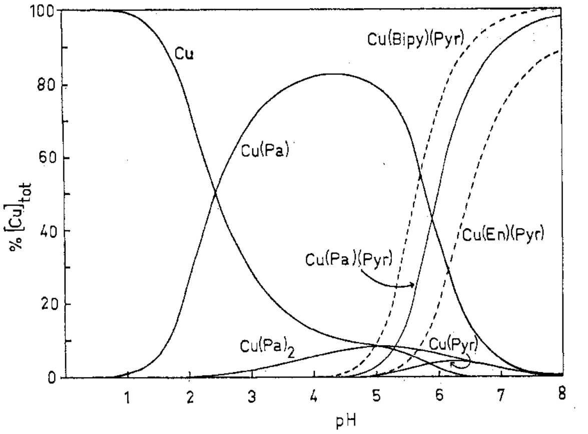

Figure 1.—Variation with pH of the concentrations (given as the percentage of the total Cu^{2+} present) of the several species present in an aqueous solution of Cu^{2+}, 2-picolylamine (pa), and pyrocatecholate (pyr) (each 10^{-3} *M*); $Cu(pyr)_2$ is less than 0.4% at pH <8. For comparison the concentration of the ternary complex in the systems containing 2,2′-bipyridyl (bipy) or ethylenediamine (en) instead of 2-picolylamine is also given (dashed lines). All data were computed with the constants given in Tables I and II.

catecholate complex (*cf.* Table II) is about 1.3 log units[2] greater than that of the ethylenediamine–Cu^{2+}–oxalate system.[16] This suggests that in complexes like 2,2′-bipyridyl–Cu^{2+}–pyrocatecholate a cooperative effect may occur between the π systems of the two ligands bound to the same Cu^{2+}.[18]

As an example, the concentrations of the several species present in the ternary system 2-picolylamine–Cu^{2+}–pyrocatecholate are given in Figure 1. At higher pH values the concentration of the mixed complex dominates strongly and all concentrations tend to approach limiting values. Of special interest is a comparison between the mentioned system and the formation of the ternary complexes containing 2,2′-bipyridyl or ethylenediamine (dashed lines) instead of 2-picolylamine. This evidently demonstrates the larger stability of the ternary 2,2′-bipyridyl–Cu^{2+}–pyrocatecholate complex, as this one is formed in the lowest pH range and reaches the highest concentration.

One of the main conclusions from this investigation is that not only the pyridyl but also the imidazole group has a stability-increasing effect on the formation of ternary Cu^{2+} complexes with ligands containing O as donor atoms. In this connection it is of interest to note the observation of Girotti and Breslow[19] that copper(II) acetate is bound more firmly to ribonuclease than Cu^{2+} and at least some of the binding sites offered by ribonuclease are imidazole groups. Considering this example, it can be hoped that by further systematic studies of mixed-ligand complexes at least in part an answer may be found to the question:[20] What are the control mechanisms that determine the coordination and coordination tendency of metal ions in biological systems?

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The Influence of π-Bonding Ligands upon the Properties of an Associated Ethylenediamine Ligand[1]

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The influence of certain π-bonding ligands upon (a) the acidity of an associated σ-bonding ethylenediamine ligand and (b) ligand lability in complexes of platinum(II) is evaluated *via* deprotonation reactions and nmr and tga data.

It has been known for some time that stability in coordinated ethylenediamine increases with increase in the charge on the transitional metal ion about which the ligand is coordinated.[2,3] More recently it has been shown that, while $[Pt(en)_2]I_2$ and its Pd analog are not deprotonated by the relatively weakly basic ammonia molecule, introduction of one bipy ligand enhances the acidity of the remaining en ligand.[4,5] Accordingly, it was of interest to investigate the effect of other π-bonding or potentially π-bonding ligands upon proton lability in an associated en ligand.

Experimental Section

Unless otherwise indicated, all experimental methods, including analytical procedures, were the same as those described in recent publications from this laboratory.[3,4,6] All of the platinum(II) complexes employed in this work were prepared and characterized as described elsewhere.[7]

Although most of the reactions reported here were carried out in liquid ammonia at or below −33.5°, it was necessary in some cases to expose the complexes to liquid ammonia at higher temperatures. For this purpose a modified Soxhlet-type extractor was employed and a typical procedure was as follows. A small sample (0.8–0.9 g) of the complex in an extraction thimble was placed in the extractor and the system was evacuated for >8

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(1) Abbreviations: 2,2′-bipyridine, bipy; pyridine, py; 1,2-bis(diphenylarsine)ethane, EDA; 1,2-bis(diphenylphosphine)ethane, EDP; ethylenediamine, en; en minus *n* protons, en-*n*H; diethylenetriamine, dien; *N*,*N*-dimethylethylenediamine, udmen; *N*,*N*′-dimethylethylenediamine, sdmen; *N*,*N*,*N*′-trimethylethylenediamine, tmen; 1,2-dicyanoethylene-1,2-dithiolato ion, MNT; 1,10-phenanthroline, phen.

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TABLE I
REACTIONS WITH POTASSIUM AMIDE

Complex	KNH_2: complex mole ratio	n (en-nH)	Anal. of deprotonated product, %					
			Calcd			Found		
			Pt	C	H	Pt	C	H
$[Pt(phen)(en)]I_2$	1:1	1	34.8	29.9	2.69	34.1	29.7	2.86
	2:1	2(?)[a]	45.0	38.8	3.26	41.8	34.6	4.14
	3:1[b]	2(?)	45.0	38.8	3.26	...	34.3	3.51
$[Pt((C_6H_5)_3P)_2(en)]I_2$	1:1	1	21.5	50.4	4.11	21.6	49.7	4.54
	2:1[c]	2	...	58.7	4.66	...	58.7	4.53
$[Pt(EDP)(en)]Br_2$	1:1	1	26.6[d]	...	...	26.7	...	...
	2:1	2	29.9	51.6	4.60[e]	29.8	51.2	4.40
$[Pt(EDA)(en)]Br_2$	1:1	1	23.8[f]	...	...	23.8	...	...
	2:1	2	26.4[g]	...	...	27.1	...	...
Pt(MNT)(en)	1:1[h]	1	...	16.6	1.61[i]	...	17.1	2.15
	2:1[h]	2	...	15.2	1.26[j]	...	15.0	2.04

[a] A sample from an independent experiment was found to contain 12.4% I. Since [Pt(phen)(en-H)]I contains 22.6% I, it follows that deprotonation in this experiment proceeded well beyond the removal of one proton. [b] A similar reaction employing a 6:1 mole ratio gave a permanganate-colored solution from which insoluble products could not be isolated except by reversion to the starting material upon addition of NH_4I. [c] With a 6:1 mole ratio, the results were only slightly different from the 2:1 case. [d] Br analysis: calcd, 10.9; found, 10.4. [e] P analysis: calcd, 9.51; found, 9.37 [f] Calcd: N, 3.44; Br, 9.76. Found: N, 3.50; Br, 9.89. [g] As analysis: calcd, 20.3; found, 20.3. [h] The products in these cases were the anionic complexes K[Pt(MNT)(en-H)] and K_2[Pt(MNT)-(en-2H)], respectively. [i] N analysis: calcd, 12.9; found, 12.8. [j] N analysis: calcd, 11.8; found, 11.6.

hr, whereupon 5 ml of liquid ammonia was condensed in the boiler at −70°. The temperature was increased to initiate refluxing which was continued for the time intervals specified below. The solvent ammonia was evaporated under reduced pressure and the extractor was transferred to a drybox for removal of ammonia-soluble and ammonia-insoluble (if any) products which were examined as described below. During refluxing, the equilibrium temperature at the thimble was *ca.* 13° and the design of the extractor[8] was such that extractions could be extended over 2 weeks without appreciable loss of ammonia.

Reactions with Ammonia. $[Pt(bipy)(en)]I_2$.—After exposure to liquid ammonia for 144 hr, the soluble product was the bright yellow starting material. The insoluble fraction consisted of dark red needlelike crystals. *Anal.* Calcd for $[Pt(bipy)(en)]I_2$ + [Pt(bipy)(en-H)]I (1:1): Pt, 32.4; C, 24.2; H, 2.62. Found: Pt, 32.4; C, 24.7; H, 3.05. X-Ray diffraction data (d spacings in ångströms, relative intensities in parentheses): 9.66 (1.0), 4.91 (0.4), 3.70 (0.4), 3.35 (0.2), 3.11 (0.2).

$[Pt(phen)(en)]I_2$.—After 100 hr, the ammonia-soluble extract consisted of a dark purple solid. *Anal.* Calcd for $[Pt(phen)(en)]I_2$ + NH_4I (1:1): Pt, 23.4; C, 20.1; H, 2.41; N, 8.40. Found: Pt, 23.0; C, 18.9; H, 2.58; N, 8.30. The presence of NH_4I was confirmed *via* an X-ray diffraction pattern; the purple solid did not react with hydrochloric acid.

A greenish brown solid remained in the thimble. *Anal.* Calcd for $[Pt(phen)(en)]I_2$ + [Pt(phen)(en-H)]I (1:2): Pt, 32.4; C, 27.0; H, 2.56. Found: Pt, 32.3; C, 27.9; H, 2.84. A 0.0766-g sample was reprotonated in 35.0 ml of 0.0499 N HCl; 30.0 ml of 0.05512 N NaOH was required to neutralize the excess HCl as compared with 30.1 ml calculated on the assumption of an equivalent weight of 906 for the mixture.

$[Pt((C_6H_5)_3P)_2(en)]I_2$.—Following extraction for 70 hr, the ammonia-soluble extract was a white solid which turned yellow when dry; both analytical and X-ray diffraction data were inconclusive.

The ammonia-insoluble product in the thimble was white. *Anal.* Calcd for $[Pt_2((C_6H_5)_3P)_4(en)I_2]$: Pt, 22.3; C, 50.7; H, 3.91; N, 1.60; I, 14.5; P, 7.07. Found: Pt, 22.2; C, 50.7; H, 3.99; N, 1.57; I, 14.5; P, 6.92. X-Ray diffraction data: 10.7 (1.0), 9.20 (0.4), 8.42 (0.5), 5.55 (0.5), 4.04 (0.4); *cf.* ref 7.

$[Pt((C_6H_5)_3P)(en)I]I$.—Extraction for 84 hr resulted in complete dissolution followed by separation of yellow crystals. *Anal.* Calcd for $[Pt((C_6H_5)_3P)(en)I]I$: Pt, 25.3; C, 31.1; H, 3.00. Found: Pt, 25.6; C, 31.6; H, 3.06.

$[Pt(EDP)(en)]Br_2$.—As above, only a yellow ammonia-soluble fraction resulted. *Anal.* Calcd for $[Pt(EDP)(en)]Br_2$: C, 41.3; H, 3.96; N, 3.44. Found: C, 41.4; H, 4.12; N, 3.53.

$[Pt(EDA)(en)]Br_2$.—Extraction for 10 hr resulted in complete dissolution followed by separation of colorless crystals. *Anal.* Calcd for $[Pt(EDA)(en)]Br_2 \cdot 1.5NH_3$: Pt, 21.0; Br, 17.3; N, 5.27. Found: Pt, 20.0; Br, 17.4; N, 5.34. The same results were obtained upon exposure to liquid ammonia for 2 hr at −60°; unchanged starting material was identified by both analytical and X-ray diffraction data.

Pt(MNT)(en).—Over 8 hr the sample dissolved completely to form a dark red solution from which a greenish yellow solid was recovered. *Anal.* Calcd for Pt(MNT)(en): Pt, 49.3; C, 18.2; H, 2.02; N, 14.2; S, 16.2. Found: Pt, 48.7; C, 18.0; H, 2.02; N, 14.3; S, 16.0. The X-ray diffraction pattern was identical with that for the starting material.

Reactions with Potassium Amide.—These were carried out at or below −33.5° in equipment described[9] and used[3,4,6] previously. A small sample of each complex listed in Table I (0.90–1.8 g) and potassium sufficient to provide KNH_2 slightly in excess of the mole ratios listed were placed in the appropriate containers and the reactor was heated at 100° under reduced pressure for at least 1 hr. Liquid ammonia (*ca.* 15 ml) was condensed on the complex and *ca.* 10 ml on the potassium (at −60°) which was converted to KNH_2 with an Fe catalyst. Slowly and with stirring the amide solution was added to the solution and/or suspension of the complex. If a solid phase resulted, it was filtered and washed with at least three 10-ml portions of ammonia; the combined filtrate and washings were collected in a trap from which the solvent was evaporated. The entire system was evacuated to remove residual ammonia prior to transfer of the equipment to a drybox for removal of samples of both the soluble and insoluble products. Elemental analysis and/or X-ray diffraction data were used to identify by-product (soluble) KI (or KBr) and any unreacted starting materials, the latter by comparison with diffraction data recorded elsewhere.[7]

Of the deprotonated complexes reported here, only [Pt(phen)-(en-H)]I gave a satisfactory X-ray diffraction pattern; the data (as above) are: 9.87 (1.0), 8.58 (0.5), 7.28 (0.5), 5.48 (0.2), 3.83 (0.8), 3.44 (0.7). (Similar data for [Pt(bipy)(en-H)]I were reported earlier.[4]) Comparison of these data with those for the corresponding parent complexes reflects the effect of deprotonation. In all other cases reported here, the deprotonated species were either opaque to X-rays or the patterns were too faint to permit indexing.

The species [Pt(phen)(en-H)]I, $[Pt((C_6H_5)_3P)_2(en\text{-}H)]I$, and $Pt((C_6H_5)_3P)(en\text{-}2H)$ were reprotonated by treatment with aqueous HI to afford the parent complex which was identified by analytical and X-ray diffraction data.[8] Reprotonation of [Pt-(EDA)(en-H)]Br with HBr was circumvented by separation of the very insoluble $Pt(EDA)Br_2$ which was identified in the same ways. In all other cases, efforts to reprotonate were unsuccessful.

The complex $[Pt((C_6H_5)_3P)_2(en\text{-}2H)]$ was methylated with methyl iodide over 5 days at 25° in the manner previously described[4] to form a dark orange solid. *Anal.* Calcd for $[Pt((C_6H_5)_3P)_2(sdmen)]I_2$: Pt, 18.4; C, 45.2; H, 3.97; N, 2.64. Found: Pt, 17.5; C, 46.5; H, 4.25; N, 2.60. X-Ray diffrac-

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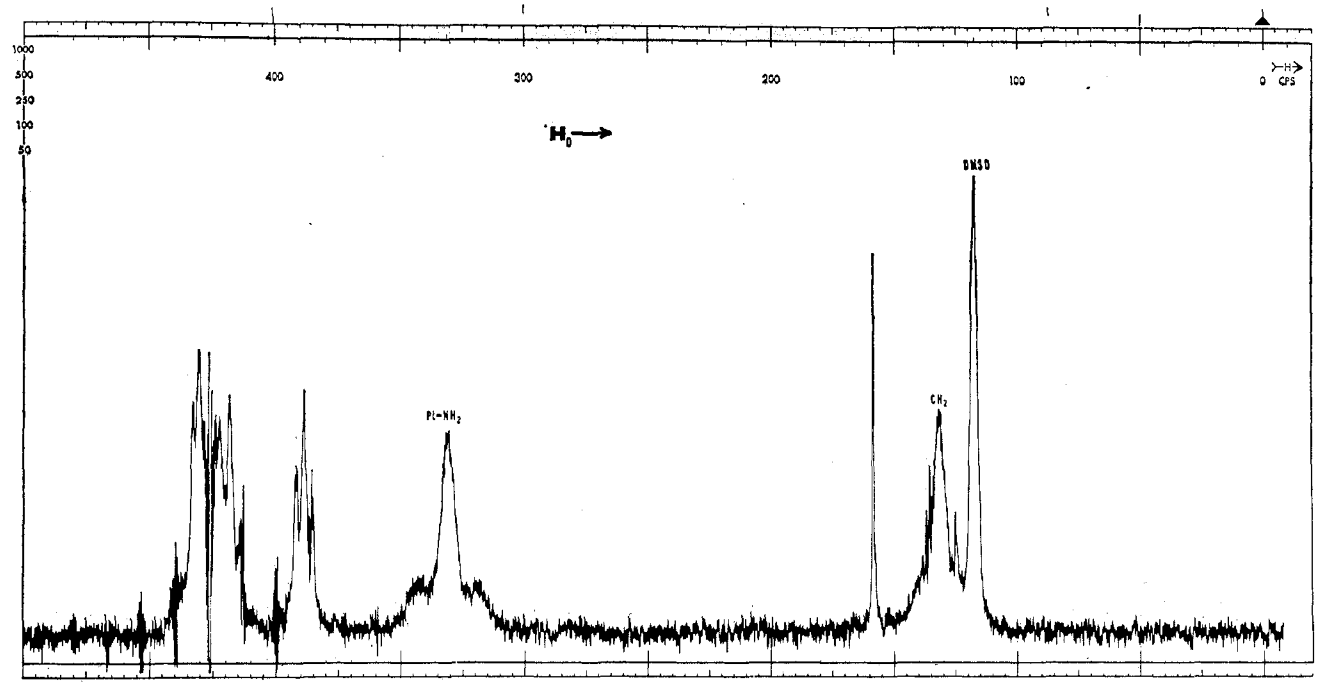

Figure 1.—The ^{1}H nmr spectrum of [Pt(phen)(en)]I_2.

tion data: 10.1 (0.8), 8.71 (1.0), 7.59 (0.8), 6.04 (0.2), 4.55 (0.5), 3.82 (0.4).

Nmr Spectra.—The proton nmr spectra of several ethylenediamine complexes of platinum(II) were obtained with a Varian HA-100 spectrometer and a 100-Mc oscillator as follows. Samples (0.05–0.06 g) of the complexes were dissolved in 0.5 ml of dry deuterated dimethyl sulfoxide (DMSO-*d*) in sample tubes in the drybox. If the complex did not contain aromatic hydrogens, 2 drops of benzene was added as the lock signal; a typical spectrum is shown in Figure 1. The amine proton chemical shifts were measured downfield from the DMSO peak owing to the 0.5% nondeuterated species present; these are listed in Table II. Complexes of [Pt(bipy)(en)]I_2 and Pt(en)$(SCN)_2$ in which the amine protons had been substituted by deuterium were examined to verify the assignment of the nitrogen proton peak.

TABLE II

CHEMICAL SHIFTS (PPM) OF AMINE PROTONS IN ETHYLENEDIAMINE COMPLEXES OF PLATINUM(II)

Complex	δ	Complex	δ
[Pt($(C_6H_5)_3P)_2$(en)]I_2	2.64	Pt(en)Br_2[b]	3.45[c]
[Pt($(C_6H_5)_3P$)(en)I]I	2.81[a]	[Pt(EDP)(en)]Br_2	3.45
Pt(udmen)$(SCN)_2$	2.81	Pt(sdmen)$(SCN)_2$	3.45
Pt$(en)_2I_2$	2.94	Pt(tmen)$(SCN)_2$	3.50
Pt(en)$(SCN)_2$	2.99	[Pt(EDA)(en)]Br_2	3.98
Pt(MNT)(en)	3.08	[Pt(bipy)(en)]I_2	4.27
Pt(en)$(NO_2)_2$	3.23	[Pt(phen)(en)]I_2	4.48

[a] δ′ 3.13. [b] Species originally placed in solution. [c] δ′ 3.77.

Thermogravimetric Analysis.—Thermal decomposition data were obtained[10] with a Stone TGA-3A instrument using samples mixed with Al_2O_3 at 25 mm in N_2 flow at 25 cm³/min and a heating rate of 10°/min; weight loss was recorded on both strip charts and an X-Y recorder (Figure 2).

To support the validity of conclusions based on tga data, [Pt(EDP)(en)]Br_2 was decomposed in a mass spectrometer which showed that the first decomposition product was en; a spectrum of en alone was used for comparison.

Discussion

The data given above show that the products of the interaction of [Pt(bipy)(en)]I_2 and NH_3 at −65 and 13° are not identical despite the fact that the elemental compositions are substantially the same.[4] The low-temperature product is a very finely divided brown-violet solid;[4] the product of reaction at 13° consists of long red needlelike crystals. Since the X-ray diffraction data for these two products are decidedly different, more detailed structural investigations will be undertaken. Substitution of phen for the bipy ligand results in much more extensive deprotonation of en by NH_3 but the analogous effect of $(C_6H_5)_3P$ ligands remains in doubt (*vide infra*). The EDP, EDA, and MNT ligands do not enhance the instability of en protons in the presence of liquid NH_3 at 13°.

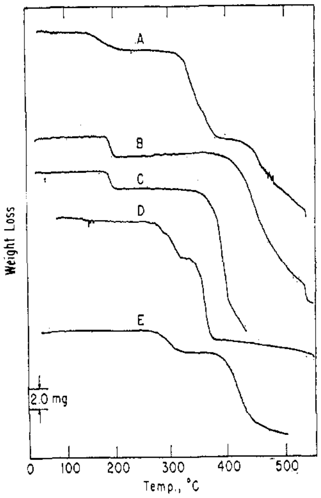

Figure 2.—Tga curves: (A) [Pt($(C_6H_5)_3P)_2$(en)]I_2; (B) [Pt(EDP)(en)]Br_2; (C) [Pt(EDA)(en)]Br_2; (D) [Pt(bipy)(en)]I_2; (E) [Pt(phen)(en)]I_2.

The interaction of [Pt($(C_6H_5)_3P)_2$(en)]I_2 and liquid NH_3 at 13° to provide $Pt_2((C_6H_5)_3P)_4(en)I_2$, a presumably binuclear complex, is of particular interest. This product is in some respects similar to the compound $Pt_2((C_6H_5)_3P)_2(N_2H_4)_2I_4$ reported by Malatesta and

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(10) Courtesy of Mr. David DeBerry, Tracor, Inc., Austin, Texas.

Cariello.[11] Correctness of the formulation of the product reported here seems unquestionable since summation of total elemental analysis amounts to 99.88%. Formulation as $Pt_2((C_6H_5)_3P_4(\text{en-2H})I_2$ cannot be ruled out and is attractive since it is compatible with the stoichiometry

$$2[Pt((C_6H_5)_3P)_2(en)]I_2 \longrightarrow Pt_2((C_6H_5)_3P)_4(\text{en-2H})I_2 + en \cdot 2HI$$

Contrary arguments however reside in the failure to detect en·2HI in the ammonia-soluble reaction product and the failure of $[Pt((C_6H_5)_3P)(en)I]I$ to react with NH_3 under the same conditions. The ammonia-insoluble product is currently the subject of more extensive chemical and structural investigations.

With the single exception of $[Pt(phen)(en)]I_2$, successive deprotonation of all of the mixed-ligand complexes examined *via* reaction with 1 and 2 molar equiv of the relatively strongly basic NH_2^- is shown by the data of Table I. There is no apparent reason for failure of uncomplicated removal of the second proton from $[Pt(phen)(\text{en-H})]I$. The species $Pt((C_6H_5)_3P)_2(\text{en-2H})$ was methylated to provide $[Pt((C_6H_5)_3P)_2(sdmen)]I_2$ to demonstrate that these deprotonated species behave as nucleophiles as reported previously for related cases.[4] More extensively deprotonated products could not be isolated and the deprotonations with NH_2^- in all cases were apparently uninfluenced by the identity of the ligand associated with en.

It was suggested earlier[2,3] that the lability of en protons is related to the strength of the Pt–N bond. Accordingly, the presence of a π-bonding ligand trans to en could result in charge transfer from ligand atom to metal ion, thus weakening the N–H bond. This amounts to a secondary trans effect[12,13] and is compatible with conclusions reached by Chatt, *et al.*,[14] by study of ν(N–H) in square-planar complexes of platinum(II). It is of interest to explore these views in relation to ir,[15] nmr, and tga data.

Because of the availability of infrared data, it is convenient to examine the influence of potentially π-bonding ligands upon ν(Pt–L) where L^- is a predominantly σ-bonding ligand, *e.g.*, Cl^-. The platinum–chlorine stretching frequencies (cm^{-1}) for a series of related complexes are as follows (symmetric and antisymmetric, respectively): $Pt(phen)Cl_2$, 355, 339; $Pt(bipy)Cl_2$, 351, 338; *cis*-$Pt(py)Cl_2$,[16] 343, 329; *cis*-$Pt((C_2H_5)_2S)_2Cl_2$,[16] 330, 318; *cis*-$Pt(NH_3)_2Cl_2$,[17] 324, 317; $Pt(EDA)Cl_2$, 320, 306; *cis*-$Pt((C_6H_5)_3P)_2Cl_2$, 316, 294; $Pt(EDP)Cl_2$, 314, 295; *cis*-$Pt((C_2H_5)_2As)_2Cl_2$,[18] 314, 287; $Pt(en)Cl_2$, 311, 290; *cis*-$Pt((C_2H_5)_3P)_2Cl_2$,[18] 305, 283. Notwithstanding the reservations implicit in correlating changes in vibrational frequencies with bond strengths,[19] the magnitude of the above frequency differences seems sufficient to warrant empirical correlations. Thus, one may establish the decreasing trans-influence[20] sequence: phen > bipy > py > $(C_2H_5)_2S$ > NH_3 > EDA > $(C_6H_5)_3P$ > EDP > $(C_2H_5)_3As$, en > $(C_2H_5)_3P$. Translation of this sequence to other σ-bonding ligands such as en seems justified by the chemical evidence presented herein. Thus, for complexes for which ν(Pt–N) data are available, the values recorded (cm^{-1}) are (symmetric only): $[Pt((C_6H_5)_3P)_2(en)]I_2$, 550; Pt(MNT)(en), 551; $[Pt(EDP)(en)]Br_2$, 558; $[Pt(EDA)(en)]Br_2$, 598; $[Pt(bipy)(en)]I_2$, 583; $[Pt(phen)(en)]I_2$, 582. These assignments are based upon previously reported data.[19,21] Where direct comparison is possible, these data conform to the trans-influence sequence given above.

To avoid concentration and solvent effects, the nmr data listed in Table II were all obtained using approximately the same concentrations of complex in DMSO. The concentration of the thiocyanate complexes was varied but the chemical shifts remained constant to ±0.05 ppm; also, use of the double-resonance technique[22] had virtually no effect upon the spectra and there was no evidence of complications arising from quadrapole broadening.[23] To ensure the validity of the assignment of the amine proton peak, samples of the SCN^- and phen complexes with en were synthesized in D_2O; the resulting spectra showed no evidence of the peak assigned to the amine proton. One of the complexes, $Pt(en)Br_2$, reacted *via* ligand substitution[8] of DMSO for one Br^-.[24,25] It can reasonably be assumed, for example, that the amine protons in the phen complex are considerably less shielded than those in the $(C_6H_5)_3P$ complex and that deshielding is attributable to a shift of electron density from N to Pt. Thus, the changes in chemical shifts seen in Table II should, and do, follow the trans-influence sequence given above.

Finally, if π-bonding ligands enhance the strength of the Pt–N bond and thus effectively labilize protons bonded to nitrogen, this should be reflected in the energy requirement for ligand dissociation. The tga data show loss of en at 155° for $[Pt((C_6H_5)_3P)(en)]I_2$, 190° for the EDP and EDA complexes, and 280° for bipy and phen. These results are in excellent agreement with the other lines of evidence presented here. It also seems noteworthy that, despite past emphasis on the π-bonding character of the $(C_6H_5)_3P$ ligand,[26,27] the data presented here indicate a predominantly σ-bonding role.

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