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Platinum(II) Dimethyl and Diphenyl Complexes with some Bidiazines and 3,6-Bis(2′-pyridyl)pyridazine

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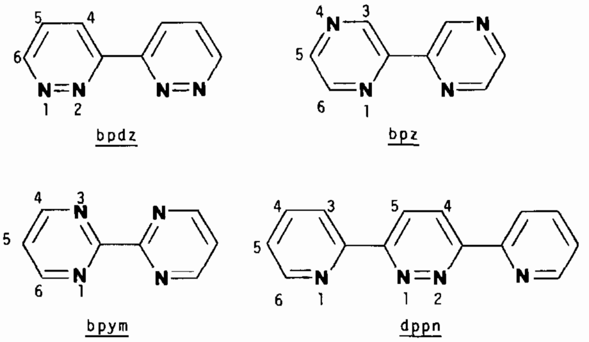
Abstract

The dimethyl and diphenyl platinum(II) complexes with 3,3′-bipyridazine (bpdz), 2,2′-bipyrazine (bpz) and 3,6-bis(2′-pyridyl)pyridazine (dppn) are reported. The newly synthesized compounds were characterized by elemental analysis, ^{1}H NMR and electronic spectroscopy. The strength of the back-bonding interaction of these nitrogen-containing ligands has been estimated on the basis of the energy of the first metal-to-ligand chaarge transfer electronic transition. In this respect the present results, together with the literature data concerning the homologous derivatives containing 2,2′-bipyridine (bipy) and 2,2′-bipyrimidine (bpym), give the following order bpdz $\simeq$ bpz > dppn > bpym > bipy.

Introduction

The bonding ability of bidiazines containing a 2,2′-bipyridine-like chelating site (Scheme 1) is related both to their σ-donor and π-acceptor behaviours, the strength of the interaction with the metal being the result of this synergistic effect. In particular, along the series bpdz, bpz, bpym theoretical and experimental studies carried out either on the free bidiazines [1–4] or on homologous metal complexes such as $(RuL_3)^{2+}$ (L = bpz [5]; L = bpdz [6]) or $ML(CO)_4$ [M = Mo, W (L = bpz [5], L = bpym [7]); M = Cr, Mo, W (L = bpdz, bpz, bpym) [4]] show the following order of back-donation: bpdz > bpz > bpym. Moreover Ernst and Kaim [4] recently reported on the energies of the first metal-to-ligand charge-transfer transitions (MLCT). For the $ML(CO)_4$ complexes (M = Cr, Mo, W; L = bpdz, bpz, bpym), in agreement with the previous results they found that the energy of the MLCT transition lowers in the order bpym > bpz $\sim$ bpdz.



Scheme 1. Ligands L: bidiazines(3,3′-bipyridazine, bpdz; 2,2′-bipyrazine, bpz; 2,2′-bipyrimidine, bpym) and 3,6-bis(2′-pyridyl)pyridazine, dppn.

These results might be a useful guide to the synthesis of coordination of organometallic compounds with predetermined features, in that they suggest the way for tuning the electronic density on the metal, which is dependent on the positions occupied in the skeleton of the ligand by the two nitrogen atoms not involved in bonds with the metal. On the other hand since all the mentioned investigations are only concerned with coordination compounds containing octahedral d^6 metal centers it appeared interesting to look at the mutual behaviours of such ligands in an homologous series of non-carbonyl square-planar d^8 platinum complexes. In addition to the symmetrical bidiazines we have also investigated dppn (Scheme 1), a bis-chelating molecule very versatile in the preparation of bimetallic compounds [8], containing both pyridine and pyridazine rings.

The platinum(II) dimethyl and diphenyl derivatives with bpym were previously reported by Sutcliffe and Young [9].

Experimental

All reactions were carried out under nitrogen and dried solvent.

Instrumentation

^{1}H NMR spectra were recorded on a Bruker WH 300 spectrometer with TMS as internal standard. Electronic spectra were obtained using a Perkin-Elmer 550 SE spectrophotometer.

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Elemental Analysis

These were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

Materials

3,6-Bis(2'-pyridyl)pyridazine was prepared according to Butte and Case [10]. 2,2'-Bipyrazine [5] and 3,3'-bipyridazine [11] were prepared by literature methods and characterized by ^{1}H NMR spectroscopy: bpz (CD_2Cl_2) δ 8.66 (s, H_6), 8.66 (s, H_5), 9.58 (s, H_3) ppm; bpdz (CD_2Cl_2) δ 9.26 (dd, H_6, $J_{6,5} = 6.0$, $J_{6,4} = 1.7$ Hz), 7.70 (dd, H_5, $J_{5,4} = 8.6$ Hz), 8.79 (dd, H_4) ppm. The complexes $(DMSO)_2Pt(CH_3)_2$ [12] and $(COD)Pt(C_6H_5)_2$ [13] were also obtained by following methods in the literature.

Preparation of Complexes

(L)Pt(CH$_3$)$_2$ L = bpz, bpdz, dppn)

In a typical preparation, a solution of $(DMSO)_2Pt(CH_3)_2$ (0.1 g, 0.26 mmol) in benzene (15 ml) was added to a stirred solution of the appropriate ligand (0.26 mmol) in benzene (15 ml). A red–brown precipitate appeared immediately. The reaction mixture was stirred for 30 min. The solid was filtered, washed with diethylether and vacuum dried. $(bpz)Pt(CH_3)_2$, yield 75%. *Anal.* Found: C, 30.74; H, 2.87; N, 13.76. Calc. for $C_{10}H_{12}N_4Pt$: C, 31.33; H, 3.15; N, 14.61%. $(bpdz)Pt(CH_3)_2$, yield 70%. *Anal.* Found: C, 30.62; H, 2.81; N, 13.60. Calc. for $C_{10}H_{12}N_4Pt$: C, 31.33; H, 3.15; N, 14.61%. $(dppn)Pt(CH_3)_2$, yield 92%. *Anal.* Found: C, 43.75; H, 3.45; N, 11.21. Calc. for $C_{16}H_{16}N_4Pt{\cdot}0.2C_6H_6$: C, 43.49; H, 3.65; N, 11.79%.

(L)Pt(C$_6$H$_5$)$_2$ (L = bpz, bpdz, dppn)

In a typical procedure, a solution of $(COD)Pt(C_6H_5)_2$ (0.15 g, 0.32 mmol) in benzene (5 ml) was added to a benzene solution (15 ml) of the appropriate ligand and the mixture was stirred under reflux for 4 h. The resultant red or red–brown solid was filtered, washed with diethylether and vacuum dried. $(bpz)Pt(C_6H_5)_2$, red, yield 63%. *Anal.* Found: C, 47.78; H, 2.93; N, 10.43. Calc. for $C_{20}H_{16}N_4Pt$: C, 47.22; H, 3.17; N, 11.00% $(bpdz)Pt(C_6H_5)_2$, red–brown, yield 50%. *Anal.* Found: C, 47.33; H, 2.95; N, 10.88. Calc. for $C_{20}H_{16}N_4Pt$: C, 47.22; H, 3.17; N, 11.00%. $(dppn)Pt(C_6H_5)_2$, red, yield 68%. *Anal.* Found: C, 53.21; H, 3.40; N, 9.70. Calc. for $C_{26}H_{20}N_4Pt$: C, 53.46; H, 3.42; N, 9.59%.

Results and Discussion

Synthesis of the Complexes

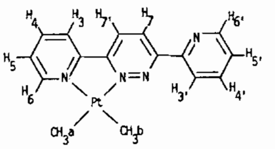
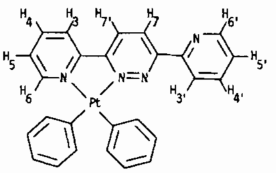
The new square-planar complexes of general formula $(L)PtR_2$ ($R = CH_3$, C_6H_5) were prepared in good yields by reacting $(DMSO)_2Pt(CH_3)_2$ (alternatively $(COD)Pt(C_6H_5)_2$) with bpdz, bpz or dppn in benzene. The new complexes were characterized by elemental analysis (see 'Experimental') and spectroscopic methods (Tables I–III). The red or red–brown products are indefinitely stable as solids. They react slowly with chlorinated solvents (dichloromethane or chloroform) or with acetonitrile, but in non-polar solvents such as benzene they are insoluble. All the methyl derivatives in DMSO partially undergo displacement reactions forming free ligands together with $(DMSO)_2Pt(CH_3)_2$.

TABLE I. ^{1}H NMR Data[a] for the Complexes $(L)Pt(CH_3)_2$ and $(L)Pt(C_6H_5)_2$ (L = bpz, bpdz)

Complex	Pt–CH$_3$		Pt–C$_6$H$_5$		L	
	δ	^2J(PtH) (Hz)	δ	J (Hz)	δ	J (Hz)
$(bpz)Pt(CH_3)_2$[b]	1.17	86.4			9.27(H_6)[c] 9.01(H_5) 9.89(H_3)	3.1($J_{5,6}$) 1.2($J_{3,6}$)
$(bpdz)Pt(CH_3)_2$[b]	1.38	89.2			9.42(H_6) 8.49(H_5) 8.82(H_4)	8.6($J_{5,4}$) 5.0($J_{5,6}$) 1.7($J_{4,6}$)
$(bpz)Pt(C_6H_5)_2$[d, e]			7.37($H_{2',6'}$) 7.05($H_{3',5'}$) 6.92($H_{4'}$)	72.5($^3J_{PtH}$)	8.61(H_6)[f] 8.81(H_5) 9.54(H_3)	3.0($J_{5,6}$) 1.3($J_{3,6}$)
$(bpdz)Pt(C_6H_5)_2$[d, e]			7.29($H_{2',6'}$) 6.95($H_{3',5'}$) 6.83($H_{4'}$)	70.5($^3J_{PtH}$)	9.33(H_6) 8.14(H_5) 8.29(H_4)	8.7($J_{5,4}$) 5.0($J_{5,6}$) 1.7($J_{4,6}$)

[a] All values (δ (ppm)) are relative to TMS. [b] In DMSO-d_6 at 25 °C. [c] ^3J(PtH) = 18.8 Hz. [d] In CD_2Cl_2 at 20 °C. [e] The calculated coupling constants for the phenyl resonances are: $J_{2',3'} = 8.4$; $J_{3',4'} = 7.4$; $J_{2',6'} = 3.3$; $J_{3',5'} = 1.9$; $J_{2',4'} = 1.5$ Hz; $J_{2',5'} = 0.0$ assumed. [f] ^3J(PtH) = 19.2 Hz.

TABLE II. ^{1}H NMR Data for dppn Complexes$^{a, b}$

Complex	Pt–CH_3		Pt–C_6H_5	L	
	δ	^2J(PtH) (Hz)	δ	δ	J (Hz)
(dppn)Pt$(CH_3)_2$^{c}	1.50 (CH_3^{a})	89.4		9.39(H_6)^d; 7.85(H_5) 8.44(H_4); 8.56(H_3)	7.8($J_{3,4}$); 7.5($J_{4,5}$) 5.5($J_{5,6}$); 1.6($J_{4,6}$)
	1.21 (CH_3^{b})	85.5		8.82($H_{6'}$); 7.60($H_{5'}$) 8.12($H_{4'}$); 7.60($H_{3'}$) 9.25(H_7); 8.77($H_{7'}$)	1.3($J_{5,3}$); 7.9($J_{3',4'}$) 7.6($J_{4',5'}$); 4.8($J_{5',6'}$) 1.8($J_{4',6'}$); 1.0($J_{5',3'}$) 1.0($J_{3',6'}$); 9.0($J_{7,7'}$)
(dppn)Pt$(C_6H_5)_2$^{e}			7.48 7.45 (H_{ortho})^f	8.63(H_6); 7.52(H_5) 8.14(H_4); 8.14(H_3)	6.9($J_{4,5}$); 5.4($J_{5,6}$) 2.0($J_{3,5}$); 1.5($J_{4,6}$) 0.9($J_{3,6}$); 8.0($J_{3',4'}$)
			7.05 7.02 (H_{meta}) 6.91 6.90 (H_{para})	8.69($H_{6'}$); 7.41($H_{5'}$) 7.80($H_{4'}$); 8.18($H_{3'}$) 9.07(H_7); 8.33($H_{7'}$)	7.6($J_{4',5'}$); 4.8($J_{5',6'}$) 1.8($J_{4',6'}$); 1.2($J_{3',5'}$) 0.9($J_{3',6'}$); 9.0($J_{7',7}$)

^{a}All values (δ (ppm)) are relative to TMS. ^{b}For convenience the H_4 and H_5 pyridazine protons were numbered H_7 and $H_{7'}$ respectively. ^{c}In acetone-d_6 at 20 °C. ^{d} ^3J(PtH) = 22.0 Hz. ^{e}In CD_2Cl_2 at 20 °C. ^{f} ^3J(PtH) = 69.2 Hz.

TABLE III. Low Energy MLCT Absorption Maxima λ_1 (cm^{-1}) of the Complexes (L)Pt$(CH_3)_2$ and (L)Pt$(C_6H_5)_2$ in Various Solvents^a

Complex	Solvent		
	Dichloromethane	Acetone	Acetonitrile
(bipy)Pt$(CH_3)_2$^{b}	21400	21200	22000
(bpym)Pt$(CH_3)_2$^{c}	20920	d	d
(dppn)Pt$(CH_3)_2$	19801	19379(3.41)	20161
(bpz)Pt$(CH_3)_2$	19083	19193(3.57)	19646
(bpdz)Pt$(CH_3)_2$	18939	18832(3.57)	19493
(bipy)Pt$(C_6H_5)_2$^{b}	22700	22800	23400
(bpym)Pt$(C_6H_5)_2$^{c}	21834	d	d
(dppn)Pt$(C_6H_5)_2$	20576	20920(3.54)	21413
(bpz)Pt$(C_6H_5)_2$	19723	20449(3.87)	20703
(bpdz)Pt$(C_6H_5)_2$	19379	20080(3.64)	20491

^{a}Log ε (ε in l mol^{-1} cm^{-1}) given in parentheses. ^{b}Ref. 10. ^{c}Ref. 9. ^{d}Unavailable.

^{1}H NMR Spectra

Bidiazine complexes

As a compromise between solubility and stability problems it has been necessary to run the ^{1}H NMR spectra of the (L)Pt$(CH_3)_2$ species in DMSO-d_6 so that, in addition to the resonances of the complex, they contained also the signals of both (DMSO-d_6)$_2$Pt$(CH_3)_2$ [δ(Pt–CH_3) = 0.5 ppm, ($^2J_{PtH}$ = 79.5 Hz) in DMSO-d_6] and uncoordinated L. For the less reactive diphenyl complexes it was possible to use CD_2Cl_2 as solvent.

The general pattern displayed by the above spectra is in agreement with the multiplicity expected for symmetrically substituted metal complexes (e.g. the methyl signals of the Pt$(CH_3)_2$ moiety appear as a single resonance with ^{195}Pt satellites at $\delta \approx 1$ ppm [14, 15]) (Table I).

Interestingly, the quality of the (L)Pt$(C_6H_5)_2$ spectra (Figs. 1 and 2), even if the Hz/point ratio prevents an accurate determination of the $J_{2',5'}$ coupling constant, is sufficient to ensure the full spectral analysis of the phenyl resonances.

The signals, showing a not-hindered rotation around the Pt–C bond, were assigned using a LACX type program for an AMM'XX' spin system. The calculated resonance values together with the estimated $^2J_{PtH}$ coupling constants are reported in Table I.

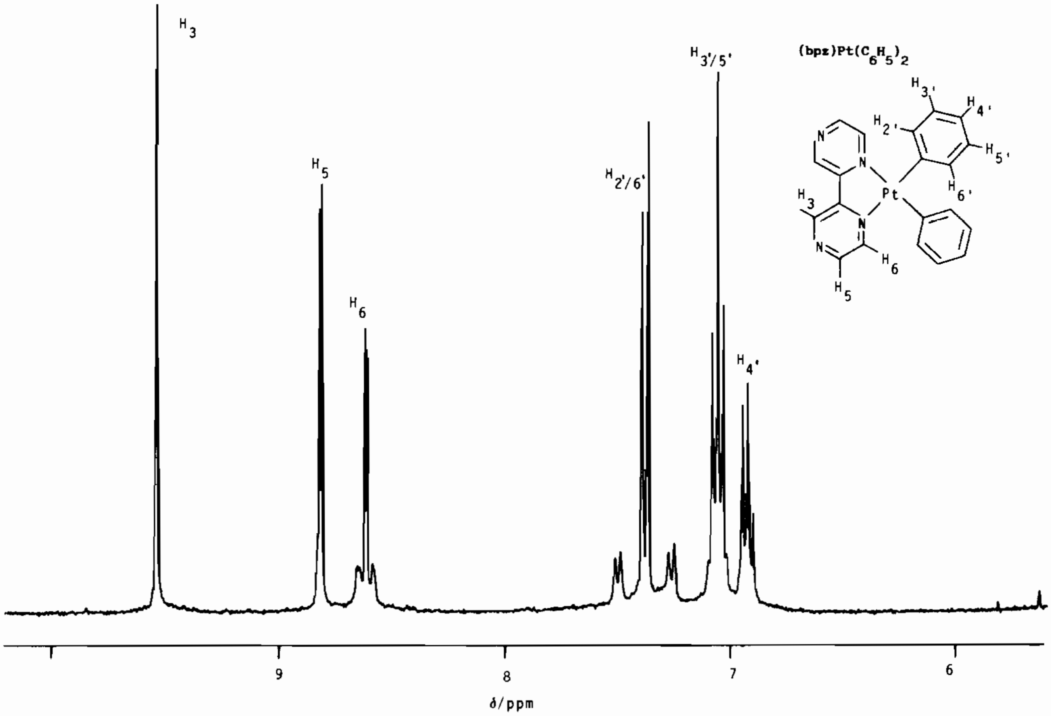


Fig. 1. ^{1}H NMR spectrum (300 MHz) of (bpz)Pt(C_6H_5)$_2$.

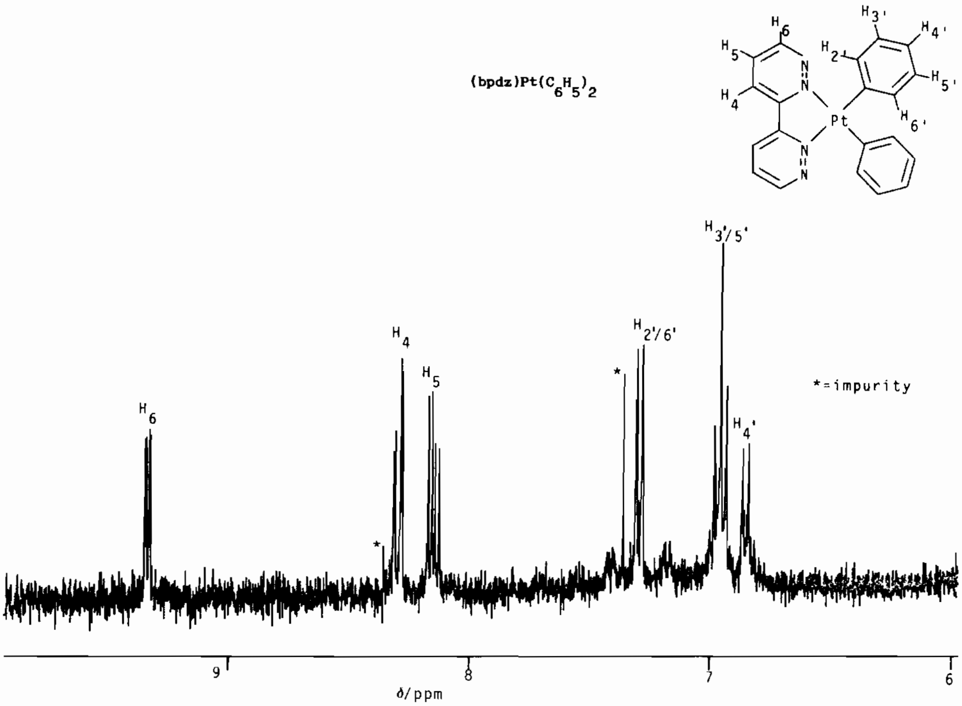


Fig. 2. ^{1}H NMR spectrum (300 MHz) of (bpdz)Pt(C_6H_5)$_2$.

3,6-Bis(2'-pyridyl)pyridazine complexes

The ^{1}H NMR spectra of the (dppn)PtR_2 complexes were performed in acetone-d_6 (R = CH_3) and CD_2Cl_2 (R = C_6H_5). Figure 3 shows the spectrum of the diphenyl complex.

The identification of the two different sets of the dppn signals (chelating and non-chelating moieties)

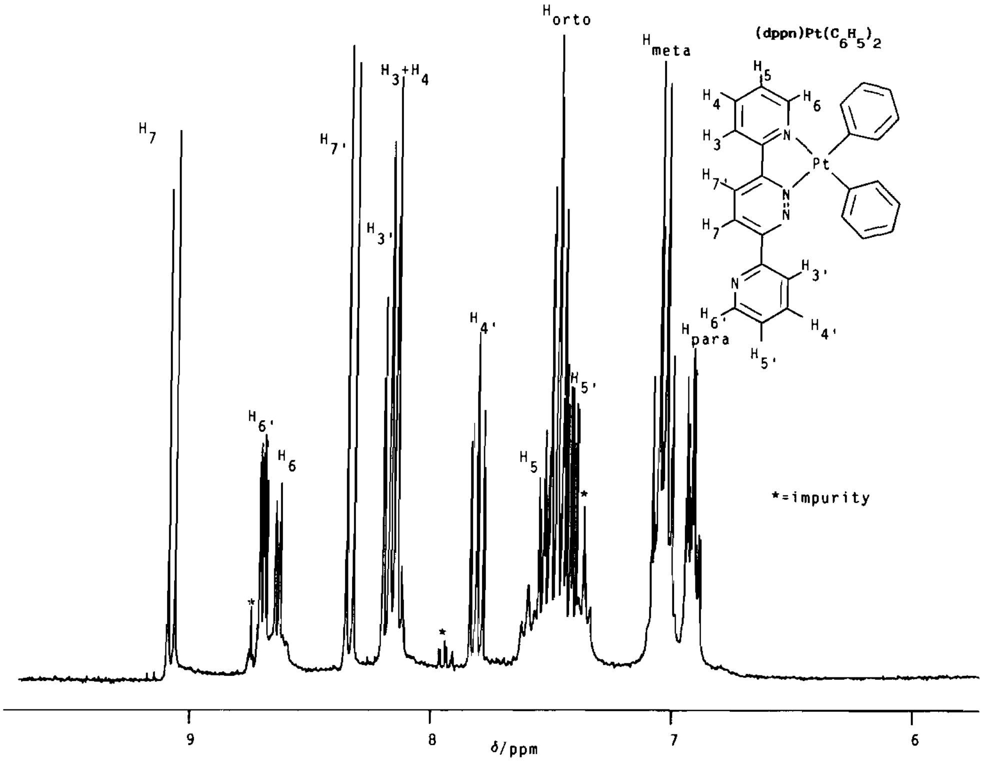


Fig. 3. ^{1}H NMR spectrum (300 MHz) of (dppn)Pt(C_6H_5)$_2$.

was made on the basis of the signals multiplicity, different line broadening and homonuclear decoupling [16]. In both complexes the PtR_2 moiety gives two distinguishable sets of signals (Table II). The spectrum of (dppn)Pt(CH_3)$_2$, taking into account both the literature data for (bipy)Pt(CH_3)$_2$ (bipy = 2,2'-bipyridine) [14] and the δ(CH_3) value found for (bpdz)Pt(CH_3)$_2$, was interpreted assigning the highfield signal to the methyl group *trans* to the pyridyl nitrogen. For the diphenyl complex the values of the different C_6H_5 resonances were only estimated on the grounds of what was previously discussed and no attempts were made to assign each resonance.

Finally, a striking feature of the (dppn)Pt(C_6H_5)$_2$ spectrum is the presence of an ABMX system, due to the coordinated pyridyl ring, where the H_3 and H_4 protons are strongly coupled.

Electronic Spectra

The electronic spectra of the platinum(II) dimethyl and diphenyl complexes were recorded in three different solvents: acetone, dichloromethane and acetonitrile. The bands which appear in the low energy region are reported in Table III. Since all these bands (extinction coefficients $\epsilon > 1000$ l M^{-1} cm^{-1}) exhibit marked solvent dependence (negative solvatochromism) they were assigned to MLCT ($\pi^* \leftarrow d$) transitions [17]. The related data concerning the similar compounds with bipy [18] and bpym [9] are included in Table III for comparison.

In the (L)Pt(CH_3)$_2$ species the lowering of the energy of the first MLCT band, in dichloromethane solution, follows the order bipy > bpym > dppn > bpz ≅ bpdz. This order remarkably parallels the one found for the bidiazine series (L)M(CO)$_4$ (M = Cr, Mo, W) [4]. The diphenyl platinum complexes display the same order, even if at higher energy values. About the above mentioned carbonyl complexes it was noted that with increasing back-bonding interaction a lowering of the λ_1 values is occurring. Thus, for the (L)PtR_2 species the previous order, in terms of back-donation strength, can be formulated as follow: bpdz ≅ bpz > dppn > bpym > bipy.

In the bidiazine series the order of the MLCT energies has been extensively discussed by Ernst and Kaim [4]; here, because of our concern about bis-chelated complexes, we are interested in comparing dppn and bpym. In this respect, since the λ_1 energy determined either in methyl or phenyl derivatives is always lower for the dppn complexes than it is for the homologous bpym, we could conclude that the former ligand undergoes the stronger back-bonding interaction. Therefore on the basis of the present data dppn appears to be the strongest stabilizing ligand. The study of the coordination chemistry of (dppn)PtR_2 (R = CH_3, C_6H_5) is currently under way, in order to establish if the dppn ligand in binuclear complexes, in comparison with the homologous bpym species [9], maintains the same features.

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References

1 V. Barone, C. Cauletti, F. Lelj, M. N. Piancastelli and N. Russo, *J. Am. Chem. Soc., 104*, 4571 (1982).
2 V. Barone, F. Lelj, C. Cauletti, M. N. Piancastelli and N. Russo, *Mol. Phys., 49*, 599 (1983).
3 V. Barone, F. Lelj, C. Cauletti, M. N. Piancastelli, M. Ghedini and N. Russo, *Congr. Naz. Chim. Inorg., [Atti], 19*, 533 (1986).
4 S. Ernst and W. Kaim, *J. Am. Chem. Soc., 108*, 3578 (1986), and refs. therein.
5 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem., 21*, 2276 (1982).
6 M. Kitamura, Y. Kawanishi and S. Tazuke, *Chem. Phys. Lett., 97*, 103 (1983).
7 C. Overton and J. A. Connor, *Polyhedron, 1*, 53 (1982).
8 M. Ghedini, F. Neve, F. Morazzoni and C. Oliva, *Polyhedron, 4*, 497 (1985), and refs. therein.
9 V. S. Sutcliffe and G. B. Young, *Polyhedron, 3*, 87 (1984).
10 W. Butte and F. H. Case, *J. Org. Chem., 26*, 4690 (1961).
11 J. J. Lafferty and F. H. Case, *J. Org. Chem., 32*, 1591 (1967).
12 C. Eaborn, K. Kundu and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 933 (1981).
13 C. R. Kistner, J. H. Hutchinson, J. R. Doyle and J. C. Storlie, *Inorg. Chem., 2*, 1255 (1963).
14 P. K. Monagham and R. J. Puddephatt, *Inorg. Chim. Acta, 65*, L59 (1982).
15 P. K. Monagham and R. J. Puddephatt, *Organometallics, 4*, 1406 (1985).
16 M. Ghedini, M. Longeri and F. Neve, *J. Chem. Soc., Dalton Trans.*, 2669 (1986).
17 D. M. Manuta and A. J. Lees, *Inorg. Chem., 22*, 3825 (1983).
18 N. Chandhury and R. J. Puddephatt, *J. Organomet. Chem., 84*, 105 (1974).