes of platinum(II) containing substituted pyridine [23] and pyridine-*N*-oxide [24] ligands.

Appleton and Hall [25] have discussed the factors affecting the three- and four-bond ¹⁹⁵Pt-¹H coupling constants (³*J*(Pt-N-C-H) and ⁴*J*(Pt-N-C-C-H) respectively) in a series of chelating diamine complexes of platinum(II). They proposed that the difference in the magnitude of the coupling constants in this series was due to a Karplus type relationship similar to that found by Erickson et al. [26] for platinum(II) amino acid complexes.

In the compounds Pt(VMN)Cl₂, Pt(VMN)Br₂, and Pt(PVMN)Cl₂ the amine methyl protons (H(4) and H(5), Table 7) are coupled to the platinum-195 nucleus through three bonds. The magnitude of this coupling is different for the two methyl groups in a given complex. This is probably due to the unequal dihedral angle between each methyl group and the platinum which would result in a coupling behaviour similar to that found by Appleton and Hall for the chelating diamine complexes [25].

There was no observable coupling between the platinum and the amine hydrogens in the complex Pt(VHN)Cl₂; presumably because the proton resonances were too broad to allow sidebands one-fourth of their intensity to be resolved.

*Ligands related to *o*-isopropenylaniline*

The isopropenylaniline ligands IHN and IMN (V and VI) were studied for the following reasons:

- (i) The ¹H NMR spectra of their platinum(II) complexes are less complicated than the spectra of the corresponding *o*-vinylaniline complexes, and
- (ii) The presence of the α-methyl group introduces four-bond allylic interproton coupling into the compounds. This type of coupling is thought to occur through a sigma-pi mechanism [17b] and it was expected that variation of the allylic coupling would provide some insight into the changes occurring in the

metal—olefin π -bond brought about by coordinating various ligands to the platinum, *trans* to the olefin group.

Chemical shifts

The chemical shift data (Table 8) for protons 2, 3, 4, and 5 in these compounds can be interpreted in a similar manner to those of the *o*-vinylaniline ligands and complexes.

Unlike H(1) in the vinylaniline ligands, H(1) in these compounds is not shielded on coordination of the ligand to the platinum. The methyl protons (H(1)) are removed from the olefin by a carbon—carbon bond, which weakens the effect of the platinum and of the magnetic anisotropy of the aromatic ring on these protons.

Interproton coupling

The interproton coupling constants (Table 9) in these ligands are more sensitive to changes in the olefinic bond than are the coupling constants in the *o*-vinylaniline ligands (Table 6).

Coordination of the isopropenyl group to the platinum results in a decrease of ca. 80 percent in the interproton coupling constants while in the vinyl complexes the decrease is only about 30 percent from the free ligand values. Assuming that in the isopropenyl group spin-spin coupling is transferred through a sigma-pi mechanism [17b] the percentage decrease in the coupling constants (J_{cisoid} and $J_{transoid}$) on coordination might be expected to exceed that of the vinyl group where the pi contribution to the coupling is not as significant. As both olefin groups have Dewar-Chatt-Duncanson type bonding interactions with the platinum it appears that the differences in coupling arise from the mode of transfer of coupling across the double bond.

^{195}Pt — ^1H coupling

Coupling between protons 2, 3, 4 and 5 and the platinum-195 nucleus (Table 10) is similar in magnitude to that of the vinylaniline complexes (Table 5). Pro-

TABLE 8

^1H CHEMICAL SHIFTS (δ) ^a FOR *o*-ISOPROPENYLANILINE LIGANDS AND PLATINUM(II) COMPLEXES

Compound	H(1)	H(2)	H(3)	H(4)	H(5)
α -methylstyrene ^b	2.10	5.29	5.00	—	—
IHN	2.03	5.27	4.98	4.9 ^c	4.9 ^c
Pt(IHN)Cl ₂	2.14	4.84	4.24	3.5	7.8
IMN	2.13	5.06 ^d	5.06 ^d	2.70 ^e	2.70 ^e
IMN(C ₆ D ₆) ^f	2.18	5.06	5.12	2.56 ^e	2.56 ^e
Pt(IMN)Cl ₂	2.24	5.03	4.30	3.45	3.47
Pt(IMN)Br ₂	2.20	5.32	4.30	3.42	3.50

^a Measured in ppm downfield from TMS as internal standard. Error = ± 0.01 ppm. ^b Included for comparison. ^c NH₂ protons; broad and equivalent in the free ligand. ^d Accidentally equivalent. ^e N(CH₃)₂ protons; equivalent in the free ligand. ^f The spectrum of IMN was also recorded in hexadeuterobenzene (C₆D₆) to separate the resonances of protons 2 and 3. This enabled measurements of the interproton coupling constants (Table 9).

TABLE 9

INTERPROTON COUPLING CONSTANTS (J)^a FOR THE *o*-ISOPROPENYLANILINE LIGANDS AND PLATINUM COMPLEXES

Compound	$J(1,2)$	$J(1,3)$	$J(2,3)$
α -methylstyrene ^b	1.6	0.9	1.7
IHN	1.7	1.0	2.2
Pt(IHN)Cl ₂	0.4	<0.1	0.8
IMN	^c	^c	^c
IMN (C ₆ D ₆) ^d	1.6	0.9	2.7
Pt(IMN)Cl ₂	0.5	<0.1	0.7
Pt(IMN)Br ₂	0.4	0.1	0.6

^a Measured in Hz. Error = ± 0.1 Hz. ^b Included for comparison. ^c Not measurable due to the accidental equivalence of protons 2 and 3. ^d See footnote *f* to Table 8.

ton 1 exhibits a smaller coupling to platinum in the isopropenylaniline complexes owing to the additional C—C bond.

o-Isopropenyl-*N,N*-dibenzylaniline

Apart from the aromatic protons the NMR spectrum of the ligand *o*-isopropenyl-*N,N*-dibenzylaniline (VII) contains peaks which can be attributed to four types of proton. When the ligand is coordinated to platinum(II) these are split into resonances which can be assigned to the seven magnetically non-equivalent protons (Table 11).

Chemical shifts

The coordination shifts of H(1) and H(3) in the platinum complexes Pt(IHN)Cl₂ and Pt(IMN)Br₂ are unusually large (Table 11a) compared to the shift of the corresponding protons in the platinum IMN complexes (Table 8). Proton 1 is shielded by ca. 1 ppm while the upfield shift of H(3) is about 3 ppm. We believe that this increased shielding is due to the *N*-benzyl groups, which are so positioned in the complex that their aromatic rings provide greater shielding of H(1) and H(3) than occurs on coordination of IMN.

Proton 2 does not appear to be significantly affected by the position of the benzyl aromatic rings as its coordination shift (0.4 and 0.8 ppm for the dichloro and dibromo complexes, respectively) is similar to that found for the IHN and IMN complexes.

Coordination of the nitrogen results in a splitting of the single peak due to

TABLE 10

¹⁹⁵Pt—¹H COUPLING CONSTANTS (J)^a FOR DIHALO(*o*-ISOPROPENYLANILINE)PLATINUM(II) COMPLEXES

Compound	$J(\text{Pt}-1)$	$J(\text{Pt}-2)$	$J(\text{Pt}-3)$	$J(\text{Pt}-4)$	$J(\text{Pt}-5)$
Pt(IHN)Cl ₂	38.1	69.5	73.2	^b	^b
Pt(IMN)Cl ₂	32.2	70.1	75.7	32.0	29.7
Pt(IMN)Br ₂	34.5	71.5	77.8	33.2	31.4

^a Measured in Hz. Error = ± 0.2 Hz. ^b Not measurable; N—H protons.

the N—CH₂ protons (H(4) to H(7)) into four doublets. These protons are fixed in non-equivalent positions by the geometry of the complex and geminal coupling results in the observation of eight peaks.

Interproton coupling

The changes which occur in the coupling constants (Table 11b) between the olefinic protons of IBN as a result of complex formation are similar to those observed for the ligands IHN and IMN (Table 9) and will not be discussed further.

The coupling constants (ca. 12 Hz) observed for the benzylic-CH₂- protons in the complexes Pt(IBM)Cl₂ and Pt(IBM)Br₂ are of the order expected for coupling between geminal protons bound to an sp³ carbon [17c].

¹⁹⁵Pt—¹H coupling

Coupling between the platinum-195 nucleus and the olefinic protons (Table 11c) is similar in magnitude to that found in the complexes of IHN and IMN (Table 10).

It can also be seen from the data presented in Table 11c that the benzylic protons (H(4) to H(7)) are coupled to the platinum to different degrees. The extent of this coupling appears to be determined by the configuration of the complex in a manner similar to that observed by Appleton and Hall [25] for diamine complexes of platinum(II) and platinum(IV).

Complexes of the type Pt(IMN)ClL

As mentioned previously, the dihalo-*o*-isopropenylanilineplatinum(II) com-

TABLE 11

¹H NMR SPECTRAL DATA FOR *o*-ISOPROPENYL-*N,N*-DIBENZYLANILINE (IBN) AND ITS PLATINUM(II) COMPLEXES

(a) Chemical shifts ^a							
Compound	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
IBN	2.31	5.17	5.11	4.21 ^b	4.21 ^b	4.21 ^b	4.21 ^b
Pt(IBM)Cl ₂	1.28	4.75	2.05	4.58	6.00	5.00	5.55
Pt(IBM)Br ₂	1.24	4.37	2.00	4.45	5.83	4.93	5.32
(b) Interproton coupling constants ^c							
Compound	J(1,2)	J(1,3)	J(2,3)	J(4,5)	J(6,7)		
IBN	1.5	1.0	2.4	^b	^b		
Pt(IBM)Cl ₂	0.4	0.1	1.3	11.7	12.6		
Pt(IBM)Br ₂	0.5	0.2	1.1	12.0	12.5		
(c) ¹⁹⁵ Pt— ¹ H coupling constants ^d							
Compound	J(Pt—1)	J(Pt—2)	J(Pt—3)	J(Pt—4)	J(Pt—5)	J(Pt—6)	J(Pt—7)
Pt(IBM)Cl ₂	30.8	73.5	77.8	57.5	12.5	65.0	12.5
Pt(IBM)Br ₂	31.8	75.5	81.1	62.0	13.0	66.0	10.5

^a Measured in ppm downfield from TMS as internal standard. Error = ±0.01 ppm. ^b N—CH₂ protons; equivalent in the uncomplexed ligand. ^c Measured in Hz. Error = ±0.1 Hz. ^d Measured in Hz. Error = ±0.2 Hz.

plexes were prepared in an attempt to study the changes in allylic coupling as various ligands were substituted for the chlorine *trans* to the olefin group. To this end the complexes $\text{Pt}(\text{IMN})\text{CIL}$ where $\text{L} = \text{Cl}^-$, Br^- , I^- , NCO^- , SCN^- and N_3^- , were prepared and their ^1H NMR spectra recorded*. Chemical shifts, interproton coupling constants and $^{195}\text{Pt}-^1\text{H}$ coupling constants are given in Tables 12, 13 and 14 respectively.

As can be seen from the data in Table 13 we were unable to obtain any significant information from the allylic coupling constants. It seems that the π -bond of the olefin is so depleted in electron density on coordination, or its nature so changed, that the allylic coupling is virtually eliminated. Consequently, variations in this coupling arising from the nature of the ligand L are insignificant.

Several groups of workers [27–29] have derived *trans*-influence series based on variations in the hydride chemical shifts of platinum(II)-hydrido complexes. It was assumed that the difference in shielding of the hydride, observed on altering the *trans*-ligand, was due only to a change in the platinum–hydrogen distance [31].

Although the chemical shift and interproton coupling constant data (Tables 12, 13) did not allow us to formulate a *trans*-influence series for the ligands, it is possible to use the $^{195}\text{Pt}-^1\text{H}$ (isopropenyl) coupling constants (Table 14) to deduce such a series.

Previous workers [30–32] have shown that changes in the ligand *trans* to an olefin in platinum(II) complexes affect the strength of the metal–olefin bond. Evidence for this was provided by changes in the platinum–hydrogen [30–31] and platinum–carbon [32] coupling constants, $J(^{195}\text{Pt}-^1\text{H}(\text{olefin}))$ and $J(^{195}\text{Pt}-^{13}\text{C}(\text{olefin}))$. This coupling has been interpreted in various ways. Holloway et al. [33] have suggested that ‘. . . the $^{195}\text{Pt}-^1\text{H}$ coupling constants of the olefin are more complicated in origin than would be expected from consideration of only the Fermi Contact term, and that they are not a reliable indication of the *s*-character of the metal–olefin bond.’ However, the majority opinion suggests that the Fermi Contact term is of over-riding importance and that coupling between the platinum-195 nucleus and an olefinic proton occurs predominantly via a sigma pathway.

For example, Braterman [34] and Manzer [35] have argued that in platinum(II)-olefin compounds the symmetry of the complex is such that the metal $\rightarrow$ olefin back π -bond has no metal *s*-orbital character and is not involved in coupling between the metal and the olefinic protons. The coupling must therefore arise entirely from the olefin $\rightarrow$ metal σ -bond.

A similar conclusion was reached by Kato [36] from theoretical studies with Zeise’s salt. He estimated $J(^{195}\text{Pt}-^1\text{H})$ from molecular orbital calculations using the Fermi Contact equation developed by Pople and Santry [37] and found the value of this constant (40.4 Hz) to be close to the experimental value of 34.0 Hz [38].

We have therefore used the coupling constants between the platinum-195 nucleus and the protons of the coordinated isopropenyl moiety to estimate the

* Complexes of this type where $\text{L} = \text{phenolato}$ or thiophenolato have been reported in a previous publication [23].

TABLE 12
CHEMICAL SHIFT VALUES ^a FOR THE COMPLEXES Pt(IMN)CIL

L	H(1)	H(2)	H(3)	H(4)	H(5)
N ₃ ⁻	2.26	4.89	4.16	3.28	3.28
NCO ⁻	2.29	4.87	4.23	3.35	3.37
SCN ⁻	2.35	5.03	4.49	3.43	3.45
Cl ⁻	2.24	5.03	4.30	3.45	3.47
Br ⁻	2.20	5.11	4.43	3.52	3.59
I ⁻	2.11	5.23	4.62	3.66	3.78

^a Measured in ppm downfield from TMS as internal standard. Error = ±0.01 ppm. Solvent = DMF-*d*₇.

TABLE 13
INTERPROTON COUPLING CONSTANTS ^a FOR THE COMPLEXES Pt(IMN)CIL

L	J(1,2)	J(1,3)	J(2,3)
N ₃ ⁻	0.3	0.2	0.7
NCO ⁻	0.4	0.4	0.7
SCN ⁻	0.5	0.2	0.7
Cl ⁻	0.5	0.1	0.7
Br ⁻	0.4	0.1	<i>b</i>
I ⁻	0.7	0.2	<i>b</i>

^a Measured in Hz. Error = ±0.1 Hz. *b* Not measurable.

TABLE 14
¹⁹⁵Pt—¹H COUPLING CONSTANTS ^a FOR THE COMPLEXES [Pt(IMN)CIL]

L	J(Pt-1)	J(Pt-2)	J(Pt-3)	J(Pt-4)	J(Pt-5)
N ₃ ⁻	28.7	65.2	70.3	34.6	34.6
NCO ⁻	29.0	67.8	72.8	35.4	34.2
SCN ⁻	30.8	69.0	74.4	34.4	32.5
Cl ⁻	32.2	70.1	75.7	32.0	29.7
Br ⁻	33.9	71.0	76.3	32.2	28.7
I ⁻	35.7	70.9	76.3	33.7	32.8

^a Measured in Hz. Error = ±0.2 Hz.

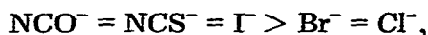
relative strengths of the olefin → platinum σ-bond in the complexes Pt(IMN)CIL. The order of increasing strength of this bond, based on the order of increasing *J*(¹⁹⁵Pt—¹H(olefin)) (Table 12), is



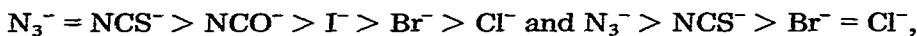
Since the strength of the olefin → metal σ-bond is inversely related to the *trans*-influence of the ligand opposite, the ligands may be arranged in the following order of decreasing *trans*-influence;



This series differs from that of several other authors. For example Clegg et al. [39] have obtained a series,



by measuring $^2J(\text{Pt}-\text{C}-\text{H})$ in a series of trimethyl-platinum(IV) complexes. Allen and Pidcock [40] have derived two orders,



from the measurement of $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$ and $J(^{195}\text{Pt}-^{31}\text{P})$ in complexes of the type *trans*-PtMeX(Et₃P)₂ and *cis*-PtMeX(Et₃P)₂, respectively.

It is evident from the examples quoted above that the order of the *trans*-influence series is dependent upon the system chosen. Clearly the *trans*-influence series for the anionic ligands studied in the complexes Pt(IMN)ClL should be distinguished from those derived from other types of complexes.

That the *trans*-influence series vary with the type of complex studied is probably due to the different properties of the bond between the metal and the ligands under consideration (e.g. Pt-H vs Pt-CH₃ vs Pt-olefin vs Pt-P).

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