Journal of Organometallic Chemistry, 361 (1989) 123–138
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis and spectroscopic characteristics of bis(ethenyldimethylsilylmethyl)platinum(II) complexes containing nitrogen donor ligands

Robert D. Kelly and G. Brent Young *

Inorganic Chemistry Laboratories, Imperial College of Science, Technology and Medicine, London, SW7 2AY (Great Britain)

(Received June 13th, 1988)

Abstract

Complexes of the type $LPt(CH_2SiMe_2CH:CH_2)_2$ have been synthesised by diene displacement from $(nbd)Pt(CH_2SiMe_2CH:CH_2)_2$ [L = bipy, Me_2bipy, Bu^t_2bipy, bipym, bipyz, phen, Me_4phen, Ph_2phen, tmeda] *. With a monodentate nitrogen donor ligand (such as pyridine), the product is the complex $(py)\overline{Pt(CH_2SiMe_2CH}:CH_2)(CH_2SiMe_2CH:CH_2)$, in which η^2-binding of one ethenylsilyl ligand completes tetracoordination of platinum. All these compounds have been characterised by ^1H and ^{13}C NMR, infrared and electronic spectroscopy.

Introduction

Controllable, heterogeneous activation of C–H bonds by transition metal systems is still an important goal in organic chemistry. Despite immense effort little precise insight in to the reaction mechanisms has been achieved [1]. On the other hand, homogeneous systems have provided much more detailed knowledge of C–H activation [2]. Early studies established intramolecular α- and β-H abstractions as major rearrangement pathways for transition-metal alkyls [3]. Where steric constraints preclude β-activation, more remote H-transfers have been observed [4]. More significant, perhaps, has been the recent emergence of organometallic species which show intermolecular activity in aliphatic and aromatic C–H activation [5].

---

* Abbreviations: nbd = bicyclo[2.2.1]hepta-2,5-diene; bipy = 2,2′-bipyridine, Me_2bipy = 4,4′-dimethyl-2,2′-bipyridine; Bu^t_2bipy = 4,4′-ditertiarybutyl-2,2′-bipyridine; bipym = 2,2′-bipyrimidine; bipyz = 2,2′-bipyridizyl; phen = 1,10-phenanthroline; Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; tmeda = *N,N,N′,N′*-tetramethylethylenediamine; py = pyridine.

0022-328X/89/$03.50

Our recent studies have focused on intramolecular, δ(C-H) activation involving the neophyl * ligand bound to platinum(II) [6]. In order to compare the reactivities of analogous olefinic C–H bonds, we have synthesised complexes $LPt(CH_2SiMe_2CH:CH_2)_2$ and $(py)\overline{Pt(R)(CH_2SiMe_2CH}:CH_2)$ [$R = CH_2SiMe_2CH:CH_2$]. Here, we describe their syntheses and some interesting spectroscopic characteristics.

These ligands are more correctly termed "ethenyldimethylsilylmethyl", but for the sake of brevity we shall refer instead to "sila-neohexenyl" groups. We have previously described analogues with phosphorus-donor ligands [10].

Experimental

General and instrumental

Elemental analyses were by the Imperial College Microanalytical Laboratories. NMR spectra were recorded on Bruker WM 250 (^1H, 250.13 MHz; ^{13}C, 62.9 MHz), Bruker W 400 (^1H, 400.13 MHz) and JEOL FX 90 Q (^1H, 89.55 MHz; ^{13}C, 22.51 MHz) spectrometers. IR data were collected for 4% KBr dispersions on a Perkin–Elmer 683 or 1720 Fourier Transform instrument. Electronic spectra were recorded on a Philips PU8740 UV/VIS spectrometer.

All reactions were carried out under nitrogen or argon unless otherwise noted, by standard anaerobic techniques [7]. Solvents were distilled under nitrogen prior to use; diethyl ether and hexane from sodium/benzophenone, toluene from sodium.

Chloromethyldimethyl(vinyl)silane and 2,2′-bipyrimidyl were used as supplied by Lancaster Synthesis. Bicyclo[2.2.1]hepta-2,5-diene, 2,2′-bipyridyl, 4,4′-dimethyl-2-2′-bipyridyl, 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 2,2′-bipyrazyl, pyridine-d_5, toluene-d_8 and benzene-d_6 were supplied by the Aldrich Chemical Co. and used without further purification. *N,N,N′,N′*-tetramethylethylenediamine (Aldrich) and pyridine (Rose Chemicals) were distilled under argon from sodium hydroxide prior to use. A sample of 4,4′-di-t-butyl-2,2′-bipyridyl was synthesised by a modification of a published procedure [8]. The precursor $(nbd)PtCl_2$ was synthesised by appropriate modification of the method used for $(cod)PtCl_2$ [9].

Preparation of bis(sila-neohexenyl)(bicyclo[2.2.1]hepta-2,5-diene)platinum(II)

The Grignard reagent $Mg(CH_2SiMe_2CH:CH_2)Cl$ was prepared by addition of $ClCH_2SiMe_2CH:CH_2$ (8.0 g, 59.2 mmol) in diethyl ether (30 cm^3) to a stirred suspension of Mg shot (6.1 g, 0.25 mol) in diethyl ether (30 cm^3) at room temperature. After 12 h stirring at room temperature, the solution was filtered and analysed (0.9 mol dm^{-3}, 91% yield). A portion of this solution (15.83 cm^3, 14.25 mmol) was added dropwise to a stirred suspension of $(nbd)PtCl_2$ (1.70 g, 4.75 mmol) in diethyl ether (40 cm^3) at $-20\,^\circ C$. The mixture was allowed to reach room temperature and stirred for a further 4 h. The resulting suspension was cooled to $-15\,^\circ C$ and quenched by dropwise addition of degassed, saturated ammonium chloride solution (40 cm^3). The ethereal layer was separated and the aqueous phase washed with diethyl ether (20 cm^3) and the combined ether extracts dried over anhydrous magnesium sulphate and decolourised with activated charcoal. Removal of the solvent in vacuo gave a pale yellow oil (1.89 g, 82%).

---

* neophyl = 2-methyl-2-phenylpropyl.

IR: 3041m, 3002m, 2954s, 2897s, 2849m, 1590w, 1434m, 1402m, 1357w, 1309m, 1246s, 1187m, 1153w, 1050m, 1009s, 946s, 831(d)vs, 770s, 756s, 726s, 680m, 604w, 518w, 362w.

Preparation of bis(sila-neohexenyl)(2,2'-bipyridyl)platinum(II)

A solution of bipy (0.13 g, 0.86 mmol) and (cod)PtR_2 [10] (0.43 g, 0.86 mmol) in the minimum amount of toluene (15 cm^3) was stirred at room temperature for 7 d. Removal of the solvent in vacuo, extraction into the minimum amount of toluene/hexane, and cooling of the extract to −25 °C gave the product as bright red crystals (0.30 g, 63%).

IR: 3100w, 3040m, 2990w, 2940m, 2880m, 2840m, 1600s, 1585w, 1470s, 1445vs, 1430m, 1400m, 1235(d)vs, 1020s, 1000s, 965m, 940vs, 835vs, 815vs, 780s, 770s, 755vs, 730s, 715s, 680m, 655m, 560w, 525w.

Preparation of bis(sila-neohexenyl)(4,4'-dimethyl-2,2'-dipyridyl)platinum(II)

To a stirred solution of (cod)PtR_2 (0.20 g, 0.40 mmol) in toluene (15 cm^3) was added Me_2bipy (0.07 g, 0.40 mmol). After 10 d at room temperature the reaction was complete. Removal of the solvent in vacuo, extraction into the minimum of hexane, concentration of the extract, and cooling to −25 °C gave red crystals (0.06 g, 25%). IR: 3030w, 2950m, 2860m, 2840m, 1615s, 1590w, 1480m, 1445w, 1415m, 1400m, 1385w, 1300w, 1240s, 1015m, 950m, 940m, 835s, 825vs, 770s, 745m, 720m, 680w, 605w, 555w, 525w.

Preparation of bis(sila-neohexenyl)(4,4'-ditertiarybutyl-2,2'-dipyridyl)platinum(II)

A solution of (cod)PtR_2 (0.20 g, 0.40 mmol) and Bu^t_2bipy (0.11 g, 0.40 mmol) in toluene (10 cm^3) was kept at room temperature for 21 d. Removal of the solvent in vacuo, extraction into hexane, concentration of the extract and cooling to −25 °C gave red crystals (0.13 g, 49%).

IR: 3045m, 2974vs, 2880s, 2849s, 1618s, 1598w, 1547m, 1485s, 1469m, 1450w, 1414s, 1371m, 1305w, 1265s, 1242s, 1207w, 1160w, 1101m, 1019s, 944s, 901w, 894m, 827(d)vs, 772s, 749m, 725s, 694m, 682m, 608m, 553w, 522w, 369w.

Preparation of bis(sila-neohexenyl)(2,2'-bipyrimidyl)platinum(II)

To a stirred solution of (cod)PtR_2 (0.25 g, 0.50 mmol) in toluene (15 cm^3) was added bipym (0.08 g, 0.51 mmol). After 10 d at room temperature, reaction was complete. Removal of the solvent in vacuo, extraction into hexane, concentration of the extract and cooling to −25 °C gave purple crystals (0.07 g, 26%). IR: 3050s, 2950s, 2880s, 2840s, 1590m, 1575vs, 1550s, 1450m, 1410vs, 1370m, 1335w, 1265m, 1240s, 1115w, 1105w, 1080m, 1070w, 1010s, 955s, 945s, 840vs, 815vs, 770vs, 750vs, 720s, 685s, 665s, 605w, 565w, 520w, 445w, 365w.

Preparation of bis(sila-neohexenyl)(2,2'-bipyrazyl)platinum(II)

A solution of (nbd)PtR_2 (0.14 g, 0.28 mmol) and bipyz (0.04 g, 0.28 mmol) in toluene (10 cm^3) was kept at room temperature for 26 d. Removal of the solvent in vacuo gave the purple product (0.07 g, 45%).

IR: 3036m, 2946s, 2882s, 2838s, 1614w, 1580m, 1495w, 1465m, 1401s, 1321w, 1306w, 1263s, 1243s, 1175s, 1165s, 1091s, 1070s, 1016s, 944s, 810(d)vs, 720s, 679s, 658s, 603m, 561m, 515m, 474m, 358m.

Preparation of bis(sila-neohexenyl)(1,10-phenanthroline)-platinum(II)

To a stirred solution of (cod)PtR$_2$ (0.20 g, 0.40 mmol) in ether (45 cm^3) was added phen (0.71 g, 3.6 mmol) and the orange suspension stirred for 7 d at room temperature. The orange suspension was transferred through a tube into a stirred solution of FeSO$_4$ (0.9 g, 3.23 mmol) in water (12 cm^3). The mixture was cooled to −78 ° C and the ethereal layer filtered from the frozen aqueous layer. The latter was thawed, and then washed with ether (3 × 15 cm^3) and the extracts were combined. Removal of the solvent in vacuo followed by washing with cold hexane (1 × 15 cm^3) gave the red product (0.17 g, 72%).

IR: 3040s, 2950s, 2870s, 2830s, 1630w, 1590w, 1580w, 1510w, 1495w, 1450m, 1425s, 1415s, 1400s, 1300w, 1240s, 1220m, 1205m, 1145m, 1095w, 1010s, 945s, 830vs, 820vs, 765s, 720vs, 680s, 610w, 600w, 560w, 510w, 495w, 455w, 435w, 370w.

Preparation of bis(sila-neohexenyl)(3,4,7,8-tetramethyl-1,10-phenanthroline)platinum-(II)

A solution of (cod)PtR$_2$ (0.20 g, 0.40 mmol) and Me$_4$phen (0.09 g, 0.40 mmol) in toluene (50 cm^3) was stirred at room temperature for 14 d. Concentration of the solution gave the orange product (0.14 g, 56%).

IR: 3045m, 2966s, 2880s, 2849s, 1622w, 1583w, 1524w, 1430m, 1399m, 1265s, 1242s, 1101s, 1019s, 941s, 823vs, 811vs, 768s, 725s, 690m, 666m, 580w, 525w, 365w.

Preparation of bis(sila-neohexenyl)(4,7-diphenyl-1,10-phenanthroline)platinum(II)

A solution of (cod)PtR$_2$ (0.31 g, 0.60 mmol) and Ph$_2$phen (0.20 g, 0.60 mmol) in toluene (40 cm^3) was kept at room temperature for 8 d. Removal of the solvent in vacuo, extraction into the minimum of hexane, concentration of the extract and cooling to −25 ° C gave the product as purple crystals (0.10 g, 23%). IR: 3040s, 3000m, 2950s, 2870s, 2840s, 1620m, 1590m, 1555m, 1495m, 1445m, 1440m, 1420s, 1415s, 1400s, 1365w, 1235s, 1075w, 1010s, 1000s, 940s, 905w, 850s, 830vs, 810vs, 765vs, 735s, 700vs, 630m, 600w, 580w, 555w, 520w, 495w, 410w, 365w.

Preparation of bis(sila-neohexenyl)(N,N,N′,N′-tetramethylethylenediamine)platinum-(II)

To (nbd)PtR$_2$ (0.30 g, 0.62 mmol) was added TMEDA (4 cm^3, 26.50 mmol). The solution was kept in the dark for 14 d at room temperature. Removal of the solvent in vacuo gave the product as a pale yellow oil (0.30 g, 96%).

IR: 2949s, 2885s, 2838s, 1678w, 1587w, 1553w, 1470s, 1460s, 1401m, 1285m, 1238s, 1187w, 1164w, 1126m, 1097w, 1063m, 1045m, 1016s, 953s, 832vs, 816vs, 800vs, 770s, 729m, 676m, 600w, 518w, 496m, 479w, 360w.

Preparation of cis-bis(sila-neohexenyl)-bis-(pyridine-d_5)platinum(II)

To (nbd)PtR$_2$ (0.30 g, 0.62 mmol) was added pyridine-d_5 (4 cm^3, 49.92 mmol). The solution was kept in the dark at room temperature for 24 h. The solvent was removed in vacuo.

Preparation of cis-(sila-neohexenyl)(η^2-cycloplatinasilaneohexenyl)(pyridine)platinum-(II)

A solution of (nbd)PtR$_2$ (0.30 g, 0.62 mmol) in pyridine (3 cm^3, 37.09 mmol) was kept at room temperature with exclusion of light for 3 h. Removal of the solvent in vacuo gave the yellow product (0.29 g, 98%).

IR: 3037m, 2949s, 2890s, 2274w, 1916w, 1601s, 1501w, 1481m, 1447vs, 1401m, 1388m, 1350m, 1241s, 1210m, 1152m, 1068s, 1044s, 1014s, 836vs(d), 775s, 756vs, 696s, 636w, 604m, 594s, 401m, 360w, 261w.

Results and discussion

A. Synthesis

A number of new bis(sila-neohexenyl)platinum(II) complexes have been made by methods similar to those previously reported [10]. Metathetical displacement of the diene in (nbd)PtR_2 or (cod)PtR_2 by nitrogen-donor ligands produces LPtR_2 [L = bipy, Me_2bipy, Bu^t_2bipy, bipym, bipyz, phen, Me_4phen, Ph_2phen, tmeda]. Conversion is generally complete in 2–26 d at ambient temperature. Qualitatively, nbd is more labile than cod.

The diene and tmeda compounds are air-inert, pale yellow oils, whilst the other bis-nitrogen complexes are air-inert, brightly-coloured crystalline solids. All gave satisfactory elemental analyses (Table 1). Their spectroscopic characteristics are discussed later. Most of these complexes decompose rapidly when their toluene solutions are exposed to air, and so oxygen was rigorously excluded. In addition, the bis-nitrogen derivatives react with chlorocarbon solvents to give as yet unidentified products. Chloroform and dichloromethane were avoided as recrystallisation solvents.

Table 1

Analytical data

Compound	Element (found (calc) (%))		
	C	H	N
(nbd)PtR_2	40.62	6.43	–
	(42.0)	(6.23)	(–)
(bipy)PtR_2	43.86	5.51	4.93
	(43.70)	(5.50)	(5.10)
(Me_2bipy)PtR_2	45.80	6.09	4.66
	(45.73)	(5.93)	(4.85)
(Bu^t_2bipy)PtR_2	50.61	7.11	4.15
	(50.81)	(7.00)	(4.23)
(bipym)PtR_2	39.39	5.24	9.63
	(39.19)	(5.12)	(10.16)
(bipyz)PtR_2	37.45	4.89	9.13
	(39.19)	(5.12)	(10.16)
(phen)PtR_2	46.45	5.32	4.70
	(46.06)	(5.27)	(4.88)
(Me_4phen)PtR_2	50.09	6.13	4.44
	(49.58)	(6.08)	(4.45)
(Ph_2phen)PtR_2	56.56	5.38	3.81
	(56.25)	(5.28)	(3.86)
(tmeda)PtR_2	35.59	7.80	5.60
	(37.70)	(7.51)	(5.50)
(py)$\overline{\text{PtR(R}}$)	36.49	5.22	2.86
	(38.12)	(5.76)	(2.96)

Table 2

^{1}H NMR characteristics [a,b]

Compound	$\delta(^1H)$ (ppm) [c]: Hydrocarbyl ligands (J(Pt–H)) [Assignment]			$\delta(^1H)$ (ppm): Ancillary ligands (J(Pt–H)) [Assignment]
	Pt-CH_2	Si(CH_3)$_2$	ALKENE (J_{trans}, J_{cis}, J_{gem})	
(nbd)PtR_2	1.07(102.0)	0.16	6.31 dd [H_A]; 5.85 dd [H_B]; 5.66 dd [H_C] (20.2, 14.6, 4.1)	4.52(41.1) [A]; 3.32 [B]; 1.03 [C]
(bipy)PtR_2	1.26(89.6)	0.39	6.58 dd [H_A]; 5.93 m [H_B]; 5.86 m [H_C]; [d]	9.00 d (22.2) ($^3J(H_6–H_5) = 5.4$) [H_6] 6.46 m [H_5]; 7.01 m [H_4]; 6.71 d ($^3J(H_4–H_3) = 8.1$) [H_3]
(Me_2bipy)PtR_2	1.21(89.5)	0.43	6.64 dd [H_A]; 5.96 m [H_B]; 5.89 m [H_C]; [d]	8.84 d (21.9) ($^3J(H_6–H_5) = 5.6$) [H_6] 6.29 d ($^3J(H_6–H_5) = 5.6$) [H_5]; 6.76 s [H_3]; 1.57 [Me]
(Bu^t_2bipy)PtR_2	1.32(89.6)	0.47	6.69 m [H_A]; 5.99 s [H_B]; 5.92 m [H_C]; [d]	9.01 d (21.9) ($^3J(H_6–H_5) = 6.0$) [H_6] 6.61 dd ($^3J(H_6–H_5) = 5.9$, $^4J(H_5–H_3) = 1.7$) [H_5]; 7.42 d ($^4J(H_5–H_3) = 1.9$) [H_3]; 0.94 [CMe_3]
(bipym)PtR_2	1.26(91.3)	0.36	6.48 dd [H_A]; 5.88 m [H_B]; 5.81 m [H_C]; [d]	8.85 dd (21.8) ($^3J(H_6–H_5) = 5.7$; $^4J(H_6–H_4) = 2.1$) [H_6]; 6.06 m [H_5]; 8.21 dd ($^3J(H_5–H_4) = 4.5$, $^4J(H_6–H_4) = 2.1$) [H_4]
(bipyz)PtR_2	1.70(90.8)	0.43	6.56 dd [H_A]; 5.98 m [H_B]; 5.91 m [H_C]; [d]	8.83 dd (21.6) ($^3J(H_6–H_5) = 3.1$, $^5J(H_6–H_3) = 1.1$) [H_6]; 7.92 d

				(^3J(H_6–H_5) = 3.1) [H_5]; 8.09 d (^5J(H_6–H_3) = 1.0) [H_3]
(phen)PtR_2	1.45(90.6)	0.42	6.60 m [H_A]; 5.93 m [H_B]; 5.86 m [H_C]; ^{d}	9.25 dd (23.0) (^3J(H_2–H_3) = 5.3, ^4J(H_2–H_4) = 1.3) [H_2]; 6.72 dd (^3J(H_2–H_3) = 5.2, ^3J(H_3–H_4) = 8.1) [H_3]; 7.44 dd (^4J(H_2–H_4) = 1.3 ^3J(H_3–H_4) = 8.1) [H_4]; 6.88 s [H_5]
(Me_4phen)PtR_2	1.40(89.7)	0.50	6.67 dd [H_A]; 5.98 m [H_B]; 5.91 s [H_C]; ^{d}	9.06 s (23.5) [H_2]; 7.26 s [H_5]; 1.87 [Me_3]; 1.74 [Me_4]
(Ph_2phen)PtR_2	1.57(90.3)	0.51	6.71 m [H_A]; 6.00 m [H_B]; 5.94 m [H_C]; ^{d}	9.40 d (23.0) (^3J(H_2–H_3) = 5.4) [H_2] 6.84 d (^3J(H_2–H_3) = 5.3) [H_3]; 7.3 s [H_5]; 7.19–7.06 [Ph]
(tmeda)PtR_2	0.17(102.7)	0.31	6.60 dd [H_A]; 5.89 dd [H_B]; 5.77 dd [H_C] (20.2, 14.5, 4.4)	1.69(11.8) [CH_2]; 2.12(22.2) [NMe_2]
(py-d_5)$_2$PtR_2	0.74(88.5)	0.17	6.47 dd [H_A]; 5.84 dd [H_B]; 5.76 dd [H_C] (20.1, 14.7, 4.4)	
(py)$\overline{\mathrm{PtR(R)}}$	1.04(103.9) 1.51(105.1) ($^2J_{H-H}$ = 10.4)	0.05 0.06 0.13 0.49	6.27 dd [H_A]; 5.75 dd [H_B]; 5.61 dd [H_C] (20.1, 14.6, 4.3) 3.87 dd (30.8) [H_A']; 3.26 dd (28.0) [H_B']; 4.11 dd (48.0) [H_C'] (16.8, 11.4, 2.2)	8.11 dd (20.6) (^3J(H_2–H_3) = 6.4, ^4J(H_2–H_4) = 1.6) [H_2, H_6]; 6.39 tt (^3J(H_3–H_2) = 6.4, ^3J(H_3–H_4) = 7.7) [H_3, H_5]; 6.75 dd (^4J(H_4–H_2) = 1.6, ^3J(H_4–H_3) = 7.7) [H_4]

---

^{a} Recorded in benzene-d_6 at 250 MHz. ^{b} Coupling constants J in Hz where observed. ^{c} Referenced to internal benzene-d_5 (δ 7.15 ppm). ^{d} 2nd order resonances (coupling constants obscured).

Recently, we described a tricyclohexylphosphine complex in which the unsaturated function of one sila-neohexenyl ligand is η^2-coordinated to platinum [10]. We have also prepared and characterised an analogous complex containing pyridine as the neutral donor ligand [10]. This is easily achieved by reaction of (nbd)PtR_2 in pyridine. First, $(py)_2PtR_2$ is formed by displacement of diene and then, as the pyridine is evaporated off intramolecular displacement of one coordinated pyridine by alkene forms $(py)\overline{PtR(R})$. Its NMR (^1H and ^{13}C) characteristics (vide infra) are comparable with those of the tricyclohexylphosphine complex [10].

Although the bis-pyridine complex could not be isolated, it has been characterised by NMR (^1H and ^{13}C) spectroscopy as the deuterated analogue $(py\text{-}d_5)_2PtR_2$.

B. Spectroscopic studies

(i) ^1H NMR (Table 2)

(a) $LPtR_2$. A notable feature of the spectra for $LPtR_2$ complexes is the pattern associated with the vinylic hydrogens. Measured at 250 MHz, for L = nbd, tmeda and $(py\text{-}d_5)_2$, the expected three sets of double doublets are observed, with $J_{trans} > J_{cis} > J_{gem}$ (as in the analogous tertiary phosphine complexes [10]). The other compounds, however, show second order patterns due to the convergence in chemical shifts of H_B and H_C. H_A shows two additional lines ascribable to normally forbidden transitions [11] (Fig. 1a). Second-order character is still evident at 400 MHz.

Precise chemical shifts and coupling constants were confirmed by computer-simulation of the vinylic hydrogens (Fig. 1b, Table 3). These illustrate the convergence of the H_B and H_C resonances as L varies, while the internal couplings remain constant.

Relative to the unperturbed first-order spin systems (L = nbd, cod, tmeda, py or P-donors) the olefinic hydrogens in the second-order spectra invariably display a net downfield shift, particularly H_C. This indicates that the effect does not stem from a direct metal–alkene interaction, since η^2-coordination of one alkene in these complexes leads to marked upfield shifts for the corresponding hydrogens (vide infra and cf. Ref. 10). More plausibly, the modified chemical shifts are due to the local magnetic effect of the extended π-electron system in the planar platinum-heteroaromatic skeleton. As the area of delocalised π-electron density increases, the magnitude of its anisotropic magnetic influence would be expected to grow correspondingly. This accords with the observation that the effect is most marked for Ph_2phen, where the opportunities for π-conjugation are maximised, and progressively diminishes as the extent of the π-framework and/or the electron availability in the rings is reduced. Clearly, the olefinic substituents predominantly occupy coordination space where the induced field is deshielding. Among complexes of N-donors, that of pyridine (with unconjugated rings which are not constrained coplanar with the metal coordination plane) and tmeda (which has no aromatic conjugation) display first-order spectra for olefinic hydrogens.

The ^1H chemical shifts of the platinum-bound methylene groups are doubtless sensitive to additional electronic influences within the complex, such as σ-effects of ligands. The same π-electron deshielding may, though, account in part for the fact

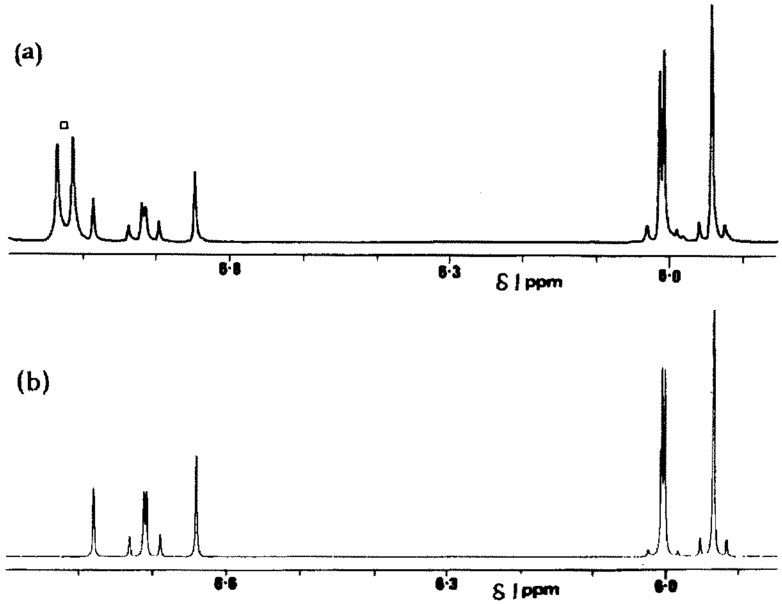

Fig. 1. (a) Observed and (b) simulated ^{1}H NMR spectra for (Ph$_2$phen)Pt(CH$_2$SiMe$_2$CH:CH$_2$)$_2$; □ H$_3$ from Ph$_2$phen ring.

Table 3

^{1}H NMR data from spectrum simulation [a]

Compound	$\delta(^1H)$ (ppm): Alkene [assignment] (J_{trans}, J_{cis}, J_{gem})	rms error [b] (Hz)
(nbd)PtR$_2$	6.31 dd [H$_A$]; 5.85 dd [H$_B$]; 5.66 dd [H$_C$] (20.4, 14.5, 4.0)	0.05
(bipy)PtR$_2$	6.58 dd [H$_A$]; 5.91 m [H$_B$]; 5.88 m [H$_C$] (20.3, 14.5, 4.3)	0.06
(Me$_2$bipy)PtR$_2$	6.64 dd [H$_A$]; 5.95 m [H$_B$]; 5.92 m [H$_C$] (20.3, 14.5, 4.3)	0.13
(Bu$^t_2$bipy)PtR$_2$	6.69 m [H$_A$]; 5.96 m [H$_B$]; 5.96 m [H$_C$] (20.5, 14.9, 4.4)	0.64
(bipym)PtR$_2$	6.48 dd [H$_A$]; 5.87 m [H$_B$]; 5.83 m [H$_C$] (20.4, 14.5, 4.2)	0.09
(bipyz)PtR$_2$	6.56 dd [H$_A$]; 5.98 m [H$_B$]; 5.92 m [H$_C$] (19.9, 14.7, 4.0)	0.39
(phen)PtR$_2$	6.60 m [H$_A$]; 5.90 m [H$_B$]; 5.90 m [H$_C$] (20.4, 14.5, 4.3)	0.07
(Me$_4$phen)PtR$_2$	6.66 dd [H$_A$]; 5.92 m [H$_B$]; 5.94 s [H$_C$] (20.0, 14.9, 4.2)	0.11
(Ph$_2$phen)PtR$_2$	6.71 m [H$_A$]; 5.97 m [H$_B$]; 5.97 m [H$_C$] (20.0, 14.9, 4.4)	0.10
(tmeda)PtR$_2$	6.59 dd [H$_A$]; 5.89 dd [H$_B$]; 5.77 dd [H$_C$] (20.3, 14.4, 4.3)	0.08
(d_5-py)$_2$PtR$_2$	6.47 dd [H$_A$]; 5.84 m [H$_B$]; 5.76 dd [H$_C$] (20.3, 14.4, 4.3)	0.11

[a] Coupling constants J in Hz. [b] rms ≡ root-mean-square.

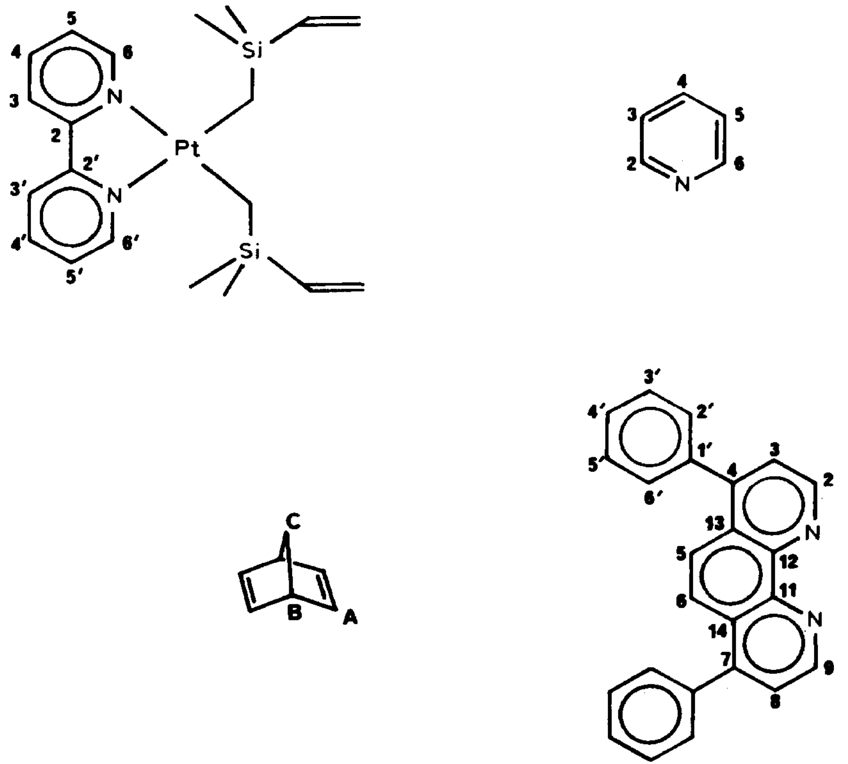

Fig. 2. ^1H and ^{13}C NMR numbering systems for neutral donor ligands.

that the heteroaromatic ligands with three rings generally induce shifts for these hydrogens downfield from their two-ring counterparts (Table 2).

The platinum satellites of the methylene protons are noticeably broader in the complexes with nitrogen-donor ligands than with the diene. This may be attributed to enhanced relaxation of the ^{195}Pt nucleus by quadrupolar ^{14}N. A similar effect was observed in the ^1H NMR spectrum of CH_3HgI, in which $^2J(Hg–H)$ is not observed owing to rapid relaxation of ^{199}Hg by ^{127}I [12]. It appears to be general for alkylplatinum complexes of this class [13].

Comparison of $^2J(Pt–H)$ couplings with the tertiary phosphine complexes shows that the nitrogen values are ca. 10 Hz larger [10]. This implies more *s*-orbital character in the Pt–C–H skeleton for the nitrogen donors, reflecting their weaker *trans*-influence [14].

The resonances assigned to the neutral donor ligands are largely as expected, with $^3J(Pt–H)$ = ca. 22 Hz for hydrogens adjacent to the chelating nitrogen atoms [6]. The bipyz complex appeared to show unusual internal H–H couplings; H_6 interacts with both H_5 (^3J) and H_3 (^5J), while H_5 does not couple to H_3 (^4J) (see Fig. 2 for numbering). Coupling through four bonds might be expected to be greater than that through five. The free ligand, though, shows the same pattern, which has also been observed in complexes with Ru, Mo and W [15].

(b) $L\overline{PtR(R)}$. The ^1H NMR spectrum for (py)$\overline{PtR(R)}$ is complex. A face-bound η^2-alkene generates a metallacyclic ring which leaves the molecule with no axis or plane of symmetry. This results in magnetic inequivalence of the two hydrogens on

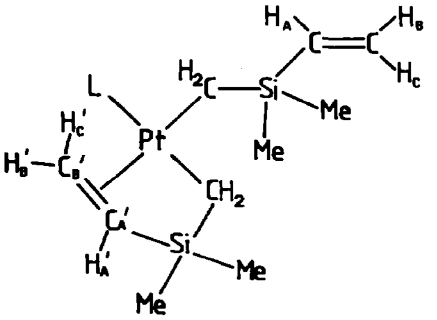

Fig. 3. ^{1}H and ^{13}C NMR assignments for $(L)\overline{Pt(CH_2SiMe_2CH}:CH_2)(CH_2SiMe_2CH:CH_2)$.

each ligating methylene group and also between the two methyl environments on each silicon atom (Fig. 3). In the latter case, four equal-intensity singlets (integral 3H) are seen in the region 0.05–0.49 ppm. Each methylene group should generate an AB spin pattern with ^{195}Pt satellites; one is clearly visible centred at ca. 1.3 ppm (rel.intensity, 2H) while the other is obscured by the methyl peaks.

The most diagnostic features of η^2-coordination are three doubled doublets with ^{195}Pt-satellites observed for H_A', H_B' and H_C' (Fig. 4).

In the past, ^{1}H NMR parameters have been widely used as guides to steric and electronic aspects of metal–alkene bonding [16]. There are three major ways in which alkene coordination can deviate from the ideal, symmetrical geometry (Fig. 5). ^{1}H NMR data has been the basis of estimations of the extent, in particular, of those shown in Fig. 5c and 5d.

There is the expected upfield coordination shift for all three η^2-alkene hydrogens, attributable to partial rehybridisation at carbon toward *sp*^{3} leading to an increase in shielding [16,17]. Coupling between olefinic hydrogens is reduced, for the same reason. The largest decrease is for the geminal coupling $J(H_B'–H_C')$, which may indicate more rearrangement around the terminal carbon upon coordination.

Couplings between ^{195}Pt and olefinic hydrogens are governed by complex factors, including the nature of the *trans*-ligand and possibly the dihedral angles between transmission vectors. Earlier work also suggests a relation between the size of

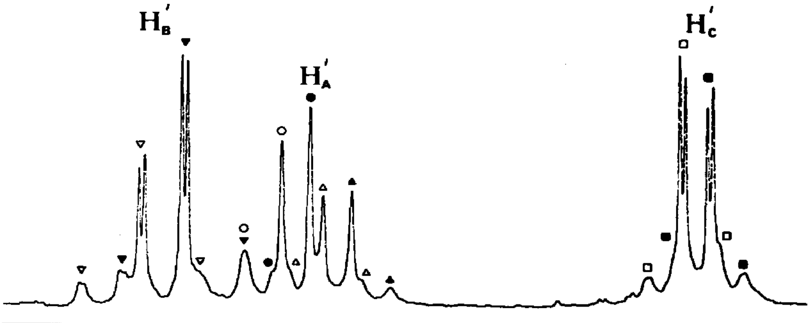

Fig. 4. ^{1}H NMR spectrum of the η^2-alkene region for $(C_5H_4N)\overline{Pt(CH_2SiMe_2CH}:CH_2)(CH_2SiMe_2CH:CH_2)$.

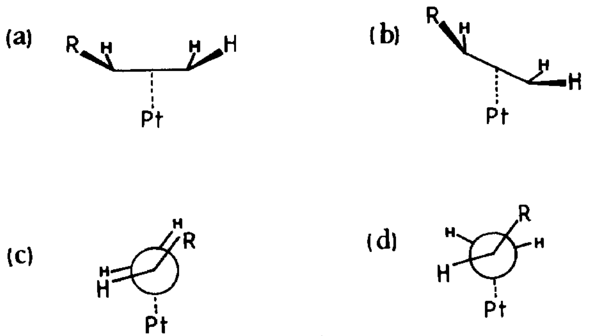

Fig. 5. Deviations from ideal η^2-alkene–Pt coordination.

J(Pt–H) and the closeness of approach between the two nuclei [16,18]. While J(Pt–H_A') and J(Pt–H_B') are similar, J(Pt–H_C') is much larger suggesting that H_C' and the silicon atom are held closer to the metal. Such a tilt about the C–C axis is not surprising since Si is linked to Pt via the methylene group. A comparison with the phosphine complexes shows similar η^2-alkene environments [10]. The slightly larger J(Pt–H) values for the pyridine complex reflect the greater *trans*-influence of phosphine [14].

The pyridine ligand itself shows the expected resonances, with ^3J(Pt–H) similar in size to those for bidentate nitrogen ligands.

(ii) ^{13}C NMR (Table 4)

For sila-neohexenyl complexes, ^1J(Pt–C) values (for methylene carbon) are ca. 200 Hz smaller than for neophyl analogues but are very similar to sila-neophyl * [6,13]. As we have argued elsewhere, this coupling is dominated by Fermi-contact and differences derive from changes in *s*-orbital character contributed to the Pt–C bond [10]. For example, a comparison of (nbd)Pt$(CH_2SiMe_2CH:CH_2)_2$ with (nbd)Pt$(CH_2CMe_2Ph)_2$ [19] shows that ^1J(Pt–C) increases from 748 Hz to 928 Hz for the alkyl ligands. Thus, neophyl concentrates more Pt 6*s*-character in the Pt–C bond, presumably in response to a greater 2*s* contribution by carbon. This is in agreement with Bent's propositions of isovalent hybridisation [20]. For (nbd)Pt$(CH_3)_2$, ^1J(Pt–C) [816 Hz] is intermediate between neophyl and sila-neohexenyl, in accord with the electronegativity order C > H > Si [21].

The chemical shifts and coupling constants of the sila-neohexenyl ligand remain essentially constant as the bis-nitrogen ligand is varied, indicating similar electronic and steric environments for the Pt$(CH_2SiMe_2CH:CH_2)_2$ skeleton in this series. Comparison with the tertiary phosphine analogues reveals that ^1J(Pt–C) for the bis-nitrogen complexes is ca. 200 Hz larger, in accord with their weaker *trans*-influence [10].

The spectrum for (py)$\overline{\text{PtR(R}}$) is complicated by the absence of symmetry planes (Fig. 3). Hence, the two methyl groups on each Si are magnetically non-equivalent, which might generate four resonances. Only three distinct signals are observed, however. The peak at 1.22 ppm [^3J(Pt–C) = 29.9 Hz] is assigned to shift-coincidence of the methyl groups on the η^1-sila-neohexenyl ligand (it has roughly twice the

---

* sila-neophyl = phenyldimethylsilylmethyl.

Table 4

^{13}C NMR characteristics [a,b]

Compound	δ(^{13}C) (ppm) [c]: Hydrocarbyl ligands (J(Pt–C))				δ(^{13}C) (ppm): Ancillary ligands (J_{Pt-C}) [assignment]
	Pt-CH_2	Si(CH_3)$_2$	CH=CH$_2$	CH=CH_2	
(nbd)PtR$_2$	14.79(748.2)	1.98(34.4)	144.49(30.3)	129.10	85.22(55.0) [A]; 72.89 (53.6) [C] 48.91(39.9) [B]
(bipy)PtR$_2$	−8.72(743.5)	1.46(34.9)	146.17(37.0)	[d]	156.12 [C$_2$]; 126.14(20.2) [C$_3$]; 134.84 [C$_4$]; 121.82 [C$_5$]; 147.55 (32.3) [C$_6$]
(Me$_2$bipy)PtR$_2$	−9.48(741.9)	1.53(34.8)	146.42(38.3)	[d]	156.15 [C$_2$]; 127.00(18.3) [C$_3$]; 146.56 [C$_4$]; 122.69(11.0) [C$_5$]; 147.11(32.9) [C$_6$]; 21.11 [Me]
(Bu$^t_2$bipy)PtR$_2$	−9.42(740.6)	1.56(34.0)	146.47(38.8)	127.80	156.61(11.3) [C$_2$]; 123.61(20.3) [C$_3$]; 159.52 [C$_4$]; 118.49(12.6) [C$_5$]; 147.47(33.3) [C$_6$]; 35.13 [CMe$_3$]; 29.75 [CMe_3]
(bipym)PtR$_2$	−8.82(749.1)	1.32(35.6)	145.64(35.5)	[d]	162.67 [C$_2$]; 155.34 [C$_4$]; 122.96(16.3) [C$_5$]; 152.82(27.7) [C$_6$]
(bipyz)PtR$_2$	−5.91(747.1)	1.26(35.1)	145.11(35.0)	128.29	149.13 [C$_2$]; 149.23(17.6) [C$_3$]; 144.23(10.0) [C$_5$]; 140.23(29.8) [C$_6$]
(phen)PtR$_2$	−9.51(746.6)	1.52(35.1)	146.27(38.1)	[d]	148.20 [C$_{11}$]; 130.35 [C$_{13}$]; 134.30 [C$_4$]; 125.12(21.1) [C$_3$]; 147.26(33.2) [C$_2$]; 126.52 [C$_5$]
(Me$_4$phen)PtR$_2$	−9.92(741.3)	1.62(35.7)	146.73(36.0)	[d]	146.91 [C$_{11}$]; 129.56 [C$_{13}$]; 140.91 [C$_4$]; 133.14(21.0) [C$_3$]; 148.47(34.1) [C$_2$]; 122.43 [C$_5$]; 16.93 [Me$_3$]; 14.37 [Me$_4$]
(Ph$_2$phen)PtR$_2$	−9.14(742.3)	1.70(35.1)	146.44(37.8)	128.45	148.85 [C$_{11}$]; [d] [C$_{13}$]; 137.73 [C$_4$]; 125.83(21.9) [C$_3$]; 146.87(33.0) [C$_2$]; [d] [C$_5$]; 147.44 [C$_1'$]; [d] [C$_2'$, C$_3'$, C$_4'$, C$_5'$, C$_6'$]
(tmeda)PtR$_2$ [e]	−23.09(765.7)	2.73(39.5)	147.29(39.1)	126.68	48.77 [NMe_2]; 61.46 [CH_2]
(d$_5$-py)$_2$PtR$_2$ [f]	−13.56(735.5)	1.08(33.7)	146.23(41.4)	127.41	[d]
(py)$\overline{\text{PtR(R)}}$ [g]	16.90(779.7)	1.22(29.9)	145.15(41.5)	127.94	150.29(52.7) [C$_2$, C$_6$]
		8.63(44.6)			
	−26.00(540.6)	−1.10	81.85	84.18(83.2)	125.00(19.7) [C$_3$, C$_5$]; 135.99 [C$_4$]

---

[a] Recorded in benzene-d_6, unless otherwise noted. [b] Coupling constants J in Hz. [c] Referenced to internal benzene-d_6 (δ 128.00 ppm) or toluene-d_8 (δ 128.00 ppm). [d] Resonance obscured by solvent. [e] Recorded at 0 °C in toluene-d_8. [f] Recorded at −20 °C in toluene-d_8. [g] Recorded at −10 °C in toluene-d_8.

intensity of either remaining methyl signal). The two peaks at 8.63 ppm [^3J(Pt–C) = 44.6 Hz] and −1.10 ppm are thus assigned to silicon-methyls in the η^2-coordinated fragment. The zero coupling in the latter case has been ascribed to self-cancellation of multi-path couplings with opposed signs [10]. The unusually large coupling for the other methyl may be due to some geometrical anomaly caused by the η^2-coordination.

The two methylene groups bound to platinum occur as "triplet" resonances at ca. −26 ppm [^1J(Pt–C) = 540 Hz] and ca. 17 ppm [^1J(Pt–C) = 780 Hz]. Comparison with $LPtR_2$ indicates that the smaller coupling arises *trans*- to pyridine and the larger, *trans*- to the η^2-alkene.

The alkene carbons show upfield coordination shifts (40–60 ppm). By analogy with their phosphine counterparts, the "triplet" resonance [J(Pt–C) = ca. 80 Hz] at lower field is due to C_B', whilst the methylene carbon (C_A') shows no coupling [10]. This may be attributed, as before, to self-cancellation.

^{13}C NMR data have also given rise to speculation on the nature of metal–alkene bonding. As with the phosphine analogues of this complex [10], similar structural contradictions emerge from chemical shift and coupling constants. The extent of depopulation of olefin π-orbitals (with concomitant population of π^*) is supposedly reflected in the upfield coordination shifts ($\Delta\delta$C) [22]. Unequal shifts have been interpreted as reflecting asymmetric coordination of alkene, with one carbon nearer to platinum (Fig. 5b) [23]. On this basis, C_A' ($\Delta\delta C = -63.3$ ppm) might be presumed closer to the metal than C_B' ($\Delta\delta C = -43.8$ ppm).

On the other hand, the distance of carbon from platinum is also proposed to correlate with the value of J(Pt–C) [23,24]. On this basis, C_B' is closer to the platinum centre, as would be expected in view of the metal connection and in agreement with ^{1}H NMR indications.

(iii) Infrared spectroscopy

IR data for these compounds are listed in the Experimental section. The very strong doublet centred at ca. 825 cm^{-1} is assigned to the Si–C stretching vibrations, whilst a strong singlet at ca. 1240 cm^{-1} is particularly indicative of $Si-CH_3$ stretching. The expected weak band at ca. 1590 cm^{-1} characteristic of an alkene C=C vibration is observed for $LPtR_2$ [L = nbd, tmed]. This band is obscured by the strong vibrations of the aromatic rings in the other complexes. For $(py)\overline{PtR(R})$ though, it occurs at 1571 cm^{-1} with a stronger band at ca. 1501 cm^{-1} assigned to the platinum-coordinated C=C vibration [cf. $(Cy_3P)\overline{PtR(R})$ [10]].

(iv) Electronic spectroscopy (Table 5)

The electronic spectra of platinum(II) complexes with chelating aromatic nitrogen ligands have been used as indicators of electronic energetics [25]. The complexes $LPtR_2$ [L = bipy, Me_2bipy, Bu^t_2bipy, bipym, bipyz, phen, Me_4phen, Ph_2phen] are characterised by two absorptions attributed to metal–ligand charge transfer (MLCT) $d\pi-\pi^*$ transitions. While the higher energy band often may be obscured, the lower energy band (λ_1) is always observed. This absorption reflects the energy difference between the HOMO on platinum and the LUMO on the ligand.

As observed for related complexes [26b], λ_1 for the bipym complex occurs at a longer wavelength than for bipy. This accords with the generally observed lowering of λ_1 in complexes of N-bonded heteroaromatic ligands with additional electro-

Table 5

First MLCT transition (λ_1) for LPtR$_2$

Compound	λ_1 max (nm)		
	Acetone	CH$_2$Cl$_2$	Hexane
(bipy)PtR$_2$	479.2	482.4	540.1
(Me$_2$bipy)PtR$_2$	470.7	470.4	532.0
(Bu$^t{}_2$bipy)PtR$_2$	468.5	470.4	526.4
(bipym)PtR$_2$	495.7	506.4	563.6
(bipyz)PtR$_2$	532.0	545.7	581.7
(phen)PtR$_2$	477.7	476.0	532.4
(Me$_4$phen)PtR$_2$	432.6	432.8	494.7
(Ph$_2$phen)PtR$_2$	485.2	484.8	536.3

negative ring atoms or substituents [26]. In contrast, the electron-releasing substituents in Me$_2$bipy and Bu$^t{}_2$bipy raise the LUMO energy, giving shorter wavelength transitions. The increased conjugation available in phenanthroline might suggest lower energy transitions relative to bipy but λ_1 is similar for the two, implying a comparable degree of π back-bonding.

The MLCT band energy is solvent-dependent; on changing from acetone to dichloromethane, while a relatively small shift occurs in λ_1 for the bipy and phen complexes, the bipym and bipyz complexes show significant energy reduction (ca. 12 nm). In hexane, all the complexes exhibit a large bathochromic shift (relative to acetone solution). Generally, this is ca. 58 nm to longer wavelength, except for bipyz (ca. 36 nm). In closely related *cis*-dialkyl platinum(II) complexes, similar solvatochromism has been ascribed to the direct interaction of solvent molecules with the metal [27]. The analogous sila-neophyl complexes show very similar electronic effects [13].

Acknowledgements

We thank Sue Johnson and Dick Sheppard of this Department, and Dr. Geoff Hawkes and his staff at Queen Mary College, London, for NMR measurements; and Dr. Henry Rzepa for invaluable advice. We are indebted to the SERC for the award of a studentship (to RDK) and to Johnson-Matthey Inc., for a generous loan of platinum salts.

References

1 (a) C.B. Lebrilla and W.F. Maier, J. Am. Chem. Soc., 108 (1986) 1606; (b) F.G. Gault, Gazz. Chim. Ital., 109 (1979) 255.

2 For reviews see: I.P. Rothwell, Polyhedron, 4 (1985) 177; S.D. Chappell and D.J. Cole-Hamilton, ibid, 1 (1982) 739.

3 (a) D.S. Edwards and L.V. Bland, J.W. Ziller, M.R. Churchill and R.R. Schrock, Organometallics, 2 (1983) 1505; (b) L.R. Chamberlain, A.P. Rothwell and I.P. Rothwell, J. Am. Chem. Soc., 106 (1984) 1847; (c) K. Kropp and G. Erker, Organometallics, 1 (1982) 1246; (d) P.J. Fagan, J.M. Marinquez, E.A. Maatta, A.M. Seyam and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 6650.

4 See, for example: (a) P. Foley, R. DiCosimo and G.M. Whitesides, ibid., 102 (1980) 6713; (b) R.A. Anderson, R.A. Jones and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1978) 446; (c) P. Diversi, G. Ingrosso, A. Lucherini and D. Fasse, J. Chem. Soc., Chem. Commun., (1982) 945; (d) J.W. Bruno,

T.J. Marks and V.W. Day, J. Am. Chem. Soc., 104 (1982) 7357; (e) J.A. Duff, B.L. Shaw and B.L. Turtle, J. Organomet. Chem., 66 (1974) C18; (f) S.D. Chappell, D.J. Cole-Hamilton, A.M.R. Galas and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1982) 1867.
5 See, for example: (a) C.S. Cundy, B.M. Kingston and M.F. Lappert, Adv. Organomet. Chem., 11 (1973) 253; (b) R. DiCosimo, S.S. Moore, A.F. Sowinski and G.M. Whitesides, J. Am. Chem. Soc., 104 (1982) 124; (c) A.H. Janowicz and R.G. Bergman, ibid., 105 (1983) 3929; (d) W.D. Jones and F.J. Feher, ibid., 107 (1985) 620; (e) J.K. Hoyano, A.D. McMaster and W.A.G. Graham, ibid., 105 (1983) 7190; (f) R.H. Crabtree, Chem. Rev., 85 (1985) 245; (g) P.L. Watson and G.W. Parshall, Acc. Chem. Res., 18 (1985) 51; (h) C.M. Fendrick and T.J. Marks, J. Am. Chem. Soc., 108 (1986) 425; (i) A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, Reidel, Dordrecht, 1984, Ch. 5.
6 (a) D.C. Griffiths and G.B. Young, Polyhedron, 2 (1983) 1095; (b) D.C. Griffiths and G.B. Young, Organometallics, in press.
7 (a) D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969; (b) H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Synthesis via Boranes, Wiley, New York, 1975.
8 S.I. Black and G.B. Young, Polyhedron, in press.
9 J.X. McDermott, J.F. White and G.M. Whitesides, J. Am. Chem. Soc., 98 (1976) 6521.
10 R.D. Kelly and G.B. Young, Polyhedron, in press.
11 D.W. Mathieson, NMR for Organic Chemists, Associated Press, 1967, p. 89.
12 D.N. Ford, P.R. Wells and P.C. Lauterbur, J. Chem. Soc., Chem. Commun., (1967) 616.
13 B.C. Ankianiec and G.B. Young, Polyhedron, in press.
14 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
15 R.J. Crutchley and A.B.P. Lever, Inorg. Chem., 21 (1982) 2276.
16 (a) R. Lazzaroni and C.A. Veracini, J. Organomet. Chem., 33 (1971) 131; (b) M.L. Maddox, S.L. Stafford and H.D. Kaesz, Adv. Organomet. Chem., 3 (1965) 1; (c) C.E. Holloway, G. Hulley, B.F.G. Johnson and J. Lewis, J. Chem. Soc. (A), (1970) 1653; (d) P.D. Kaplan and M. Orchin, Inorg. Chem., 6 (1967) 1096; (e) H.P. Fritz and D. Sellmann, Z. Naturforsch. B, 22 (1967) 610.
17 P.S. Braterman, Inorg. Chem., 5 (1966) 1085.
18 (a) H.P. Fritz, K.E. Schwarzhaus and D. Sellmann, J. Organomet. Chem., 6 (1966) 551; (b) B.F.G. Johnson, C.E. Holloway, G. Hulley and J. Lewis, J. Chem. Soc., Chem. Commun., (1967) 1143.
19 B.C. Ankianiec and G.B. Young, unpublished results.
20 H.A. Bent, Chem. Rev., 61 (1961) 275.
21 H.C. Clark, L.E. Manzer and J.E.H. Ward, Can. J. Chem., 52 (1974) 1165.
22 L.E. Manzer, Inorg. Chem., 15 (1976) 2354 and references cited therein.
23 (a) D.G. Cooper and J. Powell, ibid., 15 (1976) 1959; (b) R. Lazzaroni and B.E. Mann, J. Organomet. Chem., 164 (1979) 79.
24 A.C. Jesse, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 32 (1979) 87.
25 N. Chaudhury and R.J. Puddephatt, J. Organomet. Chem., 84 (1975) 105.
26 (a) R.R. Rumininski and J.D. Peterson, Inorg. Chem., 21 (1982) 98; (b) V.F. Sutcliffe and G.B. Young, Polyhedron, 3 (1984) 87.
27 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 3350.