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Solution Studies of Complexes of the Types *trans*-$PtCl_2L$(1,4-diazine) and *trans*-$LCl_2Pt(\mu$-1,4-diazine)$PtCl_2L$ (L = Phosphine, C_2H_4). X-ray Structures of $Pt_2Cl_4L_2$(ppz) (L = C_2H_4, PEt_3; ppz = 2,5-Dimethylpyrazine) and the Relative Trans Influence of Alkene and Tertiary Phosphine Ligands

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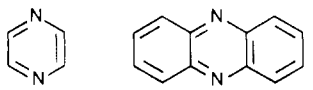
Solution studies of the complexes $PtCl_2L$(1,4-diazine) and *trans*-LCl_2Pt(1,4-diazine)$PtCl_2L$ (L = PEt_3, PMe_2Ph, $PMePh_2$, P-*n*-Bu_3, C_2H_4; diazine = pyrazine, 2-methylpyrazine, 2,3-, 2,5- and 2,6-dimethylpyrazine, 2,3,5-trimethylpyrazine, 2,3,5,6-tetramethylpyrazine, phenazine) have been carried out. It is shown that (a) coordination of the "$PtCl_2L$" fragment does not significantly weaken the donor capacity of the still uncoordinated nitrogen atom of the heterocycle, (b) these complexes are dynamic in solution, the ethene complexes being more labile than the corresponding phosphine complexes, and (c) the presence of methyl substituents near the coordinated nitrogen atom slows down the dynamic process. The X-ray crystal structures of $(C_2H_4)Cl_2Pt$(2,5-dimethylpyrazine)$PtCl_2(C_2H_4)$ (E_2ppz) and $(PEt_3)Cl_2Pt$(2,5-dimethylpyrazine)$PtCl_2(PEt_3)$ (A_2ppz) were determined. The crystals of E_2ppz are monoclinic and belong to the space group $P2_1/n$ with unit cell dimensions a = 7.048 (3) Å, b = 13.407 (3) Å, c = 9.219 (2) Å, β = 69.81 (3)°, V = 817.7 Å^3, and Z = 2. The structure was refined to R = 0.044. The crystals of A_2ppz are monoclinic and belong to the space group $P2_1/c$ with unit cell dimensions a = 12.149 (3) Å, b = 8.231 (6) Å, c = 15.464 (5) Å, β = 108.95 (2)°, V = 1462.6 Å^3, and Z = 2. The structure was refined to R = 0.038. Each platinum atom shows normal square-planar geometry with bonding parameters that are typical of the complexes *trans*-$PtCl_2L$(N-ligand) (L = alkene, tertiary phosphine). The differences in Pt-N distances in the two complexes clearly show the higher trans influence of the phosphine relative to that of the alkene.

Introduction

The coordination chemistry of pyrazine (**1**) and related ligands has been extensively investigated.[2] The main points of interest



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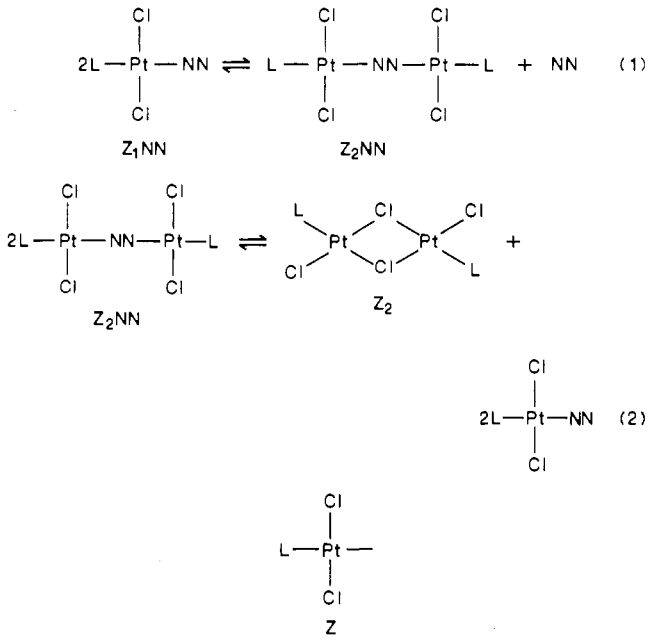
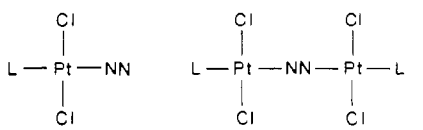
of this study are (1) the transmission of electronic effects across the heterocycle[3] and (2) the formation of polymeric materials.[4] Furthermore, reports on several platinum(II) complexes containing ligands of this type have been published in recent years.[5] Of particular interest is the report that the phenazine (**2**) complex *trans*-$PtCl_2(C_2H_4)$(**2**) and related compounds are effective hydrosilylation catalysts.[6] Our interest in ligands of this type arose from the formation of 2,5-dimethylpyrazine during the workup of products obtained from the Wacker-type oxidation of allylamine.[7] Furthermore, we have recently carried out a study of the coordination behavior of 1,3,5-triazine with phosphine complexes of platinum(II).[8]

Scheme I



Z = A (L = PEt_3), B (L = PMe_2Ph), C (L = $PMePh_2$), D (L = P-*n*-Bu_3), E (L = C_2H_4)

This paper reports the preparation in solution of complexes of the types



L = tertiary phosphine, ethylene; NN = pyrazine or related ligand

Results and Discussion

Pyrazine-type ligands react with the binuclear platinum(II) complexes $Pt_2Cl_4L_2$ (Z_2; L = PR_3, C_2H_4), giving the species shown in Scheme I. The systems investigated are listed in Table I.

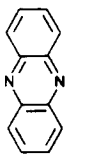
As found for the corresponding complexes with 1,3,5-triazine reported earlier,[8] different species are simultaneously present in

(1) (a) Università di Milano. (b) ETH Zürich.
(2) Substructure search (Feb 12, 1987), CAS Registry File (STN), fragments: *trans*-$PtX_2(P)L$ (X = halogen; P = phosphorus; L = 1,4-diazine, pyridine); M-(1,4-diazine), M-(1,4-diazine)-M (M = transition metal).
(3) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086.
(4) Salt, N. J. S.; Rourke, J. P.; Maitlis, P. M. Poster Contribution, 3rd International Conference on the Chemistry of Platinum Group Metals, Sheffield, England, 1987.
(5) (a) Benayache, F.; Julien, J.; Solgadi, D. *J. Chem. Res., Miniprint* **1981**, 1957. (b) Foulds, G. A.; Thornton, D. A.; Yates, J. *J. Mol. Struct.* **1983**, *98*, 315. (c) Siedle, A. R.; Mann, K. R.; Bohling, D. A.; Filipovich, G.; Toren, P. E.; Palensky, F. J.; Newmark, R. A.; Duerst, R. W.; Stebbings, W. L.; Mishmash, H. E.; Melancon, K. *Inorg. Chem.* **1985**, *24*, 2216. (d) Hall, P. S.; Thornton, D. A.; Foulds, G. A. *Polyhedron* **1987**, *6*, 85.
(6) Newmark, R. A.; Siedle, A. R. *Magn. Reson. Chem.* **1985**, *23*, 67.
(7) Kaufmann, W. Dissertation, ETH Zürich, 1987, No. 8449.
(8) Kaufmann, W.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1988**, *27*, 1178.

0020-1669/89/1328-1112$01.50/0

Table I. Investigated Complexes of the Types *trans*-$PtCl_2L(NN)$ and *trans*-$LCl_2Pt(\mu\text{-}NN)PtCl_2L$

NN	L = PEt_3	L = PMe_2Ph	L = $PMePh_2$	L = $H_2C{=}CH_2$
 pyrazine (pz)	A_1pz A_2pz	B_1pz B_2pz	C_1pz C_2pz	E_1pz E_2pz
 2,5-dimethylpyrazine (ppz)	A_1ppz A_2ppz	B_1ppz B_2ppz	C_1ppz C_2ppz	E_1ppz E_2ppz
 2,3,5,6-tetramethylpyrazine (tpz)	A_1tpz A_2tpz	B_1tpz B_2tpz	C_1tpz C_2tpz	E_1tpz E_2tpz

NN	L = PEt_3	NN	L = PEt_3
 2-methylpyrazine (mepz)	A_1mepz[a] $A_1'mepz$[b] A_2mepz	 2,3,5-trimethylpyrazine (trpz)	A_1trpz[c] $A_1'trpz$[d] A_2trpz
 2,3-dimethylpyrazine (opz)	A_1opz A_2opz	 phenazine (phz)	A_1phz A_2phz
 2,6-dimethylpyrazine (mpz)	A_1mpz[e] $A_1'mpz$[f] A_2mpz		

[a] Coordinated at N(4). [b] Coordinated at N(1). [c] Coordinated at N(1). [d] Coordinated at N(4). [e] Coordinated at N(4). [f] Coordinated at N(1).

Table II. Equilibrium Amounts of Complexes $PtCl_2(NN)L$ and $LCl_2Pt(NN)PtCl_2L$ (NN = Pyrazine or Related Ligand, L = Tertiary Phosphine) Obtained by Mixing Appropriate Amounts of $Pt_2Cl_4L_2$ and NN[a]

compd[b,c]	amt, %	compd[c,d]	amt, %
A_1pz (**1a**)	81	C_1pz	85
A_1ppz (**2a**)	82	C_1ppz	86
A_1mpz[e] (**3a**)	84	*f*	
A_1tpz (**4a**)	81	C_1tpz	86
A_2pz (**5a**)	99	C_2pz	99
A_2ppz (**6a**)	99	C_2ppz	99
A_2mpz (**7a**)	99	*f*	
A_2tpz (**8a**)	97	C_2tpz	95

[a] In $CDCl_3$ or CD_2Cl_2 solutions at room temperature. [b] A = $PtCl_2(PEt_3)$. [c] pz = pyrazine; ppz = 2,5-dimethylpyrazine; mpz = 2,6-dimethylpyrazine; tpz = tetramethylpyrazine. [d] C = $PtCl_2(PMePh_2)$. [e] Mixture of two isomers, i.e., that where N(1) is bonded to platinum and that where N(4) is bonded to platinum in the approximate ratio 1:10. [f] Not measured.

solution and dynamic processes are occurring on the NMR time scale at room temperature. Thus, the solution studies will be discussed first.

Equilibria in Solution. Chloroform or dichloromethane solutions containing mainly complexes either of the type $Z_2(NN)$ or of the type $Z_1(NN)$ resulted on mixing the appropriate amounts of Z_2 and NN. The relative amounts of the species thus formed were established by ^1H NMR measurements.

Phosphine Complexes. The reaction between Z_2 species and NN ligands in a 1:1 ratio resulted in the formation of compounds of the type $Z_2(NN)$ in amounts that were in excess of 95%, while solutions containing Z_2 and NN in a 1:2 ratio produced $Z_1(NN)$ in amounts ranging from 80 to 86%, together with the appropriate amounts of $Z_2(NN)$ and free NN (see Scheme I and Table II).

These results indicate that the uncoordinated nitrogen atom in $Z_1(NN)$ retains a significant donor capacity. An estimate of this donor capacity relative to that of free NN can be obtained by using the data given in Table II. Thus, for equilibrium 1 in Scheme I, in the case of the fragment $PtCl_2(PMePh_2)$ (C) and pyrazine (pz) one obtains a constant of ca. 7×10^{-3}. This value cannot be related to comparable data because of the unusual solvent used here. However, it indicates that the coordinating power of the uncoordinated nitrogen in a complex of type $Z_1(NN)$ is reduced about 2 orders of magnitude relative to that of the corresponding free NN.

Furthermore, the data in Table II show that this "basicity" difference is not significantly affected either on changing the phosphine on the fragment Z or on adding methyl substituents to the pyrazine ring.

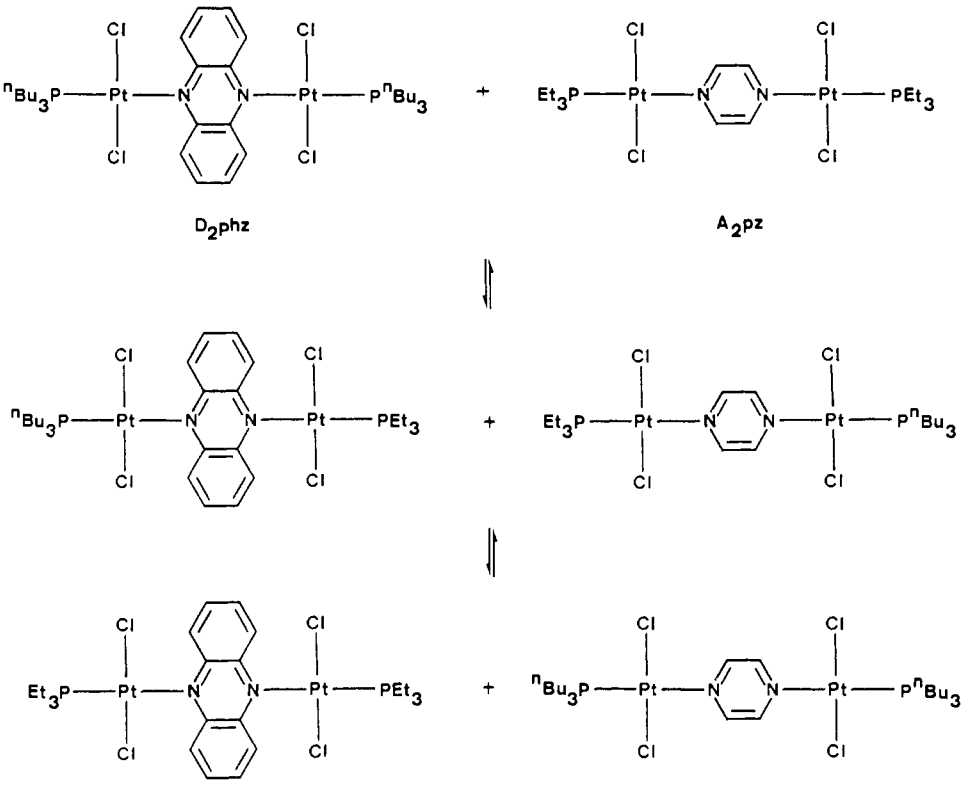
As found for the corresponding complexes with pyrimidine,[8] equilibrium 1 of Scheme I is almost temperature-independent as indicated by the ^{31}P NMR spectra, which in the case of the fragment $PtCl_2(PEt_3)$ (A) and pyrazine (pz) give the following ratios: at +30 °C A_2pz:A_1pz is 1:4, and at −50 °C it is 1:5.

As can also be seen from the data given in Table II, 1:1 mixtures of Z_2 and NN ligands, in which the two nitrogen atoms have inequivalent substitution patterns, result in the simultaneous formation of the two possible complexes of the type Z_1NN; e.g., the complex with 2,6-dimethylpyrazine (mpz), of the type Z_1mpz, can exist in two isomeric forms, i.e., one where N(1) is bonded and the other where N(4) is bonded to the platinum atom (see Table I). These isomers are present in the approximate ratio of 1:10, and this effect is likely to be of steric origin. Similar ratios are found also for the other two pyrazines with this type of substitution pattern, i.e., 2-methylpyrazine (mepz) and 2,3,5-trimethylpyrazine (trpz).

The observation that coordination of one nitrogen atom of pyrazine to platinum weakens the donor capacity of the second nitrogen atom is in apparent contrast to the report[9] that the free nitrogen atom of pyrazine in $[Ru(NH_3)_5(pz)]^{2+}$ ($pK_a = 2.5 \pm 1$) is 2 orders of magnitude more basic than in the free heterocycle ($pK_a = 0.61$). This effect has been attributed[9] to "back-donation

(9) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

Scheme II



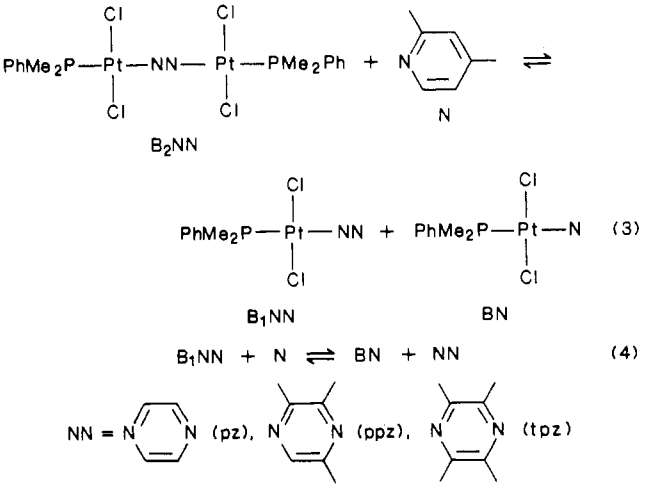
of electron density from the filled t_{2g} orbitals into the unoccupied π-antibonding orbitals of the ligand".

A plausible explanation for the relative differences in coordinating power between uncoordinated pyrazine and the free nitrogen atom in $[Ru(NH_3)_5(pz)]^{2+}$ on one hand and uncoordinated pyrazine and the free nitrogen atom in $PtCl_2(PEt_3)(pz)$ on the other may be sought in the different π-donor capacities of the two fragments $Ru(NH_3)_5^{2+}$ and $PtCl_2(PR_3)$. The coordination chemistry of complexes containing the ruthenium fragment indicates that it is a very electron-rich species, as indicated by the redox potential of the couple *trans*-$[RuCl_2(NH_3)_4]^+$/*trans*-$[RuCl_2(NH_3)_4]$ (E° = −0.166 V)[10] and the great affinity of $[Ru(H_2O)(NH_3)_5]^{2+}$ for N_2 (K(25 °C) = 3.3 × 10^4).[11]

This is in contrast to the behavior of compounds containing the fragment $PtCl_2(PR_3)$, which are air-stable. Furthermore, the couples *trans*-$[PtCl_2(NH_3)_4]^{2+}$/$[Pt(NH_3)_4]^{2+}$ and *trans*-$[PtCl_4(P\text{-}n\text{-}Pr_3)_2]$/*trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)_2]$ have E° values of 0.600[12] and 0.349 V,[13] respectively. Thus, the platinum system is expected to be a poorer π-electron donor than the ruthenium unit. It follows that if the increase in basicity of the uncoordinated nitrogen, relative to that of the free ligand, is due to π-back-bonding,[9] this effect will be less significant (if at all present) in the pyrazine-containing platinum complexes. Thus, in the latter case the electrostatic effect due to the coordination of the first nitrogen atom would be dominant although it would not be as strong as that of a proton, which is a positively charged Lewis acid.

Ethene Complexes. Several complexes of the types $E_1(NN)$ and $E_2(NN)$ (E = $PtCl_2(C_2H_4)$; see Table I) have been reported in the literature.[5] While these can be obtained from the general reactions shown in Scheme I, they can also be obtained by adding the heterocyclic ligand to an aqueous solution of $K[PtCl_3(C_2H_4)]$. The known complexes[5] E_1pz and E_2pz (pz = pyrazine) and E_1tpz (tpz = 2,3,5,6-tetramethylpyrazine) and the new species E_1ppz and E_2ppz (ppz = 2,5-dimethylpyrazine) and E_2tpz were investigated. Solubility problems (pz complexes) and ligand volatility

Scheme III



problems (ppz), coupled with dynamic behavior, prevented a reliable study of equilibria in solution as was done for the corresponding phosphine complexes. However, a study of the tpz complexes shows that when the E:tpz ratio is 2:1 the formation of E_2tpz is >99% and when this ratio is 1:1 the formation of E_1tpz is also >99%. In this context it is noteworthy that, at parity of the nitrogen donor, the phosphine-containing Lewis acid appears to be weaker than the corresponding ethene-containing Lewis acid.

Dynamic Behavior. As mentioned earlier, NMR spectroscopic studies of these complexes show that dynamic processes occur in solution.

Phosphine Complexes. Dynamic behavior at room temperature is shown by all the complexes of the types Z_1NN and Z_2NN (Z = $PtCl_2L$; L = PEt_3 (A), PMe_2Ph (B), $PMePh_2$ (C), P-*n*-Bu_3 (D); NN = pyrazine-type ligand; see Table I.) An example of the temperature dependence of the ^1H NMR spectra of a complex of the type Z_1NN is shown in Figure 1. However, although dynamic processes are also occurring in solutions of Z_2NN complexes, one observes sharp ^1H NMR spectra at room temperature. The occurrence of exchange processes in these complexes was shown by the observation of the set of reactions shown in Scheme

(10) Elson, C. M.; Itzkovitch, I.; McKenney, J.; Page, J. A. *Can. J. Chem.* **1975**, *53*, 2922.
(11) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1970**, *92*, 6170.
(12) Grinberg, A. A. *An Introduction to the Chemistry of the Complex Compounds*; Pergamon Press: New York, 1962.
(13) Ahrland, S.; Chatt, J. *J. Chem. Soc.* **1957**, 1379.

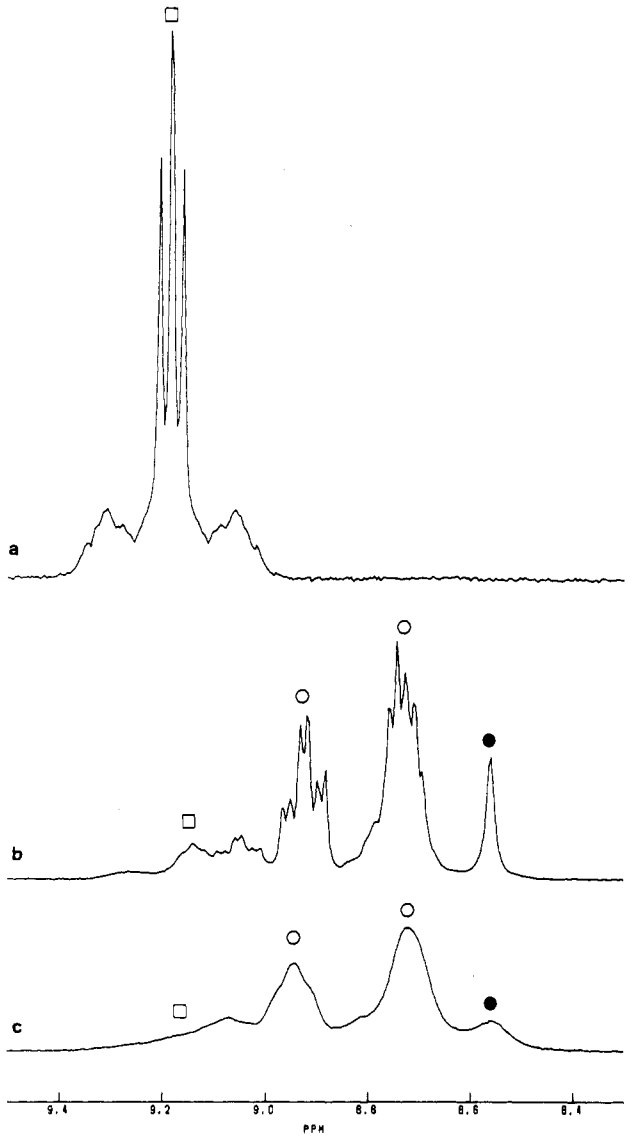


Figure 1. ^1H NMR spectra in CD_2Cl_2 of the diazine protons in *trans*-$(PMe_2Ph)Cl_2Pt(\mu\text{-}pz)PtCl_2(PMe_2Ph)$ (B_2pz) at 27 °C (a) and in *trans*-$PtCl_2(PMe_2Ph)(pz)$ (B_1pz) (b) at 0 °C and (c) at 27 °C. The signals marked with a square refer to B_2pz, those with an empty circle to B_1pz, and those with a full circle to free pyrazine.

II. The ^{31}P NMR spectrum of a 1:1 mixture of D_2phz and A_2pz, after 20 min, showed the formation of equivalent amounts of all the complexes shown in Scheme II. This behavior parallels that previously reported[8] for the corresponding pyrimidine (1,3-diazine) complexes.

As for the corresponding complexes of pyrimidine we postulate that the observed dynamic behavior is associated with the reactions described in equilibria 1 and 2 and we formulate these reactions as being of S_N2 type. These processes have been discussed previously[8] and will not be reported here.

Qualitative studies of the temperature dependence of the NMR spectra of complexes of pyrazine and its methyl-substituted derivatives indicated that the observed dynamic processes were slowed down as the number of methyl substituents increased. This effect was further investigated by the reactions shown in Scheme III. It was found that when 1 equiv of the pyrazine complex B_2pz was reacted with 2 equiv of 2,4-lutidine (N) at 0 °C, an equilibrium mixture of B_1pz and BN, in the approximate ratio 1:10, was produced within 2 min. However, when 1 equiv of the 2,5-dimethylpyrazine complex B_2ppz was reacted with 2 equiv of N at ca. 27 °C, after 2 min, one observed the presence of ca. 5% unreacted B_2ppz together with equimolecular amounts of B_1ppz and BN, while after 10 min all starting material had disappeared and B_1ppz and BN were present in a 4:5 ratio. This ratio changed

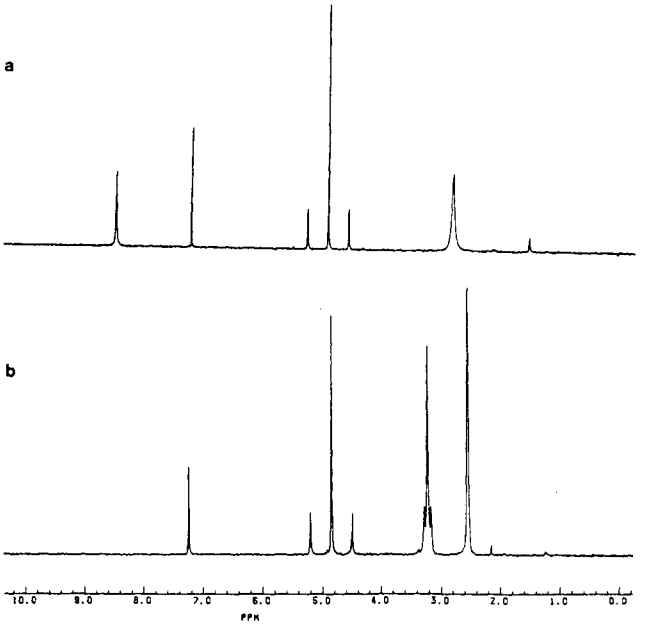
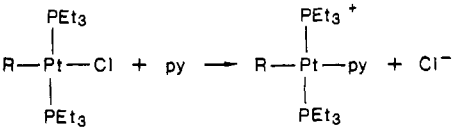


Figure 2. Room-temperature ^1H NMR spectra (in $CDCl_3$) of (a) *trans*-$PtCl_2(C_2H_4)(ppz)$ (E_1ppz) and (b) *trans*-$PtCl_2(C_2H_4)(tpz)$ (E_1tpz).

with time, and after 24 h it was about 1:10. Finally, at the same reagent ratios, when the tetramethylpyrazine complex B_2tpz was used, only detectable amounts of B_1tpz and BN were observed after 5 min; it was only after ca. 1.5 h that comparable amounts of starting material B_2tpz and of B_1tpz and BN were present in solution. However, all the starting material had disappeared after 24 h and equivalent amounts of B_1tpz and BN were present. This is obviously due to steric effects, i.e., shielding of the platinum by the methyl substituents as observed in the kinetic study of the reaction



(R = phenyl, *o*-tolyl, mesityl), where is was shown that the relative decrease in reaction rates was 30:6:1.[14]

Olefin Complexes. The complexes E_1NN (NN = pz, mpz, tpz) are reported to be very dynamic in solution: thus, even at −73 °C only one type of aromatic proton signal could be observed in the complex E_1pz. As found for the phosphine complexes discussed earlier, the compounds E_1NN become less dynamic with increasing methyl substitution on the aromatic ring. Thus, we observe that the room-temperature ^1H NMR spectrum of E_1tpz shows separate signals due to the methyl groups in α-positions to the coordinated nitrogen and to the methyl groups in β-positions to the coordinated nitrogen; i.e., exchange, if it occurs, is slow on the NMR time scale (see Figure 2).

As expected from the relative trans effects of olefins and phosphines (the former having greater effect than the latter), the complexes with the olefin fragment E (E_1NN and E_2NN) are more dynamic than the corresponding species containing a phosphine, e.g., A_1NN and A_2NN.

The observation that the rates of NN exchange in the complexes E_1ppz and E_1tpz differ significantly provides supporting evidence for the postulate that olefin complexes of the type $PtCl_2L(olefin)$ react with nucleophiles by an associative mechanism.

Isolated Complexes. As found for the analogous complexes of pyrimidine,[8] it did not prove possible to isolate the complexes Z_1NN (Z = A–D), but the corresponding Z_2NN species were

(14) Basolo, F.; Chatt, J.; Gray, H. R.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207.

Table III. ^{31}P and ^{195}Pt NMR Data[a] for the Complexes $PtCl_2(NN)L$ and $LCl_2Pt(NN)PtCl_2L$ (NN = Pyrazine or Related Ligand,[b] L = Tertiary Phosphine[c])

complex[d] or param	$\delta(^{31}P)$	$^1J(Pt,P)$	$\delta(^{195}Pt)$	complex[d] or param	$\delta(^{31}P)$	$^1J(Pt,P)$	$\delta(^{195}Pt)$
A_1pz	1.53	3428	−3603	$\Delta\delta_{2-1}$	1.25		−45
A_2pz	2.58	3472	−3602	Δ^1J_{2-1}		69	
$\Delta\delta_{2-1}$	1.05		1	A_1phz	0.80	3500	
Δ^1J_{2-1}		44		A_2phz	1.43	3574	
A_1mepz	1.17	3411		$\Delta\delta_{2-1}$	0.63		
A_1*mepz	0.23	3449		Δ^1J_{2-1}		74	
A_2mepz[e]	2.54	3463		B_1pz	−23.93	3483	
f	1.33	3495		B_2pz	−23.08	3536	
$\Delta\delta_{2-1}$[e]	1.37			$\Delta\delta_{2-1}$	0.85		
$\Delta\delta_{2-1}$[f]	1.10			Δ^1J_{2-1}		53	
ΔJ_{2-1}[e]		52		B_1ppz	−25.17	3490	−3515
ΔJ_{2-1}[f]		46		B_2ppz	−24.51	3558	−3534
A_1opz	0.04	3444		$\Delta\delta_{2-1}$	0.66		−19
A_2opz	1.29	3500		Δ^1J_{2-1}		68	
$\Delta\delta_{2-1}$	1.25			B_1tpz	−25.82	3561	
Δ^1J_{2-1}		56		B_2tpz	−25.32	3634	
A_1ppz	−0.05	3430	−3588	$\Delta\delta_{2-1}$	0.50		
A_2ppz	1.25	3484	−3608	Δ^1J_{2-1}		73	
$\Delta\delta_{2-1}$	1.30		−20	C_1pz	−12.04	3569	−3574
Δ^1J_{2-1}		54		C_2pz	−11.55	3622	−3573
A_1mpz	0.88	3391	−3611	$\Delta\delta_{2-1}$	0.49		1
A_1*mpz	−0.25	3497	−3624	Δ^1J_{2-1}		53	
A_2mpz[e]	2.26	3444	−3607	C_1ppz	−13.49	3568	−3571
f	0.80	3547	−3587	C_2ppz	−12.88	3633	−3590
$\Delta\delta_{2-1}$[e]	1.38			$\Delta\delta_{2-1}$	0.61		−19
$\Delta\delta_{2-1}$[f]	1.05			ΔJ_{2-1}		65	
ΔJ_{2-1}[e]		53		C_1tpz	−14.79	3644	−3491
ΔJ_{2-1}[f]		50		C_2tpz	−14.37	3727	−3519
A_1*trpz	−0.21	3425		$\Delta\delta_{2-1}$	0.42		−28
A_1trpz	−0.61	3499		Δ^1J_{2-1}		83	
A_2trpz[f]	1.08	3483		D_1ppz	−8.16	3412	
e	0.64	3561		D_2ppz	−6.91	3472	
$\Delta\delta_{2-1}$[f]	1.29			$\Delta\delta_{2-1}$	1.25		
$\Delta\delta_{2-1}$[e]	1.25			Δ^1J_{2-1}		60	
ΔJ_{2-1}[f]		58		D_1phz	−7.58	3500	
ΔJ_{2-1}[e]		62		D_2phz	−6.31	3559	
A_1tpz	−0.89	3498	−3531	$\Delta\delta_{2-1}$	1.27		
A_2tpz	0.36	3567	−3576	Δ^1J_{2-1}		59	

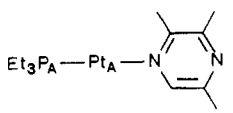
[a] Chemical shifts are given in ppm; $^1J(Pt,P)$ values are in Hz. Measurements were in $CDCl_3$ solutions at room temperature. ^{31}P data collected at 36.43 MHz are given relative to external H_3PO_4, and ^{195}Pt data collected at 53.3 MHz are given relative to external Na_2PtCl_6. Negative values indicate resonances upfield to the reference. [b] pz = pyrazine; mepz = 2-methylpyrazine; opz = 2,3-dimethylpyrazine; ppz = 2,5-dimethylpyrazine; mpz = 2,6-dimethylpyrazine; trpz = 2,3,5-trimethylpyrazine; tpz = 2,3,5,6-tetramethylpyrazine; phz = phenazine. [c] A = $PtCl_2(PEt_3)$; B = $PtCl_2(PMe_2Ph)$; C = $PtCl_2(PMePh_2)$; D = $PtCl_2(P\text{-}n\text{-}Bu_3)$. [d] The complexes marked with an asterisk denote those monometallic complexes in which the platinum atom is bonded to N(1). [e] These values refer to the phosphorus atom in a position trans to N(4). [f] These values refer to the phosphorus atom in a position trans to N(1).

easily obtained in crystalline form.

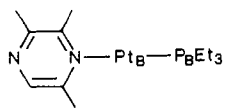
It is noteworthy that several groups[5] were able to isolate monometallic complexes containing olefins, e.g., E_1NN, as well as the corresponding bimetallic complexes, e.g., E_2NN, the only exception being E_1ppz, which could not be isolated in solid form.

^{31}P and ^{195}Pt NMR Spectra. The relevant data for the complexes examined are listed in Table III.

A direct assignment of the ^{31}P NMR resonances of isomeric species of complexes of the type Z_2NN, formed because of the methyl substitution patterns on the heterocycle (mepz, mpz, and trpz), was possible only in the case of the trpz complex (see I and II). Of the two signals arising from the only aromatic proton,



I

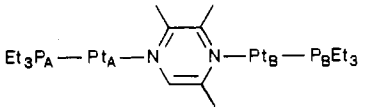


II

one of them was coupled to ^{195}Pt and the other was not. As their intensity ratios showed that the former corresponded to isomer I, the ^{31}P signal of the predominant isomer was assigned to P_A.

Direct assignment in the case of the mepz and mpz complexes was not possible because of signal overlap in the ^1H aromatic signals. Therefore, it was assumed that the predominant isomer present in solution was that where the nitrogen atom coordinated to platinum had fewer methyl groups in the 2,6-position(s).

The assignment of the ^{31}P NMR resonances in the complexes Z_2NN with mepz, mpz, and trpz (see III) was done by comparing the observed signals with those found in related complexes with symmetrical substitution patterns. Our data for complexes with



III

only one type of P atom show that the coordination of a second platinum atom, Pt_B, to a unit such as I causes a downfield shift of the ^{31}P resonance of P_A in the range of 1.0–1.4 ppm and an increase of the Pt_A–P_A coupling constant in the range 44–69 Hz. Our assignments are based on the assumption that this generalization can be extended to the other pyrazine complexes. Indeed, the observed ΔJ values (see Table III) fall within the above-mentioned range. As a larger value of $^1J(Pt,P)$ is associated with a weaker Pt–X bond in a position trans to P–Pt, the observed decrease in the ^1J values is not unexpected as other data (see earlier) indicate that the "ligand" Z_1NN has a weaker donor capacity than free NN.

The ^{195}Pt NMR spectra of some of the complexes were recorded, and the δ values are listed in Table III. The numerical values of the chemical shifts are typical for complexes of this type, e.g., those reported earlier for the complex $PtCl_2$(pyrimidine)(PEt_3)

and $(PEt_3)Cl_2Pt(\mu$-pyrimidine$)PtCl_2(PEt_3)$.[8]

^{1}H NMR Spectra. These data for the free heterocyclic ligands, NN, and their complexes are listed in Tables IV–VI.

The chemical shifts of the phosphine complexes (Table IV) and their coupling constants (Table V) move to lower field on complex formation, and the $\Delta\delta$ values ($\delta_{complex} - \delta_{free\ ligand}$) depend on the number of platinum atoms present in the complex and on the proximity of the proton in question to the platinum center(s).

As found for the analogous complexes with triazine ligands,[8] the coordination of the $PtCl_2L$ unit, Z, to the pyrazine ligand causes chemical shift changes that are additive. Changes of phosphine ligands on Z have negligible effect on the proton spectra. The systematic changes observed are as follows.

(1) The coordination of the first platinum unit to N(1) causes downfield shifts of the 2,6-protons H(2) and H(6) of ca. 0.42 ppm and downfield shifts of the 3,5-protons H(3) and H(5) by ca. 0.20 ppm.

(2) The coordination of a second Z unit to pyrazine to N(4) causes downfield shifts of H(2) and H(6) of ca. 0.23 ppm, as they are also in 3,5-position to a Pt atom, while H(3) and H(5) move by ca. 0.45 ppm by the above-mentioned 2,6-position effect.

The spectra of the other diazines and their complexes show the same regular behavior although the values of the downfield shifts differ slightly from those of the pyrazine system.

All the signals due to the individual aromatic protons appear as multiplets (see Figure 1). The H–H couplings were not analyzed, and the chemical shift values reported in Table IV are those corresponding to the center of each multiplet.

Systematic changes occur to the methyl substituents on the pyrazine ring on coordination of a platinum unit. It is found that these downfield shifts are also additive and that the values of the protons of a 3,5-CH_3 group are ca. 0.07 ppm and those for an 2,6-CH_3 group are ca. 0.7 ppm.

It was indeed the strict additivities of the δ values that allowed a reliable assignment of resonances in the monomethyl- (mpz) and trimethylpyrazine (trpz) complexes.

Furthermore, the close similarities between protons in analogous environments confirmed the assignments made on the basis of the additivity rules mentioned earlier.

The coupling constants $^3J(Pt,H)$ and $^4J(Pt,H_{CH_3})$ were also observed. These are listed in Table V. These also showed the expected values.[7,8] It is observed that for all complexes the coordination of a second platinum atom to the heterocycle causes a slight decrease in J values.

These couplings proved to be particularly valuable for structural assignment of the complexes as the presence or absence of coupling between an aromatic proton or a CH_3 group to platinum could be taken as an indication whether that atom (or group) was in a 2,6-position to the platinum atom.

The ^{1}H NMR spectra of the olefin complexes with pyrazine (pz) and 2,5-dimethylpyrazine (ppz) are indicative of fast exchange processes occurring in solution at room temperature; e.g., in the E_1pz and E_1ppz complexes only one aromatic H resonance without platinum satellites is observed. Our observations are in agreement with published data.[5] However, these exchange processes were sufficiently slow in the tetramethylpyrazine (tpz) complex so that a value of $^4J(Pt,H_{CH_3})$ could be observed (see Table VI and Figure 2).

Finally, as found in these and related complexes,[5] the dynamic processes occurring in solution involve mainly the Pt–N bond as, even at room temperature, one observes coupling between platinum and the olefin protons.

Crystal Structures of $Pt_2Cl_4L_2$(ppz) (L = C_2H_4, PEt_3; ppz = 2,5-Dimethylpyrazine). ORTEP views of these molecules with the atomic numbering schemes are shown in Figures 3 and 4, respectively, while a selection of bond lengths and angles is given in Table VII. Both molecules lie on an inversion center, and thus only half of each molecule is independent. The platinum in each of these structures shows square-planar coordination with trans geometry. Each square-planar unit shows the expected bond lengths and angles for complexes of these types. The major differences between the two structures are the Pt–N bond lengths

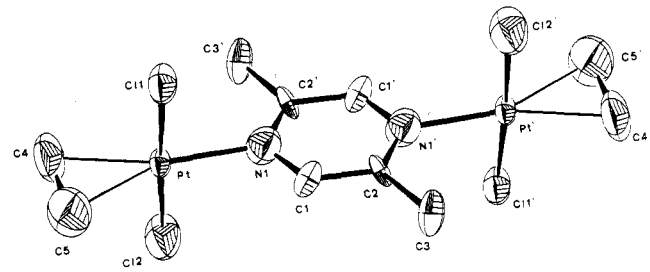


Figure 3. ORTEP view of *trans*-$(C_2H_4)Cl_2Pt(ppz)PtCl_2(C_2H_4)$.

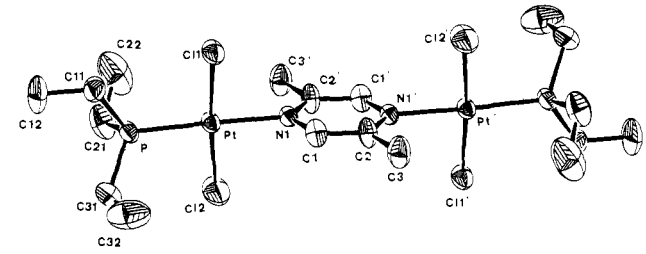


Figure 4. ORTEP view of *trans*-$(PEt_3)Cl_2Pt(ppz)PtCl_2(PEt_3)$.

(see Table VII): 2.059 (9) Å when trans to PEt_3. These provide the most direct evidence obtained to date for a higher trans influence of a phosphine ligand for an alkene.[15] It is noteworthy that the Pt–N bond is of comparable length with (a) that found for $Pt_3Cl_6(PEt_3)_3$(1,3,5-triazine) (2.15 (1) Å)[8] although, in this case, three platinum atoms are bonded to the same heterocycle and (b) that in *trans*-$PtCl_2(PEt_3)$(quinoline-8-carbaldehyde) (2.160 (2) Å).[16] On the other hand, the Pt–N distance for the ethene complex E_2ppz, 2.059 (9) Å, is comparable with that of several compounds of the type *trans*-$PtCl_2(C_2H_4)$(N-heterocycle) (N-heterocycle = 4-methylpyridine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine) (2.082 (16), 2.084 (11), and 2.084 (12) Å, respectively).[17] Thus, it appears that the presence of two coordinated nitrogen atoms in the heterocycle does not influence the Pt–N bond length and thus the nature of the Pt–N bond.

The Pt–Cl bonds in the phosphine complex are slightly longer than those in the corresponding ethene complex. This difference may be significant as it is observed also in the related complexes mentioned above.

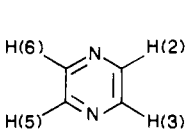
As can be seen in Table VII, the two Pt–Cl distances in A_2ppz differ by 0.021 Å, ca. 5 standard deviations. This is probably due to a repulsive interaction between one chlorine atom and one methyl ring substituent.

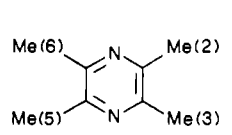
The angles between the coordination planes ($PtCl_2NP$ in one case and $PtCl_2N$ in the other) and that of the heterocycles in the two complexes are slightly different, i.e., for E_2ppz 93.6° and for A_2ppz 103.3°. Literature data show that all complexes of palladium(II)[18] and platinum(II)[8,17] with aromatic N-heterocycles having a phosphine or arsine ligand in a trans position show tilting of the coordination and heterocycle planes. However, in analogous alkene-containing complexes these two planes either can be tilted or can be at ca. 90° as found for E_2ppz. Although packing interactions in crystals containing these molecules could have a significant effect, it should be noted that the tilt angle is ca. 50° in complexes with unsubstituted heterocycles and ca. 80–90° when two 2,6-Me substituents are present.

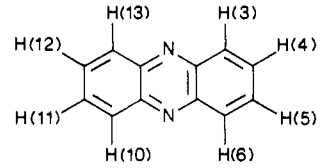
Finally, within the standard deviations, there is no significant difference in C–C and C–N bond lengths between free pyrazine and coordinated 2,6-dimethylpyrazine. However, while for py-

(15) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(16) Albinati, A.; Anklin, C. G.; Canazzoli, F.; Rüegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 503.
(17) (a) Caruso, F.; Spagna, A.; Zambonelli, L. *J. Cryst. Mol. Struct.* **1978**, *8*, 47. (b) Caruso, F.; Spagna, A.; Zambonelli, L. *Inorg. Chim. Act.* **1979**, *32*, L23.
(18) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508.

Table IV. ^{1}H NMR Chemical Shifts,[a] δ (ppm), for the Ligands NN and Their Complexes $PtCl_2(NN)L$ and $LCl_2Pt(NN)PtCl_2L$ (NN = Diazine Ligand,[b] L = Tertiary Phosphine[c])







complex[d] or param	H(2)	H(3)	H(5)	H(6)	Me(2)	Me(3)	Me(5)	Me(6)
pz	8.54	8.54	8.54	8.54				
A_1pz	8.96	8.74	8.74	8.96				
$\Delta\delta_{1-0}$	0.42	0.20	0.20	0.42				
A_2pz	9.19	9.19	9.19	9.19				
$\Delta\delta_{2-1}$	0.23	0.45	0.45	0.23				
mepz		8.42	8.33	8.43	2.54			
A_1mepz[e]		8.79	8.72	8.61	2.62			
$\Delta\delta_{1-0}$		0.37	0.39	0.18	0.08			
A_1*mepz[e]		8.55	8.55	8.75	3.06			
$\Delta\delta^*_{1-0}$		0.13	0.22	0.32	0.52			
A_2mepz[e]		8.96	8.81	9.05	3.12			
$\Delta\delta_{2-1}$		0.17	0.09	0.44	0.50			
$\Delta\delta^*_{1-0}$		0.41	0.26	0.30	0.06			
opz			8.25	8.25	2.53	2.53		
A_1opz			8.44	8.50	3.10	2.61		
$\Delta\delta_{1-0}$			0.19	0.25	0.57	0.08		
A_2opz			8.67	8.67	3.18	3.18		
$\Delta\delta_{2-1}$			0.23	0.17	0.08	0.57		
ppz		8.29		8.29	2.47		2.47	
A_1ppz		8.47		8.49	2.98		2.55	
$\Delta\delta_{1-0}$		0.18		0.20	0.51		0.08	
A_2ppz		8.69		8.69	3.05		3.05	
$\Delta\delta_{2-1}$		0.22		0.20	0.07		0.50	
mpz		8.24	8.24		2.50			2.50
A_1mpz		8.53	8.53		2.55			2.55
$\Delta\delta_{1-0}$		0.29	0.29		0.05			0.05
A_1*mpz		8.53	8.53		3.12			3.12
$\Delta\delta^*_{1-0}$		0.29	0.29		0.62			0.62
A_2mpz		8.83	8.83		3.17			3.17
$\Delta\delta_{2-1}$		0.30	0.30		0.62			0.62
$\Delta\delta^*_{1-0}$		0.30	0.30		0.05			0.05
trpz[e]				8.10	2.46	2.46	2.46	
A_1*trpz[e]				8.36	3.03	2.55	2.51	
$\Delta\delta^*_{1-0}$				0.26	0.57	0.09	0.05	
A_1trpz[e]				8.28	2.50	3.20	3.10	
$\Delta\delta_{1-0}$				0.18	0.04	0.75	0.64	
A_2trpz[e]				8.53	3.10	3.28	3.15	
$\Delta\delta^*_{2-1}$				0.17	0.07	0.73	0.64	
$\Delta\delta_{2-1}$				0.25	0.60	0.08	0.05	
tpz					2.44	2.44	2.44	2.44
A_1tpz					3.18	2.49	2.49	3.18
$\Delta\delta_{1-0}$					0.74	0.05	0.05	0.74
A_2tpz					3.27	3.27	3.27	3.27
$\Delta\delta_{2-1}$					0.09	0.78	0.78	0.09
pz	8.54	8.54	8.54	8.54				
B_1pz	8.95	8.74	8.74	8.95				
$\Delta\delta_{1-0}$	0.41	0.20	0.20	0.41				
B_2pz	9.20	9.20	9.20	9.20				
$\Delta\delta_{2-1}$	0.25	0.46	0.46	0.25				
ppz		8.29		8.29	2.47		2.47	
B_1ppz		8.51		8.51	3.01		2.54	
$\Delta\delta_{1-0}$		0.22		0.22	0.54		0.07	
B_2ppz		8.75		8.75	3.05		3.05	
$\Delta\delta_{2-1}$		0.24		0.24	0.04		0.51	
tpz					2.44	2.44	2.44	2.44
B_1tpz					3.18	2.50	2.50	3.18
$\Delta\delta_{1-0}$					0.74	0.06	0.06	0.74
B_2tpz					3.27	3.27	3.27	3.27
$\Delta\delta_{2-1}$					0.09	0.77	0.77	0.09
pz	8.54	8.54	8.54	8.54				
C_1pz	9.01	8.74	8.74	9.01				
$\Delta\delta_{1-0}$	0.47	0.20	0.20	0.47				
C_2pz	9.26	9.26	9.26	9.26				
$\Delta\delta_{2-1}$	0.25	0.52	0.52	0.25				
ppz		8.29		8.29	2.47		2.47	
C_1ppz		8.49		8.55	3.03		2.55	
$\Delta\delta_{1-0}$		0.20		0.26	0.56		0.08	
C_2ppz		8.77		8.77	3.12		3.12	

Table IV (Continued)

complex[a] or param	H(2)	H(3)	H(5)	H(6)	Me(2)	Me(3)	Me(5)	Me(6)
$\Delta\delta_{2-1}$		0.28		0.22	0.09		0.57	
tpz					2.44	2.44	2.44	2.44
C_1tpz					3.23	2.50	2.50	3.23
$\Delta\delta_{1-0}$					0.79	0.06	0.06	0.79
C_2tpz					3.32		3.32	3.32
$\Delta\delta_{2-1}$					0.09	0.82	0.82	0.09
ppz		8.29		8.29	2.47		2.47	
D_1ppz		8.45		8.47	2.96		2.54	
$\Delta\delta_{1-0}$		0.16		0.18	0.49		0.07	
D_2ppz		8.65		8.65	3.00		3.00	
$\Delta\delta_{2-1}$		0.20		0.18	0.04		0.46	

phz complex or param	H(3,13)	H(6,10)	H(4,12)	H(5,11)	phz complex or param	H(3,13)	H(6,10)	H(4,12)	H(5,11)
phz	8.23		7.81		D_1phz	9.92	7.99	8.35	7.99
A_1phz	9.90	7.97	8.32	7.97	$\Delta\delta_{1-0}$	1.60	−0.24	0.54	0.18
$\Delta\delta_{1-0}$	1.67	−0.26	0.51	0.16	D_2phz	10.05		8.11	
A_2phz	10.06		8.13		$\Delta\delta_{2-1}$	0.13	2.06	−0.24	0.12
$\Delta\delta_{2-1}$	0.16	2.09	−0.19	0.16					

[a] Chemical shifts in ppm; measurements in $CDCl_3$ solutions at room temperature; data collected at 90 MHz. [b] pz = pyrazine; mepz = 2-methylpyrazine; opz = 2,3-dimethylpyrazine; ppz = 2,5-dimethylpyrazine; mpz = 2,6-dimethylpyrazine; trpz = 2,3,5-trimethylpyrazine; tpz = 2,3,5,6-tetramethylpyrazine; phz = phenazine. [c] A = $PtCl_2(PEt_3)$; B = $PtCl_2(PMe_2Ph)$; C = $PtCl_2(PMePh_2)$; D = $PtCl_2(P\text{-}n\text{-}Bu_3)$. [d] The complexes or parameters marked with an asterisk denote those monometallic complexes in which the platinum atom is bonded to N(1). $\Delta\delta_{1-0}$ is the difference in chemical shift of a given proton in the free ligand and in the monometallic complex; $\Delta\delta_{2-1}$ is the difference in chemical shift of a given proton in the bimetallic and the monometallic complex. [e] For the assignment of resonances, see text.

razine the C–N–C bond angle is 116.3 (1)°, the corresponding angles in E_2ppz and A_2ppz are 118.4 (8) and 119.0 (6)°, respectively. This effect, albeit to a smaller extent, has been also observed in the case of 1,3,5-triazine[19] and its symmetrical triplatinum complex.[8]

Kao and Lilly[20] have recently calculated the geometry of 2,5-dimethylpyrazine and obtained the values N–C(1) = 1.317 Å, N–C(2) = 1.355 Å, C(1)–N–C(2) = 118.2°, and C(1)–C(2)–N = 119.1°, in agreement with our experimentally determined values.

Experimental Section

Instrumentation. Proton NMR spectra were recorded either on a Bruker WH 90 or on a WM 250 spectrometer and ^{31}P spectra on a Bruker HX 90 or WM 250 spectrometer. ^{13}C and ^{195}Pt spectra were also obtained by the use of a WM 250 spectrometer. Either $CDCl_3$ or CD_2Cl_2 was used as solvent. Melting points were determined on a Büchi SMP 20 apparatus. IR spectra were recorded on either a Perkin-Elmer 1430 or 883 infrared spectrometer using RbI pellets. Elemental analyses were performed at the "Mikrolabor-ETH Zürich".

Starting Materials. The 1,4-diazine ligands (Fluka, EGA, or Alfa products) were used as received. $CDCl_3$ and CD_2Cl_2 were obtained from Stohler Isotope Chemicals. Other organic solvents (99%) were used without further purification. $Pt_2Cl_4(PEt_3)_2$,[22] $Pt_2Cl_4(PMe_2Ph)_2$,[22] $Pt_2Cl_4(PMePh_2)_2$,[22] $Pt_2Cl_4(P\text{-}n\text{-}Bu_3)_2$,[21] and $Pt_2Cl_4(C_2H_4)_2$[22] were prepared as previously described.

Syntheses. Preparation of the Phosphine Complexes. General Procedure. A 0.13- or 0.26-mmol amount (depending upon the desired coordination complex) of the appropriate 1,4-diazine was added to a solution of 0.13 mmol of $Pt_2Cl_4L_2$ (L = phosphine) in 2.5 mL of $CDCl_3$ or CD_2Cl_2, and the mixture was stirred for 5 min. The resulting greenish yellow solutions were directly used for NMR measurements. A summary of ^1H NMR data of the ligand protons of the PEt_3, PMe_2Ph, $PMePh_2$, and P-*n*-Bu_3 complexes is given in Tables IV and V. The ^{31}P NMR data of all compounds can be found in Table III. Mononuclear species of the type Z_1NN (Z = A–D) could not be isolated, with the exception of *trans*-$[PtCl_2(PMePh_2)](ppz)$. Attempts to isolate these species generally yielded either greenish yellow oils with predominantly the corresponding dinuclear compounds or, in the case of the more volatile ligands, solely the dinuclear complex in nearly quantitative amounts. Dinuclear compounds were obtained by floating a layer of hexane on top of a CD_2Cl_2 or $CDCl_3$ solution of the complex.

***trans*-[$PtCl_2(PEt_3)$](pz) (A_1pz).** ^{13}C NMR ($CDCl_3$): δ 7.9, 14.8 (^1J(P,C) = 39.0 Hz, ^2J(Pt,C) = 34.1 Hz), 144.9, 147.1.

***trans*-[$PtCl_2(PEt_3)$](ppz) (A_1ppz).** ^{13}C NMR ($CDCl_3$): δ 8.0, 14.2 (^1J(P,C) = 40.6 Hz, ^2J(Pt,C) = 34.0 Hz), 21.4, 21.9 (^3J(Pt,C) = 10 Hz), 143.6, 147.4, 151.2, 153.3.

***trans*-[$PtCl_2(PEt_3)$](mpz) (A_1mpz).** Isomer with coordination at N(1): ^{13}C NMR ($CDCl_3$) δ 7.9, 14.7 (^1J(P,C) = 40.0 Hz), 22.0, 141.3, 155.6; ^{195}Pt NMR ($CDCl_3$) δ −3624 (^1J(Pt,P) = 3497 Hz). Isomer with coordination at N(4): ^{13}C NMR ($CDCl_3$) δ 7.9, 14.7 (^1J(P,C) = 40.0 Hz), 29.9, 144.7. The resonance signal of C(2) and C(6) could not be observed.

***trans*-[$PtCl_2(PEt_3)$](tpz) (A_1tpz).** ^{13}C NMR ($CDCl_3$): δ 7.8, 14.1 (^2J(P,C) = 40.5 Hz, ^2J(Pt,C) = 34.8 Hz), 21.6, 22.4, 149.1, 151.7.

***trans*-[$PtCl_2(PMePh_2)$](pz) (C_1pz).** ^{13}C NMR ($CDCl_3$): δ 12.8 (^1J(P,C) = 45.0 Hz), 128.7 (^3J(P,C) = 12.1 Hz), 130.4 (^1J(P,C) = 66.0 Hz), 131.3, 133.2 (^2J(P,C) = 9.8 Hz), 145.1, 147.2.

***trans*-[$PtCl_2(PMePh_2)$](ppz) (C_1ppz).** Floating a layer of hexane over a solution of the complex in $CDCl_3$ resulted in the formation of a small amount of crystalline C_2ppz. The mixture was subsequently stored at −20 °C for 2 weeks, during which time greenish yellow needles of C_1ppz were formed in a yield of 40%; mp 152 °C. Anal. Calcd for $C_{19}H_{21}N_2Cl_2PPt$: C, 39.73; H, 3.71; N, 4.88; Cl, 12.35. Found: C, 39.46; H, 3.69; N, 4.80; Cl, 12.51. ^{13}C NMR ($CDCl_3$): δ 12.8 (^1J(P,C) = 46.3 Hz), 21.4, 22.3, 128.6 (^3J(P,C) = 11.7 Hz), 130.3 (^1J(P,C) = 65.0 Hz), 131.3, 133.1 (^2J(P,C) = 9.8 Hz), 143.9, 147.5, 151.5, 153.4.

***trans*-[$PtCl_2(PMePh_2)$](tpz) (C_1tpz).** ^{13}C NMR ($CDCl_3$): δ 12.7 (^1J(P,C) = 45.0), 22.2, 22.4, 128.7 (^3J(P,C) = 10.6 Hz), 130.8 (^1J(P,C) = 65.1 Hz), 131.2, 133.0 (^2J(P,C) = 10.0 Hz), 149.0, 151.9.

***trans*-[$PtCl_2(PEt_3)]_2$(pz) (A_2pz).** Light green crystals were obtained in a yield of 91%; mp >240 °C. Anal. Calcd for $C_{16}H_{34}N_2Cl_4P_2Pt_2$: C, 22.65; H, 4.04; N, 3.30; Cl, 16.72. Found: C, 22.41; H, 3.81; N, 3.20; Cl, 16.95. ^{13}C NMR ($CDCl_3$): δ 7.9, 15.0 (^1J(P,C) = 41.1 Hz, ^2J(Pt,C) = 34.0 Hz), 146.8.

***trans*-[$PtCl_2(PEt_3)]_2$(mepz) (A_2mepz)**: greenish orange crystals; yield 89%; mp 170 °C. Anal. Calcd for $C_{17}H_{36}H_2Cl_4P_2Pt_2$: C, 23.68; H, 4.21; N, 3.25; Cl, 16.44. Found: C, 23.63; H, 4.24; N, 3.23; Cl, 16.50.

***trans*-[$PtCl_2(PEt_3)]_2$(opz) (A_2opz)**: light green crystals; yield 90%; mp 184 °C dec. Anal. Calcd for $C_{18}H_{38}N_2Cl_4P_2Pt_2$: C, 24.67; H, 4.37; N, 3.20; Cl, 16.18. Found: C, 24.55; H, 4.46; N, 3.12; Cl, 16.16.

***trans*-[$PtCl_2(PEt_3)]_2$(ppz) (A_2ppz)**: light green crystals; yield 95%; mp 230 °C dec. Anal. Calcd for $C_{18}H_{38}N_2Cl_4P_2Pt_2$: C, 24.67; H, 4.37; N, 3.20; Cl, 16.18. Found: C, 24.66; H, 4.22; N, 3.19; Cl, 16.50. Molecular weight: calcd, 876.5; found, 871.4. ^{13}C NMR ($CDCl_3$): δ 8.0, 14.3 (^1J(P,C) = 40.3 Hz, ^2J(Pt,C) = 35.0 Hz), 22.3, 147.7, 153.9.

***trans*-[$PtCl_2(PEt_3)]_2$(mpz) (A_2mpz)**: light green needles; yield 90%; mp 197 °C. Anal. Calcd for $C_{18}H_{38}N_2Cl_4P_2Pt_2$: C, 24.67; H, 4.37; N, 3.20; Cl, 16.18. Found: C, 24.88; H, 4.31; N, 3.35; Cl, 16.41. ^{13}C NMR ($CDCl_3$): δ 7.8, 7.9, 14.2 (^1J(P,C) = 40.8 Hz, ^2J(Pt,C) = 33.6 Hz), 14.9 (^1J(P,C) = 41.4 Hz, ^2J(Pt,C) = 32.7 Hz), 23.0, 144.4, 156.5 (^2J(Pt,C) = 20 Hz).

***trans*-[$PtCl_2(PEt_3)]_2$(trpz) (A_2trpz)**: light green crystals; yield 92%; mp >240 °C. Anal. Calcd for $C_{19}H_{40}N_2Cl_4P_2Pt_2$: C, 25.63; H, 4.53;

(19) Coppens, P. *Science* (*Washington, D.C.*) **1967**, *158*, 1577.
(20) Kao, J.; Lilly, A. C. *J. Am. Chem. Soc.* **1987**, *109*, 4149.
(21) Goodfellow, R. J.; Venanzi, L. M. *J. Chem. Soc.* **1965**, 7533.
(22) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973.

Table V. ^nJ(Pt,H) Coupling Constants[a] for the Complexes $PtCl_2(NN)L$ and $LCl_2Pt(NN)PtCl_2L$ (NN = Pyrazine or Related Ligand,[b] L = Tertiary Phosphine[c])

complex[d]	^3J(Pt,H)	^4J(Pt,H_{CH})
A_1pz	22.8	
A_2pz	22.0	
A_1mpz	23.1 [H(3)]	
	22.3 [H(5)]	
A_1*mepz	*e*	7.7
A_2mepz	21.6 [H(3)]	7.4
	20.2 [H(5)]	
	22.8 [H(6)]	
A_1opz	17.9	6.2
A_2opz	16.7	<6
A_1mpz	22.9	
A_1*mpz		9.3
A_2mpz	22.8	9.3
A_1ppz	20.4	7.7
A_2ppz	18.7	6.4
A_1*trpz	19.7	6.8
A_1trpz		7.6 [C(3)H_3]
		8.6 [C(5)H_3]
A_2trpz	18.9	<6 [C(2)H_3]
		6.4 [C(3)H_3]
		8.6 [C(5)H_3]
A_1tpz		7.3
A_2tpz		<6
B_1pz	24.1	
B_2pz	23.8	
B_1ppz	21.8	7.5
B_2ppz	21.1	7.0
B_1tpz		7.7
B_2tpz		6.5
C_1pz	25.2	
C_2pz	24.6	
C_1ppz	21.6	8.2
C_2ppz	21.1	6.8
C_1tpz		7.5
C_2tpz		<6
D_2ppz	21.7	6.9
C_2ppz	19.4	<6

phz complex	^4J(Pt,H)	phz complex	^4J(Pt,H)
A_1phz	7.7	D_1phz	8.6
A_2phz	*f*	D_2phz	*f*

[a] Coupling constants, ^nJ(Pt,H), in Hz; measurements in $CDCl_3$ solutions at room temperature; data collected at 90 MHz. [b] pz = pyrazine; mepz = 2-methylpyrazine; opz = 2,3-dimethylpyrazine; ppz = 2,5-dimethylpyrazine; mpz = 2,6-dimethylpyrazine; trpz = 2,3,5-trimethylpyrazine; tpz = 2,3,5,6-tetramethylpyrazine; phz = phenazine. [c] A = $PtCl_2(PEt_3)$; B = $PtCl_2(PMe_2Ph)$; C = $PtCl_2(PMePh_2)$; D = $PtCl_2(P\text{-}n\text{-}Bu_3)$. [d] The complexes marked with an asterisk denote those monometallic complexes in which the platinum atom is bonded to N(1). [e] Not observable because of signal overlap. [f] Not observable.

N, 3.15; Cl, 15.93. Found: C, 25.60; H, 4.54; N, 3.15; Cl, 15.94.

***trans*-[$PtCl_2(PEt_3)]_2$(tpz) (A_2tpz)**: greenish yellow crystals; yield 94%; mp >240 °C. Anal. Calcd for $C_{20}H_{42}N_2Cl_4P_2Pt_2$: C, 26.52; H, 4.68; N, 3.10; Cl 15.63. Found: C, 26.63; H, 4.64; N, 3.09; Cl, 15.75. ^{13}C NMR ($CDCl_3$): δ 7.8, 14.3 (^1J(P,C) = 41.0 Hz, ^2J(Pt,C) = 34.2 Hz), 22.9, 152.7.

***trans*-[$PtCl_2(PEt_3)]_2$(phz) A_2phz)**: red crystals; yield 90%; mp 240 °C. Anal. Calcd for $C_{24}H_{38}N_2Cl_4P_2Pt_2$: C, 30.39; H, 4.04; N, 2.95; Cl, 14.95. Found: C, 30.51; H, 4.19; N, 2.99; Cl, 15.07.

***trans*-[$PtCl_2(PMe_2Ph)]_2$(ppz) (B_2ppz)**: greenish yellow crystals; yield 90%; mp 231 °C dec. Anal. Calcd for $C_{22}H_{30}N_2Cl_4P_2Pt_2$: C, 28.83; H, 3.30; N, 3.06; Cl, 15.50. Found: C, 28.73; H, 3.24; N, 2.99; Cl, 16.04. ^{13}C NMR ($CDCl_3$): δ 12.5 (^1J(P,C) = 46.0 Hz, ^2J(Pt,C) = 36.9 Hz), 22.6, 129.9 (^3J(P,C) = 11.1 Hz), 130.4 (^1J(P,C) = 67.1 Hz), 131.3, 131.4 (^2J(P,C) = 9.6 Hz), 148.0, 154.0.

***trans*-[$PtCl_2(PMePh_2)]_2$(pz) (C_2pz)**. Pyrazine was slowly added to a solution of $Pt_2Cl_4(PMePh_2)_2$ in $CDCl_3$, resulting in the precipitation of light green product, which was washed with $CDCl_3$ and dried, yielding 85% C_2pz, mp 200 °C dec. Anal. Calcd for $C_{30}H_{30}N_2Cl_4P_2Pt_2$: 35.59; H, 2.99; N, 2.77; Cl, 14.01. Found: C, 35.19; H, 2.97; N, 2.56; Cl, 14.65. ^{13}C NMR ($CDCl_3$): δ 13.6 (^1J(P,C) = 46.2 Hz), 128.7 (^3J(P,C) = 11.9 Hz), 129.9 (^1J(P,C) = 67.5 Hz), 131.5, 133.2 (^2J(P,C) = 10.7 Hz), 147.1.

***trans*[$PtCl_2(PMePh_2)]_2$(ppz) (C_2ppz)**: light green crystals; yield 93%; mp 250 °C dec. Anal. Calcd for $C_{32}H_{34}N_2Cl_4P_2Pt_2$: C, 36.94; H, 3.29; N, 2.69; Cl, 13.63. Found: C, 36.76; H, 3.29; N, 2.53; Cl, 13.51. ^{13}C NMR ($CDCl_3$): δ 12.9 (^1J(P,C) = 46.6 Hz), 22.7, 128.7 (^3J(P,C) = 12.0 Hz), 129.9 (^1J(P,C) = 66.0 Hz), 131.4, 133.1 (^2J(P,C) = 11.1 Hz), 148.1, 154.0.

***trans*-[$PtCl_2(PMePh_2)]_2$(tpz) (C_2tpz)**: long, greenish yellow needles (when CH_2Cl_2 was used instead of $CDCl_3$, the crystals became powdery upon drying); yield 91%; mp >240 °C. Anal. Calcd for $C_{34}H_{38}N_2Cl_4P_2Pt_2$: C, 38.22; H, 3.58; N, 2.62; Cl, 13.27. Found: C, 38.11; H, 3.69; N, 2.64; Cl, 13.38. ^{13}C NMR ($CDCl_3$): δ 12.8 (^1J(P,C) = 45.8 Hz), 23.6, 128.6 (^3J(P,C) = 11.3 Hz), 130.0 (^1J(P,C) = 65.8 Hz), 131.2 (^4J(P,C) = 2.7 Hz), 132.8 (^2J(P,C) = 10.2 Hz), 152.5 (^3J(P,C) = 3.8 Hz, ^4J(P,C) = 1.0 Hz).

***trans*-$PtCl_2(PMe_2Ph)$(N) (BN)**. ^1H NMR ($CDCl_3$): δ 1.84 (d, ^2J(P,H) = 11.9 Hz, ^3J(Pt,H) = 31.9 Hz, 6 H, PCH_3), 2.35 (s, 3 H, C(4)H_3), 3.01 (s, ^4J(Pt,H) = 7.2 Hz, 3 H, C(2)H_3), 7.03 (m, 2 H, H(3)H(5)), 7.41–7.51 (m, ar H, 3 H), 7.76–8.01 (m, ar H, 2 H), 8.49 (m, ^3J(Pt,H) = 19.6 Hz, 1 H, H(6)). ^{31}P NMR ($CDCl_3$): δ −25.82 (^1J(Pt,P) = 3640 Hz).

Preparation of the Ethene Complexes. The ^1H NMR data are given in Table VI.

***trans*-[$PtCl_2(C_2H_4)$](pz) (E_1pz)**. The complex was prepared as previously described:[5a,b] greenish yellow powder; yield 90–95%; mp 60 °C dec. Anal. Calcd for $C_6H_8N_2Cl_2Pt$: C, 19.26; H, 2.16; N, 7.49; Cl, 18.95. Found: C, 19.11; H, 2.19; N, 7.46; Cl, 18.86. IR (RbI): 3111, 3071, 3050, 2989, 1481, 1459, 1420, 1161, 1123, 1053, 1011, 812, 481, 461, 338 cm^{-1}.

***trans*-[$PtCl_2(C_2H_4)$](ppz) (E_1ppz)**. The complex was prepared in solution by adding 0.34 mmol (36.8 mg) of 2,5-dimethylpyrazine to a slurry of 0.17 mmol (100 mg) of $Pt_2Cl_4(C_2H_4)_2$ in 2 mL of $CDCl_3$ or CD_2Cl_2. The greenish yellow solution was directly used for NMR measurements. Attempts to isolate E_1ppz by floating a layer of hexane on top of the CD_2Cl_2 or $CDCl_3$ solutions led to the formation of nearly quantitative amounts of E_2ppz. Taking the solution to dryness under vacuum led to the same result, as ppz sublimed during this process. Known methods for the isolated of E_1pz as mentioned above also failed in the case of E_1ppz.

***trans*-[$PtCl_2(C_2H_4)$](tpz) (E_1tpz)**. The complex was prepared as previously described;[5b] it contained small amounts of E_2tpz: greenish yellow powder; yield 90%; mp 165 °C dec. Anal. Calcd for $C_{10}H_{16}N_2Cl_2Pt$: C, 27.92; H, 3.75; N, 6.51; Cl, 16.48. Found: C, 27.19; H, 3.75; N, 6.22; Cl, 16.81. IR (RbI): 1517, 1490, 1420, 1231, 1178, 1004, 986, 812, 386, 339, 301 cm^{-1}.

***trans*-[$PtCl_2(C_2H_4)]_2$(pz) (E_2pz)**. A 0.17-mmol (13.6-mg) amount of pyrazine was added to a slurry of 0.17 mmol (100 mg) of $Pt_2Cl_4(C_2H_4)_2$ in 2 mL of $CHCl_3$ or CH_2Cl_2, and the mixture was stirred for 18 h in the absence of light, during which time the orange suspension changed to yellow. The reaction mixture was then taken to dryness, and the yellow complex was washed with $CHCl_3$: yield 90%; mp 90 °C dec. Anal. Calcd for $C_8H_{12}N_2Cl_4Pt_2$: C, 14.38; H, 1.81; N, 4.19; Cl, 21.22. Found: C, 14.32; H, 1.98; N, 4.21; Cl, 20.96. IR (RbI): 3112, 1479, 1420, 1163, 1121, 1052, 1013, 812, 797, 499, 465, 384, 341 cm^{-1}.

***trans*-[$PtCl_2(C_2H_4)]_2$(ppz) (E_2ppz)**. A greenish yellow powder of E_2ppz in a yield of 90–95% could be obtained by using the method described above for E_2pz. Dissolving the powder in $CHCl_3$ with a slight excess of ppz followed by floating a layer of hexane on top led to the formation of crystalline product, mp 210 °C dec. Anal. Calcd for $C_{10}H_{16}N_2Cl_4Pt_2$: C, 17.25; H, 2.32; N, 4.02; Cl, 20.32. Found: C, 17.35; H, 2.33; N, 4.00; Cl, 20.22. IR (RbI): 3126, 3049, 2919, 1498, 1476, 1448, 1420, 1382, 1344, 1157, 1038, 1016, 977, 887, 469, 386, 348 cm^{-1}.

***trans*-[$PtCl_2(C_2H_4)]_2$(tpz) (E_2tpz)**. Using the method described above for E_2pz led to a clear, greenish yellow solution from which intense greenish yellow crystals could be obtained in a yield of 85% by floating a layer of hexane on top of the $CHCl_3$ solution; mp 180 °C dec. Anal. Calcd for $C_{12}H_{20}N_2Cl_4Pt_2$: C, 19.90; H, 2.78; N, 3.87; Cl, 19.58. Found: C, 20.09; H, 2.74; N, 3.82; Cl, 19.50. IR (RbI): 1441, 1423, 1361, 1257, 1232, 1176, 1017, 1003, 987, 824, 812, 476, 395, 345, 338 cm^{-1}.

Exchange Reactions. General Procedure. Two equivalents (0.4 mmol, 46.0 μL) of 2,4-lutidine and 0.2 mmol of B_2pz, B_2ppz, or B_2tpz were dissolved separately in $CDCl_3$, the solutions mixed, and their ^{31}P NMR spectra measured after 0, 2, 5, 10, 30, 60, and 105 min as well as after 24 h. The measurements were carried out at 0 °C for the B_2pz system and at room temperature for the B_2ppz and B_2tpz systems. The NMR parameters of the species observed corresponded to those given in the appropriate tables.

Crystallography. Crystals suitable for X-ray diffraction of both compounds were grown as described earlier.

Data were collected on a Nonius CAD4 diffractometer using the parameters listed in Table VIII and Supplementary Table S5 with var-

Table VI. ^{1}H NMR Data[a] for the Complexes $PtCl_2(NN)(C_2H_4)$ and $(C_2H_4)Cl_2Pt(NN)PtCl_2(C_2H_4)$ (NN = Pyrazine or Related Ligand[b])

complex[c] or param	δ(arom H)[d]	δMe(2,6)	δMe(3,5)	^4J(Pt,H)[e]	δ(C_2H_4)	J(Pt,H)
pz	8.54					
E_1pz	8.92				4.99	62.3
$\Delta\delta_{1-0}$	0.38					
E_2pz	9.32				5.05	64.8
$\Delta\delta_{2-1}$	0.40				0.06	
ppz	8.29	2.47				
E_1ppz	8.51		2.83[f]		4.93	62.6
$\Delta\delta_{1-0}$	0.22		0.36			
E_2ppz	8.71		3.08		5.00	65.1
$\Delta\delta_{2-1}$	0.20		0.25		0.07	
tpz			2.44			
E_1tpz		3.22	2.54	10.0	4.85	63.3
$\Delta\delta_{1-0}$		0.78	0.10			
E_2tpz		3.37		8.2	4.92	65.8
$\Delta\delta_{2-1}$		0.15	0.83		0.07	

[a] Chemical shifts, δ, in ppm and coupling constants, ^nJ(Pt,H), in Hz, for $CDCl_3$ solutions at room temperature; data collected at 90 MHz. [b] pz = pyrazine; ppz = 2,5-dimethylpyrazine; tpz = 2,3,5,6-tetramethylpyrazine. [c] $\Delta\delta_{1-0}$ is the difference in chemical shift of a given proton in the free ligand and in the monometallic complex; $\Delta\delta_{2-1}$ is the difference in chemical shift of a given proton in the bimetallic and the monometallic complex. For the assignment of resonances see text. [d] Only an average value of this parameter for all diazine aromatic protons is observable because of rapid donor-exchange processes occurring at this temperature (see text). This process is also responsible for the failure to observe the corresponding J(Pt,H) couplings. [e] As the pz and ppz complexes are very dynamic in solution, no Pt–H coupling is observed. However, as the tpz complexes are much less dynamic, Pt–H coupling is clearly observable. [f] Average value because of dynamic behavior.

Table VII. Relevant Bond Lengths (Å) and Angles (deg) for E_2ppz and A_2ppz[a]

	E_2ppz	A_2ppz
Pt–Cl(1)	2.277 (5)	2.289 (3)
Pt–Cl(2)	2.279 (4)	2.310 (4)
Pt–P(1)		2.233 (2)
Pt–C(4)	2.13 (2)	
Pt–C(5)	2.16 (2)	
Pt–N	2.059 (9)	2.116 (7)
N–C(1)	1.32 (1)	1.34 (1)
N–C(2′)	1.35 (1)	1.33 (1)
C(1)–C(2)	1.40 (2)	1.39 (1)
C(2)–C(3)	1.49 (2)	1.51 (2)
C(4)–C(5)	1.42 (2)	
Pt–N–C(1)	118.8 (6)	117.9 (5)
Pt–N–C(2′)	122.7 (5)	123.0 (5)
Pt–C(4)–C(5)	72.1 (9)	
Pt–C(5)–C(4)	69.7 (9)	
Cl(1)–Pt–Cl(2)	177.5 (1)	175.0 (1)
Cl(1)–Pt–N	89.6 (3)	87.0 (2)
Cl(2)–Pt–N	87.9 (3)	88.1 (2)
P(1)–Pt–N		177.7 (3)
P(1)–Pt–Cl(1)		95.3 (1)
P(1)–Pt–Cl(2)		89.6 (1)
N(1)–C(1)–C(2)	124.0 (8)	121.3 (6)
C(1)–C(2)–N(1′)		119.6 (7)
C(1)–N(1)–C(2′)	118.4 (8)	119.0 (6)
C(4)–Pt–N(1)–C(1)[a]	8.6	
Cl(1)–Pt–N(1)–C(1)	98.2	79.2
C(4)–C(5)–Pt–Cl(1)	−88.2	
P(1)–Pt–N(1)–C(1)		−108.9
Pt–P(1)–C(11)–C(12)		177.6
Pt–P(1)–C(21)–C(22)		55.6
Pt–P(1)–C(31)–C(32)		−57.3

[a] Esd's in the last significant digit are given in parentheses. [b] Esd's on torsion angles are in the range 0.9–1.3°.

iable scan speed to obtain constant statistical precision on the collected intensities. Data were corrected for Lorentz and polarization factors and for absorption by using the data reduction programs of the Nonius-SDP package.[23] Reflections having $F_o > 2.5\sigma(F_o)$ were considered as observed; $F_o = 0.0$ was given to those reflections having negative net intensities. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, using a Cruickshank weighting scheme.[24] The scattering factors used were from ref 25; a correction for the real part of the anomalous dispersion was also taken into account.[25]

Table VIII. Experimental Data for the X-ray Diffraction Studies of Compounds E_2ppz and A_2ppz

	E_2ppz	A_2ppz
chem formula	$C_{10}H_{16}Cl_4N_2Pt_2$	$C_{18}H_{38}Cl_4N_2P_2Pt_2$
mol wt	692.25	876.46
space group	$P2_1/n$	$P2_1/c$
a, Å	7.048 (3)	12.149 (3)
b, Å	13.407 (3)	8.231 (6)
c, Å	9.219 (2)	15.464 (5)
β, deg	69.81 (3)	108.95 (2)
Z	2	2
V, Å	817.7	1462.6
ρ(calcd), g cm^{-3}	2.827	1.989
μ, cm^{-1}	89.54	100.9
T, °C	25	
λ, Å^3	0.71069	
R^a	0.044	0.038
R_w^b	0.056	0.042

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

$Pt_2Cl_4(C_2H_4)_2$(ppz) (E_2ppz). The yellow crystals of this compound are air stable. A crystal of prismatic shape was mounted on a glass fiber for the data collection. From the systematic absences the space group was unambiguously determined as $P2_1/n$. Cell constants were obtained by a least-squares fit of 25 high-angle reflections ($10.0 \leq \theta \leq 12.0$) using the CAD4 centering routines. Crystallographic and other relevant parameters for the data collection are given in Table VIII. Three standard reflections ($1\bar{2}\bar{5}$, $\bar{1}34$, $\bar{1}\bar{3}4$) were measured every 1 h of exposure time to monitor the stability of the crystal and of the experimental conditions: no significant variation was observed. The orientation of the crystal was checked by measuring three reflections ($\bar{1}\bar{1}4$, $02\bar{5}$, 214) every 300 reflections. An empirical absorption correction was applied by using the ψ scans of three reflections; 241, 352, 482 (at χ angles of 87.6, 83.0, and 87.6°, respectively). Transmission factors were in the range 0.85–0.97. The structure was refined by full-matrix least squares as described above, using anisotropic temperature factors for all atoms. The contribution of the hydrogen atoms in their calculated positions (C–H = 0.95 Å, B_{iso} = 5.0 Å^2) was taken into account but not refined. Final positional parameters are listed in Table IX.

$Pt_2Cl_4(PEt_3)_2$(ppz) (A_2ppz). The pale yellow crystals of prismatic shape are air stable. A suitable crystal was mounted on a glass fiber at a random orientation and used for the data collection. The space group ($P2_1/c$) and cell constants were obtained as above and are listed in Table VIII. Three standard reflections (measured every 1 h), $4\bar{1}6$, $41\bar{6}$, and $5\bar{1}2$, were used to check the crystal decay; reflections $\bar{5}\bar{1}5$, 515, $7\bar{2}\bar{2}$, were

(23) *Enraf-Nonius Structure Determination Package, SDP*; Enraf-Nonius: Delft, The Netherlands, 1980.

(24) Cruickshank, D. W. J. In *Computing Methods in Crystallography*; Ahmed, A., Ed.; Munksgaard: Copenhagen, 1972.

(25) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table IX. Final Positional Parameters for E_2ppz and A_2ppz

	x/a	*y/b*	*z/c*
		E_2ppz	
Pt(1)	0.19539 (6)	0.18337 (3)	0.16875 (5)
Cl(1)	0.39058 (82)	0.06707 (33)	0.23026 (73)
Cl(2)	-0.00759 (63)	0.29419 (28)	0.10441 (49)
N(1)	0.07392 (146)	0.07315 (77)	0.07215 (116)
C(1)	0.14694 (209)	0.06012 (92)	-0.07861 (148)
C(3)	0.17032 (232)	-0.02794 (94)	-0.32732 (149)
C(2)	0.07680 (170)	-0.01241 (91)	-0.15752 (141)
C(4)	0.40337 (244)	0.29757 (136)	0.17481 (212)
C(5)	0.25412 (290)	0.29158 (132)	0.32237 (223)
		A_2ppz	
Pt	0.17461 (3)	0.25951 (4)	0.16680 (2)
Cl(1)	0.00976 (21)	0.33738 (34)	0.19677 (19)
Cl(2)	0.33064 (27)	0.16844 (52)	0.12590 (25)
P	0.29499 (20)	0.41733 (33)	0.27359 (17)
N(1)	0.06622 (59)	0.10769 (93)	0.06362 (48)
C(1)	0.03221 (87)	-0.03412 (127)	0.08916 (65)
C(2)	-0.03311 (88)	-0.14501 (125)	0.02492 (64)
C(3)	-0.06993 (117)	-0.30398 (154)	0.05550 (77)
C(11)	0.23067 (92)	0.52549 (139)	0.34771 (79)
C(12)	0.31171 (143)	0.63850 (211)	0.41800 (110)
C(21)	0.42097 (108)	0.31128 (180)	0.34779 (97)
C(22)	0.39174 (174)	0.16409 (233)	0.39523 (112)
C(31)	0.35810 (112)	0.57408 (182)	0.22110 (94)
C(32)	0.26893 (170)	0.67686 (243)	0.15582 (143)

measured every 300 reflections to check the crystal orientation. Data were corrected for absorption by using the ψ scans of five reflections, $\bar{1}2\bar{2}$, $\bar{1}3\bar{3}$, $2\bar{4}\bar{4}$, $2\bar{5}\bar{6}$, and 266 ($\chi > 85.0°$). The range of transmission factors was 0.506-0.997. During the refinement (all atoms treated anisotropically) the contribution of the H atoms in their idealized positions (C-H = 0.98 Å, B_{iso} = 5.0 Å^2) was taken into account but not refined. Final positional parameters are listed in Table IX.

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Registry No. A_1mepz, 118516-01-1; A_1*mepz, 118516-02-2; A_1mpz, 118515-76-7; A_1*mpz, 118515-75-6; A_1opz, 118516-03-3; A_1phz, 118516-06-6; A_1ppz, 118515-74-5; A_1pz, 118515-73-4; A_1tpz, 118515-77-8; A_1trpz, 118516-05-5; A_1*trpz, 118516-04-4; A_2mepz, 118515-82-5; A_2mpz, 118515-85-8; A_2opz, 118515-83-6; A_2phz, 118515-88-1; A_2ppz, 118515-84-7; A_2pz, 118515-81-4; A_2tpz, 118515-87-0; A_2trpz, 118515-86-9; BN, 118515-92-7; B_1ppz, 118515-98-3; B_1pz, 118515-96-1; B_1tpz, 118515-99-4; B_2ppz, 118515-89-2; B_2pz, 118515-97-2; B_2tpz, 118516-00-0; C_1ppz, 118515-79-0; C_1pz, 118515-78-9; C_1tpz, 118515-80-3; C_2ppz, 118515-90-5; C_2pz, 118537-32-9; C_2tpz, 118515-91-6; D_1phz, 118516-09-9; D_1ppz, 118516-07-7; D_2phz, 118516-10-2; D_2ppz, 118516-08-8; E_1ppz, 118515-93-8; E_1pz, 78713-20-9; E_1tpz, 95662-22-9; E_2ppz, 118515-94-9; E_2pz, 78724-29-5; E_2tpz, 118515-95-0; $Pt_2Cl_4(C_2H_4)_2$, 12073-36-8; $Pt_2Cl_4(PEt_3)_2$, 15692-96-3; $Pt_2Cl_4(PMe_2Ph)_2$, 15699-79-3; $Pt_2Cl_4(PMePh_2)_2$, 16633-87-7; $Pt_2Cl_4(P\text{-}n\text{-}Bu_3)_2$, 15670-38-9.

Supplementary Material Available: For E_2ppz and A_2ppz, Table S1 (thermal factors), Table S2 (calculated hydrogen atom positions), Table S3 (extended list of bond distances and angles), and Table S5 (experimental data for the X-ray diffraction studies) (12 pages); Table S4 (listings of F_o and F_c) (20 pages). Ordering information is given on any current masthead page.

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The Electron-Deficient Planar Tetrairon Cluster $Fe_4(CO)_8L_4$ (L = Pyridine)

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A 56-electron cluster with formula $Fe_4(CO)_8(pyridine)_4$ (**1**) is formed by addition of $FeCl_2$ and $Na_2Fe(CO)_4$ in tetrahydrofuran containing a small excess of pyridine. The compound, which has a magnetic moment of 3.8 μ_B, has been structurally characterized. Crystal data for $C_{28}H_{20}N_4O_8Fe_4$: a = 21.511 (3) Å, b = 16.766 (3) Å, c = 19.253 (3) Å, β = 117.94 (2)°, monoclinic $P2_1/a$, Z = 8, R = 0.06 for 2848 observed reflections. The structure consists of a triangulated parallelogram of iron atoms, two of which are coordinated, at opposite vertices, each by four carbon monoxide molecules and the other two are each coordinated by two pyridine molecules. The Fe-Fe separations along the periphery are an average of 2.534 (4) Å, a length attributable to an Fe-Fe single bond. The length of the shortest diagonal is 2.759 (3) Å, raising the question whether there is residual Fe-Fe bonding along that direction. The question is examined by extended Hückel calculations. Simple qualitative MO arguments describe the interactions between opposite pairs of L_2Fe and L_4Fe fragments. Although they do not give a uniquely defined electronic ground-state configuration, significant pieces of information on the Fe-Fe trans-diagonal bond and on the electron distribution over the four metal atoms may be attained.

Introduction

As a part of our studies of the interaction of Lewis bases with metal carbonyl complexes,[4,5] we have observed that pyridine can induce the disproportionation of $Fe(CO)_5$ to yield the new cluster $Fe_4(CO)_8(py)_4$ (**1**). The preliminary characterization of the latter has been communicated.[5b] Now we report a straightforward method to synthesize **1** along with the results of a new single-crystal diffraction study. The number of valence electrons (56) indicates an electron deficiency which has been examined by semiempirical calculations. Within this context we present a new graphical computer program that allows threedimensional plottings of single molecular orbitals, as a whole or as a composite by separated atomic orbitals (or their hybrids). For these features the program written by C.M. and D.M.P. has been named CACAO (computer aided composition of atomic orbitals).[6]

Results

Synthesis. A few iron carbonyl complexes containing direct metal-metal bonds with elements from groups 11, 12, and 14 are known.[7] These complexes can be easily prepared by addition of

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(4) Hieber, W. *Adv. Organomet. Chem.* **1970**, *8*, 1.
(5) (a) Fachinetti, G.; Fochi, G.; Funaioli, T. *J. Organomet. Chem.* **1986**, *301*, 91. (b) Fachinetti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F. *J. Chem. Soc. Chem. Comm.* **1987**, 89. (c) Fachinetti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 680. (d) Fachinetti, G.; Funaioli, T.; Marcucci, M. *J. Organomet. Chem.* Submitted for publication.
(6) Mealli, C.; Proserpio, D. M. To be submitted for publication.
(7) Shriver, D. F.; Whitmire, K. H. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 4, pp 306-311.

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