3,6-Bis(2′-Pyridyl)pyridazine-based Ligands. Synthesis and Organometallic Complexes of Platinum(II)

MAURO GHEDINI*, FRANCESCO NEVE, MARCELLO LONGERI and MARIA CLOTILDE BRUNO
Dipartimento di Chimica, Università della Calabria, I 87030 Arcavacata (CS), Italy
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Abstract

In order to improve the solubility of bimetallic complexes in organic solvents, some new 3,6-bis(2′-pyridyl)pyridazine-based molecules have been synthesised and tested as ligands in platinum(II) organometallic complexes. The reaction of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine with terminal acetylenes gives 3,6-bis(2′-pyridyl)-4-substituted pyridazines. Their further reactivity toward $(DMSO)_2Pt(CH_3)_2$ or $(COD)Pt(C_6H_5)_2$ (1:1 molecular ratio) is reported. The characterisation of the newly synthesised compound by IR, ^1H NMR and electronic spectroscopy is described.

Introduction

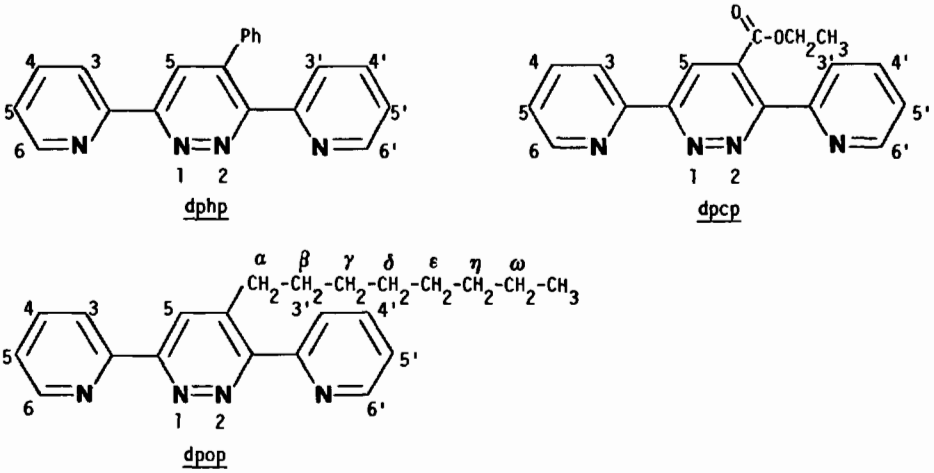
Ligands containing four nitrogen atoms in a bis-chelating arrangement have been proved to be suitable building blocks for the synthesis of bimetallic complexes [1–4]. Following this route, our group has been interested in the preparation and characterisation of the binuclear transition metal species formed from the 3,6-bis(2′-pyridyl)pyridazine (dppn) ligand [1, 5–7]. Such a molecule is very reactive but, in some instances, the final complexes are poorly soluble in the usual solvents [8], and accurate characterisation results quite difficult. The same feature has been displayed by the strictly similar ligand 7,10-bis(2′-pyridyl)-8,9-diazafluoranthene (dpaf) [9]. To overstep this limit we have explored the behaviour of different dppn-like molecules.

In this paper we report the synthesis of two new 3,6-bis(2′-pyridyl)-4-substituted pyridazines, namely carboxyethyl (dpcp) and n-octyl (dpop), shown in Scheme 1. The homologous phenyl compound (dphp in Scheme 1) was previously described by Butte and Case [10]. These ligands, as well as the above cited dpaf gave the respective organometallic derivatives when reacted with $(DMSO)_2Pt(CH_3)_2$ or $(COD)Pt(C_6H_5)_2$. The chemical and physical properties of these new complexes are reported and compared with those of the known $(dppn)Pt(CH_3)_2$ and $(dppn)Pt(C_6H_5)_2$ species [8].

Experimental

Although the complexes were not air-sensitive all reactions were carried out under nitrogen in dried solvent. The ^1H NMR spectra were recorded on a

*Author to whom correspondence should be addressed.



Scheme 1. 4-Substituted 3,6-bis(2′-pyridyl)pyridazine ligands.

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Bruker WH 300 spectrometer with Me_4Si as internal standard. Electronic spectra were obtained using a Perkin-Elmer 550 SE spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer as KBr pellets. Mass spectral (MS, 70 eV) data, reported as (assignment, relative intensity), were determined on a Varian-Mat CH-5/DF + spectrosystem 100 MS apparatus, working in Field Desorption mode. Elemental analyses were performed by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

Reagents

The ligand 7,10-bis(2'-pyridyl)-8,9-diazafluoranthene was synthesised according to the literature [11]. The complexes $(DMSO)_2Pt(CH_3)_2$ [12] and $(COD)Pt(C_6H_5)_2$ [13] were obtained by published procedures.

Preparation of Ligands

3,6-Bis(2'-pyridyl)-4-phenylpyridazine, dphp

The ligand was prepared according to Butte and Case [10] and characterised by NMR spectroscopy and mass spectrometry. ^1H NMR ($CDCl_3$): δ 8.80 [dt, 1 H, $^3J(H^3H^4) = 8$ Hz, $^4J(H^3H^5) = {}^5J(H^3H^6) = 1.0$ Hz, H^3], 8.73 [ddd, 1 H, $^3J(H^6H^5) = 4.8$ Hz, $^4J(H^6H^4) = 1.8$ Hz, $^5J(H^6H^3) = 1.0$ Hz, H^6], 8.67 [s, 1 H, H^7], 8.48 [ddd, 1 H, $^3J(H^{6'}H^{5'}) = 4.8$ Hz, $^4J(H^{6'}H^{4'}) = 1.8$ Hz, $^5J(H^{6'}H^{3'}) = 1.0$ Hz, $H^{6'}$], 7.93 [td, 1 H, $^3J(H^4H^3) = 7.8$ Hz, $^3J(H^4H^5) = 7.8$ Hz, $^4J(H^4H^6) = 1.8$ Hz, H^4], 7.90 [dt, 1 H, $^3J(H^{3'}H^{4'}) = 7.8$ Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'}) = 1.1$ Hz, $H^{3'}$], 7.80 [td, 1 H, $^3J(H^{4'}H^{3'}) = 7.7$ Hz, $^3J(H^{4'}H^{5'}) = 7.7$ Hz, $^4J(H^{4'}H^{6'}) = 1.8$ Hz, $H^{4'}$], 7.42 [ddd, 1 H, $^3J(H^5H^6) = 4.8$ Hz, $^3J(H^5H^4) = 7.5$ Hz, $^4J(H^5H^3) = 1.2$ Hz, H^5], 7.35–7.26 [m, 6 H, $H^{5'}$ and C_6H_5]. ^{13}C NMR, Table I. MS: *m/e* 310 (M^+, 45), 309 ($M^+ - 1$, 100), 262 ($M^+ - C_6H_5$, 2).

3,6-Bis(2'-pyridyl)-4-octylpyridazine, dpop

A small excess of 1-decyne (5.08 mmol) was added to a suspension of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (4.23 mmol) in *N,N*-dimethylformamide. The resulting dark violet solution stirred under reflux became brown after 24 h. The solvent was removed *in vacuo* to give a brown viscous oil, which was eluted on a silica-gel column with diethyl ether and concentrated *in vacuo*. The resulting yellow oil was redissolved in petroleum ether and the solution cooled to −20 °C. The product was obtained as a white solid, melting point (m.p.) 35 °C; yield 62%. *Anal.* Calc. for $C_{22}H_{26}N_4$: C, 76.26; H, 7.56; N, 16.17. Found: C, 75.81; H, 7.56; N, 16.26%. ^1H NMR ($CDCl_3$): δ 8.77–8.71 [m, 3 H, $H^{6,3,6'}$], 8.50 [s, 1 H, H^7], 8.10 [dt, 1 H, $^3J(H^{3'}H^{4'}) = 7.9$ Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'}) = 1.1$ Hz, $H^{3'}$], 7.91 [td, 1 H, $^3J(H^4H^3) = 7.8$ Hz, $^3J(H^4H^5) = 7.8$ Hz, $^4J(H^4H^6) = 1.8$ Hz, H^4], 7.90 [td, 1 H, $^3J(H^{4'}H^{3'}) = 7.8$ Hz, $^3J(H^{4'}H^{5'}) = 7.8$ Hz, $^4J(H^{4'}H^{6'}) = 1.8$ Hz, $H^{4'}$], 7.40 [ddd, 1 H, $^3J(H^5H^6) = 4.6$ Hz, $^3J(H^5H^4) = 7.6$ Hz, $^4J(H^5H^3) = 1.2$ Hz, H^5], 7.39 [ddd, 1 H, $^3J(H^{5'}H^{6'}) = 4.6$ Hz, $^3J(H^{5'}H^{4'}) = 7.6$ Hz, $^4J(H^{5'}H^{3'}) = 1.2$ Hz, $H^{5'}$], 3.09 [m, 2 H, CH_2^{α} (aliphatic chain)], 1.60 [m, 2 H, CH_2^{β} (aliphatic chain)], 1.32–1.22 [m, 10 H, $CH_2^{\gamma,\delta-\omega}$ (aliphatic chain)], 0.86 [t, 3 H, $^3J(HH) = 6.8$ Hz, CH_3 (aliphatic chain)]. ^{13}C NMR, Table I. MS: *m/e* 346 (M^+, 45), 347 ($M^+ + 1$, 12), 261 ($M^+ - C_7H_{15}$, 100), 247 ($M^+ - C_8H_{17}$, 19).

3,6-Bis(2'-pyridyl)-4-carboxyethylpyridazine, dpcp

This reaction was carried out as above using a small excess of ehtylpropiolate in toluene and a 96 h reflux time. The crude product was eluted on a silica-gel column with diethyl ether. Dark yellow crystals were obtained by evaporation of the solvent under vacuum, m.p. 110 °C; yield 83%. *Anal.* Calc. for $C_{17}H_{14}O_2N_4$: C, 66.66; H, 4.61; N, 18.29. Found: C, 66.33; H, 4.54; N, 18.38%. ^1H NMR ($CDCl_3$): δ 8.78–8.74 [m, 2 H, $H^{3,6}$], 8.75 [s, 1 H, H^7], 8.65 [ddd, 1 H, $^3J(H^{6'}H^{5'}) = 4.8$ Hz, $^4J(H^{6'}H^{4'}) = 1.8$ Hz, $^5J(H^{6'}H^{3'}) = 1.0$ Hz, $H^{6'}$], 8.53 [dt, 1 H, $^3J(H^{3'}H^{4'}) = 7.9$ Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'}) = 1.1$ Hz, $H^{3'}$], 7.93 [td, 1 H, $^3J(H^4H^3) = 7.8$ Hz, $^3J(H^4H^5) = 7.8$ Hz, $^4J(H^4H^6) = 1.8$ Hz, H^4], 7.92 [td, 1 H, $^3J(H^{4'}H^{3'}) = 7.8$ Hz, $^3J(H^{4'}H^{5'}) = 7.8$ Hz, $^4J(H^{4'}H^{6'}) = 1.8$ Hz, $H^{4'}$], 7.43 [ddd, 1 H, $^3J(H^5H^6) = 4.9$ Hz, $^3J(H^5H^4) = 7.6$ Hz, $^4J(H^5H^3) = 1.1$ Hz, H^5], 7.40 [ddd, 1 H, $^3J(H^{5'}H^{6'}) = 4.8$ Hz, $^3J(H^{5'}H^{4'}) = 7.6$ Hz, $^4J(H^{5'}H^{3'}) = 1.1$ Hz, $H^{5'}$], 4.40 [q, 2 H, $^3J(HH) = 7.2$ Hz, CH_2-$(CO_2CH_2CH_3)$], 1.30 [t, 3 H, $^3J(HH) = 7.2$ Hz, CH_3-$(CO_2CH_2CH_3)$]. ^{13}C NMR, Table I. MS: *m/e* 306 (M^+, 78), 277 ($M^+ - C_2H_5$, 61), 261 ($M^+ - C_2H_5O$, 33), 205 (100), 78 ($C_5H_4N^+$, 85).

Preparation of Complexes

(dphp)Pt(CH_3)$_2$

A solution of $(DMSO)_2Pt(CH_3)_2$ (0.1 g, 0.26 mmol) in benzene (15 ml) was added to a stirring solution of dphp (0.081 g, 0.26 mmol) in benzene (5 ml). The solution immediately turned deep red. A dark red solid was recovered after 1 h, which was washed with diethyl ether and vacuum dried: yield 93%; m.p. 210 °C (dec.). *Anal.* Calc. for $C_{22}H_{20}N_4Pt$: C, 49.34; H, 3.76; N, 10.46. Found: C, 50.12; H, 3.74; N, 9.99%.

^1H NMR (CD_2Cl_2): δ 1.47 [s, 3 H, $^2J(PtH) = 84.7$ Hz, CH_{3a} or $CH_{3b}Pt$], 1.24 [s, 3 H, $^2J(PtH) = 88.1$ Hz, CH_{3a} or $CH_{3b}Pt$], 9.36 [d(br), 1 H, $^3J(PtH) = 21.0$ Hz, $^3J(H^6H^5) = 5.4$ Hz, H^6], 8.98 [s, 1 H, H^7], 8.84 [dt, 1 H, $^3J(H^{3'}H^{4'}) = 8.0$ Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'}) = 1.0$ Hz, $H^{3'}$], 8.72 [ddd, 1 H, $^3J(H^{6'}H^{5'}) = 4.8$ Hz, $^4J(H^{6'}H^{4'}) = 1.8$ Hz, $^5J(H^{6'}H^{3'}) = 0.9$ Hz, $H^{6'}$], 7.98 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'}) = 7.8$ Hz,

$^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.72 [ddd, 1 H, $^3J(H^4H^3)$ = 8.2 Hz, $^3J(H^4H^5)$ = 7.6 Hz, $^4J(H^4H^6)$ = 1.6 Hz, H^4], 7.58–7.41 [m, 7 H, $H^{5,5'}$ and aromatic protons], 7.13 [dt, 1 H, $^3J(H^3H^4)$ = 8.2 Hz, $^4J(H^3H^5)$ = $^5J(H^3H^6)$ = 1.0 Hz, H^3].

(dpop)Pt(CH_3)$_2$

$(DMSO)_2Pt(CH_3)_2$ (0.1 g, 0.26 mmol) dissolved in benzene (15 ml), was added to a solution of dpop (0.09 g, 0.26 mmol) in benzene (5 ml). Immediately the solution turned light red. After 1 h the solution was concentrated by using a nitrogen stream and diethyl ether (30 ml) added to give a pale red microcrystalline solid. The product was filtered, washed with diethyl ether and vacuum dried: yield 70%; m.p. 165 °C. *Anal.* Calc. for $C_{24}H_{32}N_4Pt$: C, 50.43; H, 5.64; N, 9.80. Found: C, 49.70; H, 5.52; N, 9.45%.

^{1}H NMR (CD_2Cl_2): δ 1.32 [s, 3 H, ^2J(PtH) = 89.2 Hz, CH_{3a} or CH_{3b}Pt], 1.12 [s, 3 H, ^2J(PtH) = 84.5 Hz, CH_{3a} or CH_{3b}Pt], 9.32 [m, 1 H, ^3J(PtH) = 18.9 Hz, $^3J(H^6H^5) \simeq 5.5$ Hz, H^6], 8.73 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.8 Hz, $^4J(H^{6'}H^{4'})$ = 1.8 Hz, $^5J(H^{6'}H^{3'})$ = 1.0 Hz, $H^{6'}$], 8.24 [dt, 1 H, $^3J(H^{3'}H^{4'})$ = 8.0 Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'})$ = 1.0 Hz, $H^{3'}$], 8.21 [td, 1 H, $^4J(H^4H^6)$ = 1.6 Hz, H^4], 8.08 [dt, 1 H, $^3J(H^3H^4)$ = 7.9 Hz, $^4J(H^3H^5) = {}^5J(H^3H^6)$ = 1.0 Hz, H^3], 8.07 [s, 1 H, $H^{7'}$], 7.96 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.63 [ddd, 1 H, $^3J(H^5H^6)$ = 5.4 Hz, $^3J(H^5H^4)$ = 7.5 Hz, $^4J(H^5H^3)$ = 1.3 Hz, H^5], 7.45 [ddd, 1 H, $^3J(H^{5'}H^{6'})$ = 4.8 Hz, $^3J(H^{5'}H^{4'})$ = 7.6 Hz, $^4J(H^{5'}H^{3'})$ = 1.2 Hz, $H^{5'}$], 3.03 [m, 2 H, CH_2^{α} (aliphatic chain)], 1.61 [m, 2 H, CH_2^{β} (aliphatic chain)], 1.23 [m, 10 H, $CH_2^{\gamma-\omega}$ (aliphatic chain)], 0.87 [t, 3 H, CH_3 (aliphatic chain)].

(dpcp)Pt(CH_3)$_2$

To a solution of dpcp (0.08 g, 0.26 mmol) in benzene (5 ml) was added a solution of $(DMSO)_2Pt(CH_3)_2$ (0.1 g, 0.26 mmol) in benzene (15 ml). The solution immediately turned dark red, and after 1 h the product precipitated as a dark red solid. The solid was filtered washed with diethyl ether and vacuum dried: yield 83%; m.p. 210 °C (dec.). *Anal.* Calc. for $C_{19}H_{20}N_4O_2Pt$: C, 42.94; H, 3.79; N, 10.54. Found: C, 41.96; H, 3.73; N, 10.08%.

^{1}H NMR (CD_2Cl_2): δ 1.50 [s, 3 H, ^2J(PtH) = 89.2 Hz, CH_{3a} or CH_{3b}Pt], 1.33 [s, 3 H, ^2J(PtH) = 84.8 Hz, CH_{3a} or CH_{3b}Pt], 9.40 [d(br), 1 H, ^3J(PtH) = 19.2 Hz, $^3J(H^6H^5) \simeq 6.0$ Hz, H^6], 8.67 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.8 Hz, $^4J(H^{6'}H^{4'})$ = 1.7 Hz, $^5J(H^{6'}H^{3'})$ = 0.9 Hz, $H^{6'}$], 8.54 [dt, 1 H, $^3J(H^{3'}H^{4'})$ = 7.9 Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'})$ = 1.0 Hz, $H^{3'}$], 8.26 [s, 1 H, $H^{7'}$], 8.24 [td, 1 H, $^3J(H^4H^3)$ = 8.0 Hz, $^4J(H^4H^6)$ = 1.5 Hz, H^4], 8.12 [d(br), 1 H, $^3J(H^3H^4)$ = 8.0 Hz, H^3], 7.99 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.71 [ddd, 1 H, $^3J(H^5H^6)$ = 5.5 Hz, $^3J(H^5H^4)$ = 7.5 Hz, $^4J(H^5H^3)$ = 1.2 Hz, H^5], 7.47 [ddd, 1 H, $^3J(H^{5'}H^{6'})$ = 4.8 Hz, $^3J(H^{5'}H^{4'})$ = 7.6 Hz, $^4J(H^{5'}H^{3'})$ = 1.1 Hz, $H^{5'}$], 4.36 [q, 2 H, ^3J(HH) = 7.2 Hz, $CH_2(CO_2CH_2CH_3)$], 1.24 [t, 3 H, ^3J(HH) = 7.2 Hz, $CH_3(CO_2CH_2CH_3)$].

(dpaf)Pt(CH_3)$_2$

$(DMSO)_2Pt(CH_3)_2$ (0.213 g, 0.56 mmol) and dpaf (0.2 g, 0.56 mmol) reacted in benzene (10 ml) at room temperature for 48 h after which time a dark red precipitate had formed. The product was filtered, washed with diethyl ether and vacuum dried; yield 84%; m.p. 248 °C (dec.). *Anal.* Calc. for $C_{26}H_{20}N_4Pt$: C, 53.51; H, 3.45; N, 9.60. Found: C, 53.67; H, 3.37; N, 9.49%.

^{1}H NMR (CD_2Cl_2): δ 1.40 [s, 3 H, ^2J(PtH) = 89.0 Hz, CH_{3a} or CH_{3b}Pt], 1.28 [s, 3 H, ^2J(PtH) = 85.6 Hz, CH_{3a} or CH_{3b}Pt], 9.43 [d(br), 1 H, ^3J(PtH) = 19.8 Hz, $^3J(H^6H^5) \simeq 5.0$ Hz, H^6], 8.94 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.9 Hz, $^4J(H^{6'}H^{4'})$ = 1.8 Hz, $^5J(H^{6'}H^{3'})$ = 0.9 Hz, $H^{6'}$], 8.76 [d(br), 1 H, H^3], 8.73 [d, 1 H, $^3J(H^cH^b)$ = 7.3 Hz, H^c], 8.59 [d, 1 H, $^3J(H^{c'}H^{b'})$ = 7.4 Hz, $H^{c'}$], 8.52 [dt, 1 H, $^3J(H^{3'}H^{4'})$ = 7.9 Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'})$ = 1.0 Hz, $H^{3'}$], 8.31 [td, 1 H, $^4J(H^4H^6)$ = 1.3 Hz, H^4], 8.30 [d, 1 H, $^3J(H^aH^b)$ = 7.6 Hz, H^a], 8.23 [d, 1 H, $^3J(H^{a'}H^{b'})$ = 8.0 Hz, $H^{a'}$], 8.10 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.76 [dd, 1 H, $^3J(H^b H^{a'})$ = 8.0 Hz, $^3J(H^{b'}H^{c'})$ = 7.4 Hz, $H^{b'}$], 7.71 [dd, 1 H, $^3J(H^bH^a)$ = 8.0 Hz, $^3J(H^bH^c)$ = 7.3 Hz, H^b], 7.71 [ddd, 1 H, $^3J(H^5H^4)$ = 7.7 Hz, $^4J(H^5H^3)$ = 1.3 Hz, H^5], 7.61 [ddd, 1 H, $^3J(H^{5'}H^{4'})$ = 7.6 Hz, $^3J(H^{5'}H^{6'})$ = 4.9 Hz, $^4J(H^{5'}H^{3'})$ = 1.2 Hz, $H^{5'}$]. The two sets of protons labeled a, b, c and a', b', c' were not assigned unambiguously and may be reversed.

(dphp)Pt(C_6H_5)$_2$

The dphp (0.068 g, 0.22 mmol) was added to a solution of $(COD)Pt(C_6H_5)_2$ (0.1 g, 0.22 mmol) in benzene (10 ml) and the reaction mixture stirred under reflux for 4 h. Addition of diethyl ether (20 ml) to the red solution gave a red–orange solid, which was recovered by filtration, washed with diethyl ether and dried under vacuum: yield 79%; m.p. 230 °C (dec.). *Anal.* Calc. for $C_{32}H_{24}N_4Pt$: C, 58.26; H, 3.67; N, 8.49. Found: C, 58.18; H, 3.75; N, 8.18%.

^{1}H NMR (CD_2Cl_2): δ 7.52–7.12 [m, 10 H, C_6H_{5a} and C_6H_{5b}Pt], 9.99 [s, 1 H, H^7], 9.49 [d(br), 1 H, $^3J(H^{3'}H^{4'}) \simeq 8.0$ Hz, $H^{3'}$], 9.05 [d(br), 1 H, $^3J(H^{6'}H^{5'}) \simeq 5.0$ Hz, $H^{6'}$], 8.91 [d(br), 1 H, ^3J(PtH) ≃ 21.0 Hz, $^3J(H^6H^5)$ = 5.7 Hz, H^6], 8.75 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.9 Hz, $^4J(H^{4'}H^{6'})$ = 1.6 Hz, $H^{4'}$], 8.18 [ddd, 1 H, $^3J(H^{5'}H^{4'})$ = 7.8 Hz, $^4J(H^{5'}H^{3'})$ = 1.2 Hz, $H^{5'}$], 7.92 [t(br), 1 H, $^3J(H^4H^3) = {}^3J(H^4H^5)$ = 7.8 Hz, H^4], 7.90–7.45 [m, 5 H, aromatic protons].

(dpop)Pt(C_6H_5)$_2$

A solution of dpop (0.076 g, 0.22 mmol) and (COD)Pt(C_6H_5)$_2$ (0.1 g, 0.22 mmol) in benzene (10 ml) was stirred under reflux for 4 h. Diethyl ether (20 ml) was added to the resulting red solution giving an orange precipitate. The product was filtered off, washed with diethyl ether and vacuum dried: yield 50%; m.p. 182 °C. *Anal.* Calc. for $C_{34}H_{36}N_4Pt$: C, 58.69; H, 5.21; N, 8.05. Found: C, 57.84; H, 5.07; N, 7.63%.

^{1}H NMR (CD_2Cl_2): δ 7.45 [m, 2 H, H_{ortho} (C_6H_{5a} or $C_6H_{5b}Pt$)], 7.44 [m, 2 H, H_{ortho} (C_6H_{5a} or $C_6H_{5b}Pt$)], 7.03 [m, 2 H, H_{meta} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.95 [m, 2 H, H_{meta} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.89 [m, 1 H, H_{para} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.83 [m, 1 H, H_{para} (C_6H_{5a} or $C_6H_{5b}Pt$)], 8.66 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.7 Hz, $^4J(H^{6'}H^{4'})$ = 1.8 Hz, $^5J(H^{6'}H^{3'})$ = 1.0 Hz, $H^{6'}$], 8.61 [d(br), 1 H, $^3J(H^6H^5)$ = 5.2 Hz, H^6], 8.16–8.11 [m, 2 H, $H^{4,3}$], 8.09 [s, 1 H, $H^{7'}$], 7.97 [dt, 1 H, $^3J(H^{3'}H^{4'})$ = 8.0 Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'})$ = 1.0 Hz, $H^{3'}$], 7.79 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.50 [ddd, 1 H, $^3J(H^5H^6)$ = 5.5 Hz, $^4J(H^5H^3)$ = 2.2 Hz, H^5], 7.37 [ddd, 1 H, $^3J(H^{5'}H^{6'})$ = 4.8 Hz, $^3J(H^{5'}H^{4'})$ = 7.6 Hz, $^4J(H^{5'}H^{3'})$ = 1.1 Hz, $H^{5'}$], 3.22 [m, 2 H, CH_2^{α} (aliphatic chain)], 1.6–1.2 [m, 12 H, $CH_2^{\beta-\omega}$ (alphatic chain)], 0.87 [t, 3 H, ^3J(HH) = 6.8 Hz, CH_3 (aliphatic chain)].

(dpcp)Pt(C_6H_5)$_2$

A solution of (COD)Pt(C_6H_5)$_2$ (0.1 g, 0.22 mmol) and dpcp (0.067 g, 0.22 mmol) in benzene (10 ml) was stirred under reflux. The yellow solution turned red on heating. A red solid precipitated over 24 h, which was filtered, washed with diethyl ether and vacuum dried: yield 65%; m.p. 237 °C. *Anal.* Calc. for $C_{29}H_{24}N_4O_2Pt$: C, 53.13; H, 3.69; N, 8.54. Found: C, 52.23; H, 3.51; N, 8.29%.

^{1}H NMR (CD_2Cl_2): δ 7.45 [m, 2 H, ^3J(PtH) 68.0 Hz, H_{ortho} (C_6H_{5a} or $C_6H_{5b}Pt$)], 7.43 [m, 2 H, ^3J(PtH) 68.0 Hz, H_{ortho} (C_6H_{5a} or $C_6H_{5b}Pt$)], 7.05 [m, 2 H, H_{meta} (C_6H_{5a} or $C_6H_{5b}Pt$)], 7.01 [m, 2 H, H_{meta} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.91 [m, 1 H, H_{para} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.90 [m, 1 H, H_{para} C_6H_{5a} or $C_6H_{5b}Pt$)], 8.68 [ddd, 1 H, ^3J(PtH) = 18.4 Hz, $^3J(H^6H^5)$ = 5.3 Hz, $^4J(H^6H^4)$ = 1.6 Hz, $^5J(H^6H^3)$ = 0.9 Hz, H^6], 8.61 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.8 Hz, $^4J(H^{6'}H^{4'})$ = 1.7 Hz, $^5J(H^{6'}H^{3'})$ = 0.9 Hz, $H^{6'}$], 8.33 [s, 1 H, $H^{7'}$], 8.19 [td, 1 H, $^3J(H^4H^3)$ = 8.0 Hz, $^4J(H^4H^6)$ = 1.5 Hz, H^4], 8.15 [d(br), 1 H, $^3J(H^3H^4) \simeq$ 8.2 Hz, H^3], 8.07 [dt, 1 H, $^3J(H^{3'}H^{4'})$ = 8.0 Hz, $^4J(H^{3'}H^{5'}) = {}^5J(H^{3'}H^{6'})$ = 1.0 Hz, $H^{3'}$], 7.83 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.58 [ddd, 1 H, $^3J(H^5H^6)$ = 5.4 Hz, $^4J(H^5H^3)$ = 1.7 Hz, H^5], 7.41 [ddd, 1 H, $^3J(H^{5'}H^{6'})$ = 4.8 Hz, $^3J(H^{5'}H^{4'})$ = 7.6 Hz, $^4J(H^{5'}H^{3'})$ = 1.2 Hz, $H^{5'}$], 4.39 [q, 2 H, ^3J(HH) = 7.1 Hz, $CH_2(CO_2CH_2CH_3)$], 1.26 [t, 3 H, ^3J(HH) = 7.1 Hz, $CH_3(CO_2CH_2CH_3)$].

(dpaf)Pt(C_6H_5)$_2$

A suspension of dpaf (0.04 g, 0.11 mmol) and (COD)Pt(C_6H_5)$_2$ (0.05 g, 0.11 mmol) in benzene (5 ml) was stirred under reflux for 24 h. A red–orange precipitate formed along with a yellow solution. The precipitate was removed by filtration, washed with diethyl ether and vacuum dried: yield 72%; m.p. 258 °C. *Anal.* Calc. for $C_{36}H_{24}N_4Pt$: C, 61.10; H, 3.42; N, 7.92. Found: C, 61.31; H, 3.30; N, 8.00%.

^{1}H NMR (CD_2Cl_2): δ 7.51 [m, 2 H, H_{ortho} C_6H_{5a} or $C_6H_{5b}Pt$], 7.48 [m, 2 H, H_{ortho} C_6H_{5a} or $C_6H_{5b}Pt$], 7.06 [m, 2 H, H_{meta} C_6H_{5a} or $C_6H_{5b}Pt$], 7.00 [m, 2 H, H_{meta} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.92 [m, 1 H, H_{para} (C_6H_{5a} or $C_6H_{5b}Pt$)], 6.89 [m, 1 H, H_{para} (C_6H_{5a} or $C_6H_{5b}Pt$)], 8.99 [d, 1 H, $^3J(H^cH^b)$ = 7.2 Hz, H^c], 8.88 [ddd, 1 H, $^3J(H^{6'}H^{5'})$ = 4.9 Hz, $H^{6'}$], 8.82 [d-(br), 1 H, $^3J(H^3H^4)$ = 8.0 Hz, H^3], 8.76 [d(br), 1 H, $^3J(H^6H^5) \simeq$ 5.0 Hz, H^6], 8.61 [d, 1 H, $^3J(H^{c'}H^{b'})$ = 7.4 Hz, $H^{c'}$], 8.30 [d, 1 H, $^3J(H^aH^b)$ = 8.1 Hz, H^a], 8.28 [d, 1 H, $^3J(H^{a'}H^{b'})$ = 8.1 Hz, $H^{a'}$], 8.26 [td, 1 H, H^4], 8.05 [d(br), 1 H, $^3J(H^{3'}H^{4'})$ = 7.9 Hz, $H^{3'}$], 7.89 [td, 1 H, $^3J(H^{4'}H^{3'}) = {}^3J(H^{4'}H^{5'})$ = 7.8 Hz, $^4J(H^{4'}H^{6'})$ = 1.8 Hz, $H^{4'}$], 7.81 [dd, 1 H, $^3J(H^{b'}H^{a'})$ = 8.1 Hz, $^3J(H^{b'}H^{c'})$ = 7.3 Hz, $H^{b'}$], 7.78 [dd, 1 H, $^3J(H^bH^a)$ = 8.1 Hz, $^3J(H^bH^c)$ = 7.3 Hz, H^b], 7.60 [ddd, 1 H, $^3J(H^5H^4)$ = 7.6 Hz, $^4J(H^5H^3)$ = 1.2 Hz, H^5], 7.52 [ddd, 1 H, $^3J(H^{5'}H^{6'})$ = 4.7 Hz, $^4J(H^{5'}H^{3'})$ = 1.2 Hz, $H^{5'}$]. The two sets of protons labeled a′, b′, c′ may be interchanged.

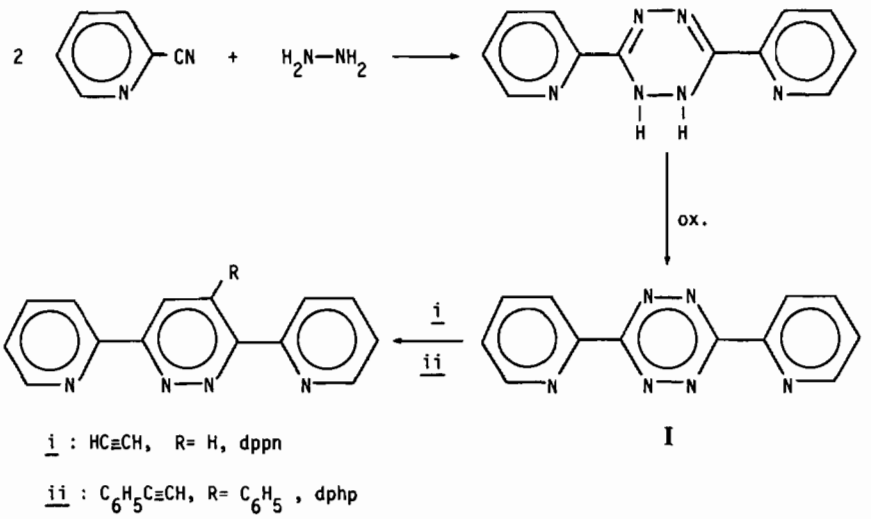
Results and Discussion

Synthesis of the Ligands

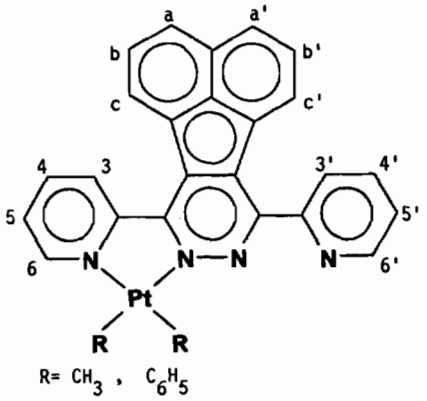
The preparation of the symmetrically 3,6-disubstituted pyridazines is achieved through a multistep reaction having aromatic nitriles and hydrazine as starting materials. As reported in the literature by Butte and Case [10], when the nitrile is 2-cyanopyridine (Scheme 2), 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**I**) is obtained. From a subsequent reaction with acetylene or phenylacetylene respectively dppn or dphp result.

Remarkably, the product dphp contains a 4-phenylsubstituted pyridazine ring. Therefore we have extended the study on the reactivity of **I** toward other terminal acetylenes in order to prepare an homologous series of ligands. In particular, 1-decyne and ethylpropiolate have been considered within this investigation.

Reactions were carried out in refluxing toluene (1-decyne) and DMFA (ethylpropiolate) to give dpop and dpcp, respectively (Scheme 1). These compounds were separated in good yields as white or yellow solids and characterised by elemental analysis, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy (data in 'Experimental' and Table I).



Scheme 2. Reaction scheme for the preparation of dppn or dphp.



Scheme 3. Proposed structure for the (dpaf)PtR_2 (R = CH_3, C_6H_5) complexes and proton numbering order.

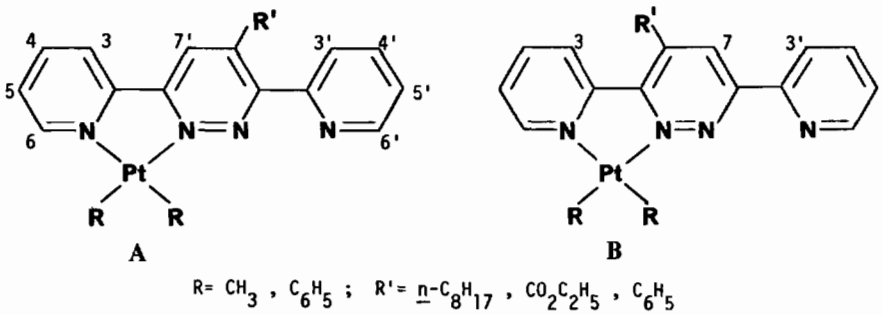
Synthesis of the Organometallic Complexes

The new nitrogen containing molecules dpop and dpcp, together with the known dpaf and dphp, have been tested as ligands in platinum(II) organometallic compounds.

The synthesis of the new complexes of general formula (L)PtR_2 (L = dpaf, dpop, dpcp and dphp; R = CH_3 and C_6H_5) have been performed reacting the ligand L with $(DMSO)_2Pt(CH_3)_2$ or (COD)Pt-$(C_6H_5)_2$ (1:1 molecular ratio) in benzene solution ('Experimental'). The resulting products were separated in high yields from the reaction mixtures as stable red or orange microcrystalline solids and characterised by elemental analysis and spectroscopic methods.

The microanalytical data account for the expected L to PtR_2 ratio as a 1:1 stoichiometry, while the monochelating bonding mode exhibited by L is confirmed by the IR spectra [1, 9].

In all these complexes the platinum(II) center is supposed to be in a square planar geometry. As to the ligand L, while in the dpaf derivatives the two chelating sites are equivalent (Scheme 3), in the 4-substituted ones, two isomeric forms, **A** and **B** in Scheme 4, are possible. Therefore, actually, their reaction products may be either single species or isomeric mixtures. Keeping into account such an



Scheme 4. Possible isomers for the (L)PtR_2 (L = dphp, dpop, dpcp; R = CH_3, C_6H_5) complexes and proton numbering order.

TABLE I. ^{13}C NMR Data for 3,6-Bis(2'-pyridyl)pyridazine-based Ligands in Chloroform-d[a]

Ligand	C-3	C-4	C-5	C-6	C-2'	C-3'	C-4'	C-5'	C-6'	C-2''	C-3''	C-4''	C-5''	C-6''
dppn; R' = H[b]	159.1	125.7			154.4	125.6	138.0	122.1	150.4					
dphp; R' = C_6H_5[c]	157.8	140.5[d]	124.8	158.4	153.6	125.6	137.0	123.2	149.4	156.0	124.6	136.3	121.8	149.0
dpop; R' = C_8H_{17}[e]	157.2	142.7	124.6	159.0	153.7	125.4	136.8	123.2	149.2	156.6	124.3	136.5	121.6	148.4
dpcp; R' = $CO_2C_2H_5$[f]	156.1	132.4	123.6[g]	158.1	153.5	124.9	137.1	123.0	149.6	152.8	124.3[g]	136.9	121.7	148.6

[a]Chemical shifts (δ/ppm) are relative to internal TMS. [b]From ref. 15. [c]Phenyl group: δ 137.2 (1C, C_{ipso}), 128.9 (2C, C_{metq}), 128.3 (2C, C_{ortho}), 128.3 (1C, C_{para}). [d]The assignments C-4 and C_{ipso} may be reversed. [e]Aliphatic chain: δ 32.3, 31.6, 29.7, 29.3, 29.0, 28.9, 22.4, 13.8 (CH_3). [f]Ethoxy group: 167.0 (C=O), 61.9 (CH_2), 13.9 (CH_3). [g]The assignment may be interchanged.

event, we have performed an ^1H NMR investigation (CD_2Cl_2 solutions).

The spectra of the dpop (Fig. 1) and dpcp complexes account for pure compounds, while those of both the (dphp)PtR_2 (R = CH_3, C_6H_5) species show the presence of a mixture containing two distinct products with a relative abundance (as determined from the integrals ratio) of about 95:5. The reported data concerning the dphp derivatives ('Experimental' and Table II) as well as the following discussion are referred to the main product.

As far as the organometallic fragments are concerned, we will pay attention only to the spectra of the (L)$Pt(CH_3)_2$ species which display, in the region of the methylplatinum(II) groups *trans* to a nitrogen, two distinct resonances of equal intensity. Moreover, for all the complexes, except (dphp)$Pt(CH_3)_2$, the smaller ^2J(PtH) value is observed for the highfield signal (Table II). In the previously reported case of (dppn)$Pt(CH_3)_2$ [8] the methyl group *trans* to the pyridyl nitrogen shows the lower δ and ^2J(PtH) values so whereas the assignment of the signals of the methyl protons for the dpcp, dpop and dpaf complexes can be tentatively achieved by comparison with the dppn compound, for (dphp)$Pt(CH_3)_2$ we are not able to suggest any appropriate attribution.

The analysis of the spectra exhibited by the nitrogen coordinated molecules was performed on the basis of the reported literature data for strictly similar compounds [8, 15, 16]. The assignment of the different signals is reported in 'Experimental' and in Table II. In particular for the complexes arising from the asymmetrical ligands the chemical shifts of both the pyridazinic H^7 (or $H^{7'}$) and the pyridinic H^3 and $H^{3'}$ protons should be geometrically influenced by the position of the R' substituent (Scheme 4). Therefore our attention has been focused on their signals in order to distinguish between the **A** and **B** isomers. The data we obtained show that in the dpop and dpcp complexes either H^3 or the pyridazinic proton are shifted upfield. By contrast, in the dphp derivatives, the $H^{3'}$ and the pyridazinic protons are shifted downfield while the H^3 again undergoes an upfield shift but to a greater extent than in the previous cases. The peculiar bchaviour of the H^3s may be attributed to a strong shielding exerted by the phenyl group present on the neighbouring pyridazine ring and, accordingly, the structure **B** (Scheme 4) is proposed for both the (dphp)PtR_2 species. Furthermore, this evidence offers the tool to elucidate the actual structure of the complexes arising from the dpop and dpcp ligands since, owing to the differences displayed from their spectral features, the formation of isomers **A** (Scheme 4) may be now suggested.

The electronic spectra of the new organometallic platinum(II) complexes were recorded in three different solvents and show a band ($\epsilon > 10^3$ l M^{-1} cm^{-1}, Table III) which displays negative solvatochromism in

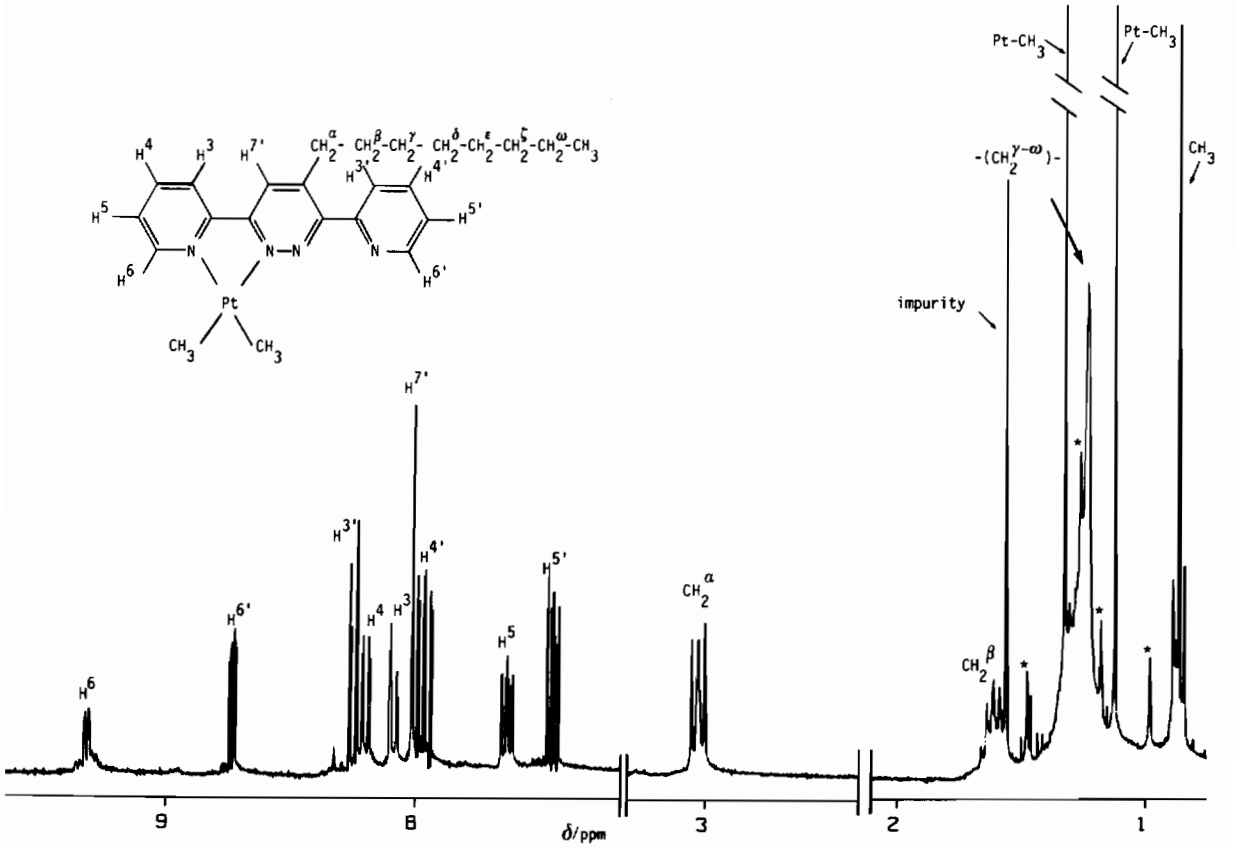


Fig. 1. ^{1}H NMR spectrum (300 MHz) of (dpop)Pt$(CH_3)_2$. ^{195}Pt satellites are indicated by asterisks.

TABLE II. ^{1}H NMR Data for Organoplatinum(II) Complexes and Free Ligands[a, b]

Compound	H^3	$H^{3'}$	H^7	$H^{7'}$	Pt–CH_3[c]
dppn	8.69		8.67		
(dppn)Pt$(CH_3)_2$[d]	8.56	8.74[e]	9.25	8.77	1.50 [J(PtH) = 89.4]; 1.21 [J(PtH) = 85.5]
(dppn)Pt$(C_6H_5)_2$	8.14	8.18	9.07	8.33	
dphp	8.80	7.90		8.67	
(dphp)Pt$(CH_3)_2$	7.13	8.84	8.98		1.47 [J(PtH) = 84.7]; 1.24 [J(PtH) = 88.1]
(dphp)Pt$(C_6H_5)_2$	[f]	9.49	9.99		
dpop	8.76	8.10		8.50	
(dpop)Pt$(CH_3)_2$	8.08	8.24		8.07	1.32 [J(PtH) = 89.2]; 1.12 [J(PtH) = 84.5]
(dpop)Pt$(C_6H_5)_2$	8.16–8.11	7.97		8.09	
dpcp	8.76	8.53		8.75	
(dpcp)Pt$(CH_3)_2$	8.12	8.54		8.26	1.50 [J(PtH) = 89.2]; 1.33 [J(PtH) = 84.8]
(dpcp)Pt$(C_6H_5)_2$	8.15	8.07		8.33	
(dpaf)Pt$(CH_3)_2$	8.76	8.52			1.40 [J(PtH) = 89.0]; 1.28 [J(PtH) = 85.6]

[a] In CD_2Cl_2 at 20 °C unless otherwise noted. Chemical shifts (ppm) are relative to TMS. [b] For convenience the H^4 and H^5 pyridazinic protons were numbered H^7 and $H^{7'}$ respectively. [c] Coupling constants (Hz) in parentheses. [d] In acetone-d_6. [e] The value given in ref. 8 must be replaced by the present value. [f] The corresponding signal was not observed because superimposed on the phenylic resonances which were observed in the range 7.90–7.45 ppm.

the lowest energy region. The energy of such a band, assigned to a MLCT ($\pi^* \leftarrow$ d) transition [17] for both the Pt$(C_6H_5)_2$ and Pt$(CH_3)_2$ derivatives and in each solvent, follows the same trend. Therefore the relative back-donation strength of the ligands is dpcp > dpaf > dppn ≃ dphp > dpop [8], wherein the dpaf and dppn mutual positions are as for the previously described group VI tetracarbonyl complexes [9].

TABLE III. Low Energy Electronic Absorption Maxima λ (cm^{-1}) in Solvents of Different Polarity[a]

Compound	Toluene	Acetone[b]	Acetonitrile
(dppn)Pt$(CH_3)_2$[c]	[d]	19379 (3.41)	20161
(dpcp)Pt$(CH_3)_2$	[d]	18832 (3.57)	19380
(dphp)Pt$(CH_3)_2$	17857	19305 (3.56)	20161
(dpop)Pt$(CH_3)_2$	18231	19755 (3.50)	20589
(dpaf)Pt$(CH_3)_2$	[d]	18935 (4.00)	19608
(dppn)Pt$(C_6H_5)_2$[c]	18999	20920 (3.54)	21413
(dpcp)Pt$(C_6H_5)_2$	18416	20161 (3.55)	20533
(dphp)Pt$(C_6H_5)_2$	18975	20703 (3.58)	21231
(dpop)Pt$(C_6H_5)_2$	19312	21141 (3.58)	21978
(dpaf)Pt$(C_6H_5)_2$	18762	20340 (3.43)	21186

[a]For a solvent polarity scale see ref. 18. [b]Log ε (ε in 1 mol^{-1} cm^{-1}) given in parentheses. [c]From ref. 8. [d]The complex is insoluble in this solvent.

Regarding the asymmetrical Ls, their back-bonding interaction capability parallels the electron-withdrawing power of the substituent on the pyridazine ring. Furthermore, if our tentative identification of the **A** ((dpop)PtR_2 and (dpcp)PtR_2) or **B** ((dphp)-PtR_2) products is correct, the reactivity of the two pyridazinic nitrogen atoms appears unaffected by the different electronic demand coming from the R′ substituent in *para* (isomer **A**) or *meta* (isomer **B**) positions. Therefore, the bonding ability of such ligands, as shown by the electronic spectra of their PtR_2 derivatives, is mainly determined by the nature of the different chelating system as a whole.

Finally, all the reported complexes were easily prepared in good yields. Moreover, as far as the solubility is concerned, the improvement observed for the dpop compounds (e.g. in acetone is *ca.* 10^{-2} M l^{-1}) indicates that such a ligand may be a good candidate for further investigations on bimetallic species, though dpcp is found to be the stronger stabilising molecule.

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