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Dineopentylplatinum(II) complexes with bidentate heteroaromatic N-donor ligands

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Abstract

The preparations are reported of several new bis-neopentylplatinum(II) complexes, viz.: $Pt(CH_2CMe_3)_2L_2$, (L_2 = 2,2′-bipyridyl (bipy), 2,2′-bipyrimidyl (bipym), 4,4′-dimethyl-2,2′-bipyridyl (Me_2bipy), 4,4′-di-t-butyl-2,2′-bipyridyl (Bu^t_2bipy), 1,10-phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), 2,2′-bipyrazine (bipyz), L = pyridine (py)), these were made by ligand displacement from the diene complex $Pt(CH_2CMe_3)_2$(nbd), (nbd = bicyclo[2.2.1]hepta-2,5-diene). Their spectroscopic properties (^{1}H and ^{13}C NMR, IR and UV/visible) are described.

Introduction

In a recent study of intramolecular aromatic C–H activation in *cis*-$Pt(CH_2CMe_2Ph)_2L_2$ [1] close mechanistic parallels were found with platinacyclobutane formation from the more inert *cis*-$Pt(CH_2CMe_3)_2L_2$ [2], where L is a monodentate tertiary phosphine; dissociation of L is a prerequisite, but is not a rate-determining, process. In contrast we observed an unexpected rate-limiting role for the ancillary ligand in metallacyclisations of dineophylplatinum complexes where L_2 is a bidentate, heteroaromatic N-donor such as 2,2′-bipyridyl or 2,2′-bipyrimidyl [1]. To evaluate the influence of N-donor ligands in neopentylplatinum reactivity, we have synthesised a suitable series. Here we report on their preparation and spectroscopic characteristics.

Experimental

General and instrumental

Elemental analyses were by the Imperial College Microanalytical Laboratories. NMR spectra were recorded on Bruker WM250 (^{1}H, 250.13 MHz; ^{13}C, 62.9 MHz)

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and JEOL FX90Q (^{1}H, 89.55 MHz) instruments. IR spectra were recorded on a Perkin–Elmer 683 spectrometer as 4% KBr dispersions. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer.

All reactions were carried out under nitrogen by standard anaerobic techniques [3]. All apparatus was flame dried, and solvents were distilled under nitrogen prior to use; diethyl ether and hexane from sodium/benzophenone and toluene from sodium.

Reagents nbd, bipy, Me_2bipy, bipyz, phen, Ph_2phen, Me_4phen, toluene-d_8 and benzene-d_6 were used as supplied by Aldrich Chemical Company. Bipym was supplied by Lancaster Synthesis, and pyridine was supplied by Rose Chemicals and distilled from sodium hydroxide under nitrogen prior to use. $Mg(CH_2CMe_3)Br$ and $PtCl_2$(nbd) were prepared by published methods.

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

A solution of $Mg(CH_2CMe_3)Br$ [2] (60 cm^3 of a 0.43 *M* solution in ether, 25.8 mmol) in ether (20 cm^3) was added during 30 min to a stirred suspension of $PtCl_2$(nbd) (2.46 g, 6.87 mmol) in ether (50 cm^3) at −78 °C. The mixture was stirred for 4 h as it was allowed to warm slowly to room temperature, and then for a further 2 h. The resulting brown solution was treated with saturated aqueous ammonium chloride solution (20 cm^3), the mixture filtered, and the ethereal layer separated from the aqueous phase, which was washed with ether (3 × 20 cm^3). The organic extracts were combined and dried over anhydrous magnesium sulphate and decolourised with charcoal. Removal of the ether left a pale yellow solid (2.15 g, 73%).

(IR: 2940vs, 2860sh, 2800sh, 1470m, 1460m, 1430sh, 1380w, 1360m, 1310vw, 1270vw, 1240m, 1190vw, 1150m, 980m, 860m, 825w, 765m, 450vw cm^{-1}).

Preparation of (2,2′-bipyridyl)bis(neopentyl)platinum(II)

A solution of $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) in toluene (15 cm^3) was transferred by cannula to a Teflon-capped vessel containing a solution of bipy (74 mg, 0.48 mmol) also in toluene (15 cm^3). Upon addition of the $Pt(CH_2CMe_3)_2$(nbd) solution, the bipy solution became red. After 14 days at ambient temperature, the toluene was removed in vacuo, to leave an orange-red microcrystalline solid (0.17 g, 76%).

(IR: 3120w,br, 2940w,br, 2880m, 2840m, 2790m, 1680w,br, 1600m, 1570w, 1470m, 1450m, 1380w, 1360m, 1310w, 1250m,br, 1220w, 1140m, 1100m, 1050m, 800w, 760vs, 740m cm^{-1}).

Preparation of (4,4′-dimethyl-2,2′-bipyridyl)bis(neopentyl)platinum(II)

A solution of $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) and Me_2bipy (0.09 g, 0.49 mmol) in the minimum amount of toluene (ca. 25 cm^3) was kept for 7 days at 60 °C. The toluene was then removed in vacuo, to leave an orange microcrystalline solid (0.20 g, 84%).

(IR: 3120w, 3090w, 2960w, 2940s, 2890m, 2860m, 2780m, 1620m, 1560w, 1480m, 1470m, 1450m, 1420m, 1370w, 1350m, 1300w, 1260m, 1240m, 1220w, 1100m, 1030m,br, 920w, 890w, 830s, 800m,br, 530m cm^{-1}).

Preparation of (4,4′-di-t-butyl-2,2′-bipyridyl)bis(neopentyl)platinum(II)

A solution of Bu^t_2bipy (0.13 g, 0.48 mmol) and $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) in the minimum amount of toluene (20 cm^3) was kept for 7 days at 60 °C. Removal of the toluene left a dark red microcrystalline solid (0.20 g, 70%).

(IR: 3100w, 3090w, 2960m, 2940s, 2890m, 2860m, 2780m, 1620m, 1560w, 1480m, 1470m, 1450m, 1420m, 1370w, 1360m, 1350m, 1260vs, 1200w, 1150sh, 1090vs,br, 900w, 870w, 840m, 800vs,br, 600m, 390m,br cm^{-1}).

Preparation of (2,2′-bipyrimidyl)bis(neopentyl)platinum(II)

A solution of bipym (80 mg, 0.5 mmol) and $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) in the minimum amount of toluene (ca. 20 cm^3) was stirred at 60 °C for 7 days. Removal of the toluene in vacuo left the product as a dark red microcrystalline solid, which was recrystallised from acetone (10 cm^3) and water (4 cm^3) to yield wine red needles (0.20 g, 90%).

(IR: 3080m, 2940s,br, 2890m, 2840m, 2780m, 1570m, 1550m, 1470m, 1460m, 1400s, 1375w, 1350m, 1240w,br, 1220w, 1145m, 1115w, 1100w, 820m, 750s, 680w, 660w cm^{-1}).

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

A solution of $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) and phen (85 mg, 0.47 mmol) in the minimum amount of toluene (30 cm^3) was kept for 7 days at 60 °C. Removal of the toluene left a scarlet microcrystalline solid (0.22 g, 84%).

(IR: 2920m,br, 2880m, 2840m,sh, 1470m,sh, 1420m,sh, 1410m,sh, 1370m, 1340s,sh, 1260s,br, 1235m, 1210w,sh, 1180m,sh, 1080s,br, 1020s,br, 760m, 715s,sh, 510w, 490w, 390w,br.

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

A solution of $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) and Ph_2phen (0.16 g, 0.48 mmol) in the minimum amount of toluene (20 cm^3) was kept for 7 days at 60 °C. Removal of the toluene in vacuo left a maroon microcrystalline solid (0.24 g, 76%).

(IR: 3030w, 2960m, 2940m, 1640m, 1620m, 1595w, 1560w, 1420w, 1350w, 1260s, 1225m, 1095s,br, 850m, 800vs,br, 760m, 735w, 700m, 630w, 585w, 555w, 400w,br cm^{-1}).

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

A solution of $Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) and Me_4phen (0.12 g, 0.50 mmol) in the minimum amount of toluene (ca. 40 cm^3) was stirred for 7 days at 60 °C. The product separated from the solution during the reaction as a bright orange microcrystalline powder in almost quantitative yield. It was recrystallised from acetone (15 cm^3) and water (5 cm^3) as bright orange needles (0.25 g, 93%).

(IR: 3060w, 2940s,br, 2880s, 2840s, 2780m, 1620w, 1580w,br, 1520w, 1090w, 1020w,br, 920w, 890w,br, 860w, 810m, 720m, 580m, 320w cm^{-1}).

Preparation of (2,2′-bipyrazyl)bis(neopentyl)platinum(II)

$Pt(CH_2CMe_3)_2$(nbd) (0.20 g, 0.47 mmol) and bipyz (75 mg, 0.47 mmol) were dissolved in the minimum amount of toluene (30 cm^3) in a Teflon-capped grease-free flask. The purple solution was kept at ambient temperature for 7 days, and the

solvent then removed in vacuo to leave a purple oil, which was recrystallised from ether and hexane to give a purple microcrystalline solid (0.16 g, 65%).

(IR: 3099m, 2938s, 2895vs, 2851s, 2785s, 1654w, 1578s, 1499w, 1466s, 1403vs, 1379m, 1354m, 1267m, 1242m, 1165s, 1148m, 1106w, 1091w, 1067m, 1036m, 1019m, 836s, 658w, 643w, 482m cm^{-1}).

Preparation of cis-bis(neopentyl)bis(pyridine)platinum(II)

A solution of $Pt(CH_2CMe_3)_2(nbd)$ (0.20 g, 0.47 mmol) in freshly distilled pyridine (10 cm^3) was kept at room temperature for 24 h. Removal of the volatiles in vacuo left a yellow/brown solid (0.22 g, 97%).

(IR: 3070w, 2930vs,br, 2940vs, 2910vs, 1980w, 1970w, 1910w, 1600s, 1470sh, 1440vs, 1375m, 1345s, 1240m, 1205m, 1145m, 1100w, 1065s, 1040m, 1010w, 800w,br, 750s, 690vs, 650w, 630w cm^{-1}).

Results and discussion

Synthesis

The complexes described were made by established methods. Reaction between $PtCl_2(nbd)$ and an excess of $Mg(CH_2CMe_3)Br$ yielded $Pt(CH_2CMe_3)_2(nbd)$ in good yield. Subsequent displacement of the diene by one equivalent of a nitrogen donor ligand produced $Pt(CH_2CMe_3)_2L_2$, also in high yields. These substitutions are slow; $Pt(CH_2CMe_3)_2(bipy)$, for example, requires 14 days at ambient temperature, but this is, more than twice as rapid as diene displacement from the cycloocta-

Table 1

Analytical data for $Pt(CH_2CMe_3)_2L_2$ complexes

Complex	Colour	Element (Found (calcd.) (%))			Yield (%))
		C	H	N	
$Pt(CH_2CMe_3)_2(nbd)$	Yellow	48.39 (48.00)	6.13 (6.12)	– (–)	73
$Pt(CH_2CMe_3)_2bipy$	Scarlet	47.63 (47.51)	6.01 (5.69)	5.68 (5.49)	76
$Pt(CH_2CMe_3)_2Me_2bipy$	Orange	50.48 (50.67)	6.41 (6.53)	5.11 (5.37)	84
$Pt(CH_2CMe_3)_2Bu^t_2bipy$	Maroon	55.33 (55.51)	7.61 (7.60)	3.80 (3.77)	70
$Pt(CH_2CMe_3)_2phen$	Orange/Red	51.14 (51.05)	5.78 (5.84)	5.30 (5.41)	84
$Pt(CH_2CMe_3)_2Me_4phen$	Orange	54.45 (54.35)	6.63 (6.64)	4.89 (4.77)	93
$Pt(CH_2CMe_3)_2Ph_2phen$	Vermillion	60.79 (60.97)	5.52 (5.72)	3.91 (4.18)	76
$Pt(CH_2CMe_3)_2bipym$	Maroon	43.48 (43.63)	5.59 (5.70)	11.19 (11.31)	90
$Pt(CH_2CMe_3)_2bipyz$	Maroon	43.94 (43.63)	5.38 (5.70)	11.54 (11.31)	65
$Pt(CH_2CMe_3)_2py_2$	Yellow/Brown	47.46 (47.17)	6.46 (6.46)	5.61 (5.18)	97

Table 2

^{1}H NMR characteristics of $Pt(CH_2CMe_3)_2L_2$ complexes [a]

Complex	δ(^{1}H) (ppm): Hydrocarbyl ligands (J(Pt–H) (Hz))		δ(^{1}H) (ppm): Neutral donor ligand (J(Pt–H)) assignment		
	CH_2	CH_3			
$Pt(CH_2CMe_3)_2$(nbd)	1.99 (96)	1.11 (5.1)	4.94 (38)	-CH-olefinic	
			3.24	-CH	
			1.07	$-CH_2$	
$Pt(CH_2CMe_3)_2$bipy	2.89 (86)	1.67	9.55 dd (21)	H(6)	J(H(6)–H(7)) = 7.0
			6.51 m	H(5)	J(H(4)–H(5)) = 7.0
			7.05 m	H(4)	J(H(4)–H(6)) = 1.5
			6.80 dd	H(3)	J(H(3)–H(5)) = 1.2
$Pt(CH_2CMe_3)_2Me_2$bipy	2.63 (86)	1.52	9.25 d (20)	H(6)	J(H(5)–H(6)) = 5.7
			7.46 d	H(3)	
			6.65 dd	H(5)	
			1.56 s	CH_3	
$Pt(CH_2CMe_3)_2Bu^t_2$bipy	2.73 (87)	1.72	9.49 d (18)	H(6)	J(H(5)–H(6)) = 6.0
			7.46 d	H(3)	J(H(3)–H(5)) = 1.9
			6.65 dd	H(5)	
			0.95 s	CH_3	
$Pt(CH_2CMe_3)_2$phen	3.05 (87)	1.69	9.75 dd (18)	H(2,9)	J(H(2)–H(3)) = 5.2
					J(H(2)–H(4)) = 1.5
			7.48 dd	H(4,7)	J(H(4)–H(3)) = 1.9
			6.90 s	H(5,6)	
			6.75 dd	H(3,8)	
$Pt(CH_2CMe_3)_2Me_4$phen	3.06 (87)	1.80	9.68 "t"(21)	H(2,9)	
			7.44 s	H(5,6)	
			1.93 s	3,8-CH_3	
			1.78 s	4,7-CH_3	
$Pt(CH_2CMe_3)_2Ph_2$phen	2.96 (86)	1.63	9.80 d (21)	H(2,4)	J(H(2)–H(3)) = 5.4
			7.34 s	H(5,6)	
			7.26-7.04 m	C_6H_5	
			6.86 d	H(3,8)	
$Pt(CH_2CMe_3)_2$bipym	2.81 (87)	1.59	9.31 dd (22)	H(6)	J(H(6)–H(5)) = 5.5
			8.32 dd	H(4)	J(H(4)–H(6)) = 2.2
			6.07 dd	H(5)	J(H(5)–H(4)) = 4.8
$Pt(CH_2CMe_3)_2$bipyz	3.02 (87)	1.50	9.19 d (19)	H(6)	J(H(5)–H(6)) = 4.2
			8.12 d	H(3)	J(H(3)–H(5)) = 1.0
			7.91 d	H(5)	
$Pt(CH_2CMe_3)_2py_2$	2.38 (84)	1.38	8.42 dd (23)	H(2,6)	J(H(2)–H(3)) = 6.0
					J(H(2)–H(4)) = 1.5
			6.74 m	H(4)	J(H(4)–H(3)) = 7.5
			6.28	H(3,5)	

[a] Obtained in toluene-d_8; shifts relative to tetramethylsilane.

1,5-diene analogue [2], which needed at least 28 days at ambient temperature. Reactions at 60 °C were generally complete in 7 days. Use of excess of the ligands did not improve the rates appreciably.

All the complexes $Pt(CH_2CMe_3)_2L_2$ are air-inert, often brightly coloured, crystalline solids, and were characterised by elemental analysis (Table 1). ^{1}H NMR and ^{13}C NMR (Tables 2, 3), as well as electronic (Table 4) and IR spectroscopy (see Experimental section). In solution the N-donor complexes are air-sensitive. They

Table 3

^{13}C NMR characteristics of $Pt(CH_2CMe_3)_2L_2$ complexes [a]

Complex	$\delta(^{13}C)$ (ppm): Hydrocarbyl ligands (J(Pt–C) (Hz))			$\delta(^{13}C)$ (ppm): neutral donor ligand (J(Pt–C) (Hz)) assignment			
	$Pt\text{-}CH_2$	$Pt\text{-}CH_2\text{-}C$	$Pt\text{-}CH_2\text{-}C(CH_3)_3$				
$Pt(CH_2CMe_3)_2$(nbd)	43.77	37.12	34.74	90.59 (40)	CH-olefinic		
	(923)	(22)	(55)	73.92 (44)	CH_2		
				49.08 (37)	CH		
$Pt(CH_2CMe_3)_2$bipy	23.60	37.40	34.96	156.47	C(2);	125.82(16.3)	C(3)
	(940)	(21)	(53)	147.87(30.7)	C(6);	121.94	C(5)
				134.59	C(4)		
$Pt(CH_2CMe_3)_2Me_2$bipy	23.28	37.43	35.03	156.50	C(2);	126.74(16.8)	C(3)
	(939)	(20)	(53)	147.46(32)	C(6);	122.82	C(5)
				146.25	C(4);	21.13	CH_3
$Pt(CH_2CMe_3)_2Bu^t_2$bipy	23.46	37.49	35.08	159.10	C(4);	123.35(16.4)	C(3)
	(938)	(20)	(53)	157.05	C(2);	118.68	(5)
				147.90(31.5)	C(6);	29.78	Bu^t
$Pt(CH_2CMe_3)_2$phen	22.73	37.54	35.14	148.29	C(11,12);	130.27	C(13,14)
	(941)	(20)	(53)	147.83(31.1)	C(2,9);	126.44	C(5,6)
				134.12	C(4,7);	124.87(16.3)	C(3,8)
$Pt(CH_2CMe_3)_2Me_4$phen	22.93	37.60	35.24	149.11	C(2,9);	129.47	C(13,14)
	(939)	(21)	(53)	147.28	C(11,12);	122.30	C(5,6)
				140.35	C(4,7);	16.96	3,8-CH_3
				132.91(18.1)	C(3,8);	14.31	4,7-CH_3
$Pt(CH_2CMe_3)_2Ph_2$phen	23.37	37.69	35.27	148.91	C(11,12);	129.21	C(2′)
	(936)	(20)	(53)	147.47(31.7)	C(2,9);	128.88	C(3′)
				147.12	C(1′);	127.06	C(3,6)
				138.00	C(4,7);	125.65(16.5)	C(3,8)
				129.46	C(13,14);	124.60	C(4′)
$Pt(CH_2CMe_3)_2$bipym	22.86	37.31	34.84	163.02	C(2);	155.25	C(4)
	(949)	(21)	(54)	153.21(27.4)	C(6);	122.82(12.9)	C(5)
$Pt(CH_2CMe_3)_2$bipyz	25.14	37.57	34.81	149.43	C(2);	148.91(12.4)	C(3)
	(932)	(20)	(52)	144.29	C(5);	140.53(20.3)	C(6)
$Pt(CH_2CMe_3)_2py_2$	22.13	37.12	34.64	150.93	C(2,6);	134.71	C(4)
	(930)	(20)	(56)	124.59	C(3,5)		

[a] Obtained in benzene-d_6; shifts relative to tetramethylsilane.

Table 4

Lowest energy MLCT absorptions (λ_1) for $Pt(CH_2CMe_3)_2L_2$ complexes

Complex	λ_1 (nm)	
	CH_2Cl_2	$C_6H_5CH_3$
$Pt(CH_2CMe_3)_2$bipy	491	524
$Pt(CH_2CMe_3)_2Me_2$bipy	480.5	515
$Pt(CH_2CMe_3)_2Bu^t_2$bipy	474.5	513.5
$Pt(CH_2CMe_3)_2$phen	489	522
$Pt(CH_2CMe_3)_2Ph_2$phen	495	531
$Pt(CH_2CMe_3)_2Me_4$phen	440	489
$Pt(CH_2CMe_3)_2$bipym	513	555
$Pt(CH_2CMe_3)_2$bipyz	561	575

react with chlorocarbon solvents, and so chloroform and dichloromethane were avoided as recrystallisation solvents. Where dichloromethane was used as a solvent for spectroscopy, spectra were recorded as soon as possible after preparation of the solutions.

Conventions

Numerical conventions for N-donors follow IUPAC recommendations, as previously [1]. In NMR discussions, resonances which show coupling to ^{195}Pt (spin = $\frac{1}{2}$, 34% abundant) are denoted by $\delta(J)$ where δ is the chemical shift and J is the observed coupling (in Hz). Such multiplets are designated "triplets" ("t") as distinct from binomial 1 : 2 : 1 triplets (t).

^1H NMR (Table 2)

The resonance particularly characteristic of the neopentyl ligand is the 1 : 4 : 1 pattern due to the platinum-bound methylene protons (δ 3.06–1.99), for which ^2J(Pt–H) lies within the range 96–84 Hz. The methyl resonances appear in the range 1.80–1.11 ppm. The hydrogens of the nitrogen donor ligand resonate downfield of the free ligand, as generally observed [1,4,5,6a,7].

Trimethylsilylmethyl complexes predictably show both the methyl and methylene ^1H signals at lower field for these neopentyl complexes than for these silylmethyl analogues [4,5,6].

For all N-donor complexes, the ^{195}Pt satellites of the methylene resonances are broadened significantly, a feature which is characteristic of this skeleton and which is attributed to quadrupolar relaxation of ^{195}Pt by ^{14}N [4,5,6b].

^{13}C NMR (Table 3)

The ^{13}C chemical shifts and J(Pt–C) show little variation as the N-donor ligands vary, although they differ appreciably from those of PtR_2(nbd). The N-donors have similar influences on Pt–C bonding. As observed previously, the presence of carbon in the β-position of the alkyl results in much larger values for ^1J(Pt–C) than in sila-alkyl analogues. For N-donors ^1J(Pt–C) is ca. 940 Hz, compared with ca. 750 Hz for trimethylsilylmethyl analogues [4]. Similarly the value for $Pt(CH_2CMe_3)_2$-(nbd) (923 Hz) is greater than that for $Pt(CH_2SiMe_3)_2$(nbd) (754 Hz). This is matched by a corresponding increase in the value of $^1J(Pt–C_{alkene})$ from 40 Hz to 54

Hz. We have attributed similar differences in other cases to variations in the Pt-6*s* and C-2*s* orbital contribution to the Pt–C bond, in accordance with rehybridisation about C as the electronegativity of its substituent alters [4,5,6a].

These data confirm that sila-alkyl ligands have weaker (NMR) *trans*-influences than their carbon analogues in complexes of this type. The implication that the Pt–C bond is stronger in neopentyl complexes is not in keeping with the conclusions from thermochemical comparisons of these ligands in other cases [8]. We are currently investigating Pt–C bond strengths in these complexes by other techniques.

These results also agree with our general observation that the *trans*-influence of η^2-alkenes is marginally greater than that of N-donors [4–6]. For the alkyl ligands the value of ^2J(Pt–C) is less than that of ^3J(Pt–C), but this, also, is not uncommon [1a].

Infrared spectroscopy

IR data for this series of compounds are listed in the experimental section. The spectra are characteristic, but of little diagnostic value owing to their complexity. There is expected correspondence with data for related complexes [4–6]. Pt–C or Pt–N stretching modes could not be assigned.

Electronic spectra (Table 4)

Electronic spectroscopy is a well established technique for investigating relative electronic influences of heteroaromatic nitrogen donor ligands [1,4,7,9,10]. The spectra of the bis(neopentyl) complexes have been recorded for both dichloromethane and toluene solutions in order allow assessment of solvatochromic effects.

These spectra are characterised by two absorptions which are attributed to $d\pi$–$\pi^\star$ metal–ligand charge-transfer (MLCT) transitions. Of these, the higher energy band (λ_2) is often obscured by the very intense π–$\pi^\star$ transitions of the ligand itself, and so for comparisons of electronic variations within the series, the lower energy absorption (λ_1) is more suitable; it is always observable, and reflects the energy difference between the HOMO of the metal and the LUMO of the ligand.

In toluene the energy of lowest MLCT increases in the order bipyz < bipym < Ph_2phen < bipy < phen < Me_2bipy < Bu^t_2bipy < Me_4phen. This is in accord with previous results [4–6], and can be explained in terms of conjugational and substituent effects. The transitions for bipyz and bipym occur at wavelengths some 25–30 nm longer than that for the analogous bipy complex as a result of the presence of the additional nitrogen atoms; this reflects the general effect of electronegative ring atoms or substituents [1,4]. Similarly, the increased $d\pi$–$\pi^\star$ energy for the Me_2bipy and Bu^t_2bipy complexes is attributed to their electron-releasing substituents.

The effect of increased conjugation can also be seen in this series of complexes when the Ph_2phen and phen complexes are compared. This suggests that π-conjugation can lower the transition energy, although the similarity in λ_1 for the bipy and phen complexes indicates that conjugation is not the only important energetic factor.

The spectra in dichloromethane show marked solvatochromic effects, notably a shift in λ_1 (and λ_2, where observable) to shorter wavelength. This effect has been noted elsewhere [4,5,6a,10], and is suggested [9] to originate from direct interaction

between the solvent and the metal centre, the nature of the interaction not yet being fully understood.

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