minimum for $\phi = 0°$. The pattern is similar to that noted by Keevoy[34] for vicinal $^{1}H-^{199}Hg$ couplings in a variety of Hg compounds.

Suggestions for Further Work. The conformation dependence of J_{Pt-H} in Pt–N–C–H fragments indicated by these data suggests further experiments, in addition to application to other ligands. A more thorough investigation of platinum complexes of other ligands of known geometry could be carried out to establish the dependence more precisely. In particular, the details of the dependence as ϕ approaches zero should be further investigated. Such investigations could also include complexes of other spin one-half nuclei (*e.g.*, ^{57}Fe, ^{89}Y, ^{103}Rh, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{113}Cd, ^{169}Tm, ^{171}Yb, ^{183}W, ^{203}Tl, ^{205}Tl, ^{207}Pb) to determine the generality of the phenomenon.

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The Secondary *trans* Effect in Platinum(II) Complexes[1]

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Abstract: Existence of a secondary *trans* effect in platinum(II) complexes has been established unequivocally by deprotonation and subsequent methylation of ions of the type $[Pt(dien)X]^+$ where $X^- = I^-$, CSN^-, and NO_2^-. The methylation of [Pt(dien-H)X] proceeds at differing rates which permits the ordering of the base strength of the deprotonated species as $I^- > SCN^- > NO_2^-$ for these ligands as X^-.

Palmer and Basolo[2] have reported results which suggested that the *trans* effect is observable not only in metal–ligand bonds but also in the bonding of atoms attached to a coordinated ligand atom. They measured two separate rates for the amine hydrogen exchange for ions of the general formula $[Pt(dien)X]^+$, where X = ligands with a single negative charge, and associated the faster rate with the hydrogen of the secondary amino group *trans* to the ligand X. It therefore became of interest to determine if this observed difference in exchange rates represented enough difference in actual chemical reactivity so that a selective deprotonation could be accomplished at a site on the coordinated diethylenetriamine that is normally less reactive than the four other possible reaction sites. To this end, ions of the same type as used by Palmer and Basolo were synthesized and treated with NH_2^- in liquid ammonia solution in an attempt to determine if such selective deprotonation could indeed be demonstrated. Such deprotonation would provide direct chemical evidence that a secondary *trans* effect does extend beyond the metal–ligand atom bond to atoms attached to the coordinated ligand atom.

Results and Discussion

Before attempting any deprotonation reactions, it was necessary to test the stability of $[Pt(dien)X]^+$ in liquid ammonia solution. As indicated in the Experimental Section, the ions were more soluble in NH_3 than in H_2O, and ammoniation occurred to produce $[Pt(dien)NH_3]^{2+}$ for $X^- = Cl^-$ and Br^-, while for $X^- = I^-$, NO_2^-, and SCN^- the complex could be recovered from solution unchanged. Inasmuch as the latter three ligands have approximately the same order and are two orders of magnitude greater than NH_3 for their *trans* effect,[3] only those ions containing I^-, NO_2^-, and SCN^- were suitable for deprotonation studies.

It was predicted[4] that the deprotonation site of [Pt(dien-H)X] could be established upon isolation of these compounds using infrared spectra as a diagnostic tool. Such, however, was not found to be the case as is evident from the spectra illustrated in Figure 1 along with the tentative assignments made in Table I. The latter were made empirically on the basis of the assignments previously made[4] for [Pd(dien)I] I since there was almost a 1:1 correlation between the spectra of the Pt and Pd complexes. Comparison of the spectra in Figures 1a and b suggests that the deprotonation occurred on the center nitrogen of dien since the two surviving peaks at 3180 and 3120 cm^{-1} correspond almost exactly to the $\nu(NH_2)$ peaks at 3200 and 3130 cm^{-1} in the starting compound. The broad, ill-defined nature of the NH_2 stretching bands in the deprotonated species precludes any unequivocal statement that the ν(NH) peak at 3070 cm^{-1} in the starting compound has disappeared. The out-of-plane deformation for the NH group at 1440 cm^{-1} in [Pt(dien)I] I might also have been obscured in the spectra of the deprotonated species, in this case by the general

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[1] Abbreviations used in this paper: dien, diethylenetriamine, where the nitrogens are designated N^1, N^2, and N^3; 2-mdien, N^2-methyldiethylenetriamine; 1-mdien, N^1-methyldiethylenetriamine; dien-H, diethylenetriamine from which a proton has been removed; n-mdien, methyldiethylenetriamine in which no specification is made as to the nitrogen to which the methyl group is bonded.

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Table I. Infrared Spectra in the 200–3800-Cm^{-1} Region for Diethylenetriamine Complexes of Platinum(II) Iodide

[Pt-(dien)I]I	[Pt(dien-H)I]	[Pt(n-mdien)I]I	[Pt(1-mdien)I]I	Tentative assignments
3450 w	3440 vs	3450 s	3450 w	ν(OH)
3200 vs	3180 vs	3200 vs	3240 s, sh	ν(NH$_2$)
3130 vs	3120 vs	3130 vs	3160 vs	ν(NH$_2$)
3070 vs		3080 vs	3100 vs	ν(NH)?
2960 w	2940 m, sh	2960 w	2970 w	ν(CH$_2$)
2880 m	2870 m	2880 m	2890 vw	ν(CH$_2$)
	1615 s	1630 w	1630 vw	δ(OH)
1590 vs	1580 s	1590 s	1580 m	δ(NH$_2$)
			1565 m	δ(NHCH$_3$)
1455 s	1450 s	1455 s	1460 s	δ(CH$_2$)
1440 w			1445 m	δ(NH)
1390 w	1380 s	1390 w	1395 w	ω(CH$_2$)
1353 w		1358 w	1358 w	ω(CH$_2$)
	1315 w	1315 m	1315 m	
1305 m	1305 w	1307 m	1305 w, sh	ω(NH$_2$)
1288 s		1288 m		γ(CH$_2$)
1257 w	1260 w	1260 s	1260 s	γ(CH$_2$)
	1170 m	1170 s	1170 s	
1155 s		1155 s		ω(NH$_2$)
1095 m		1095 s		ν(C–N)
1080 s		1077 s	1077 s	ν(C–C)
1057 m		1055 w	1043 s	ν(C–N)
1028 m		1035 s	1035 s	ν(C–C)
1005 m		1003 vw	1020 w	
995 s		993 vw		γ(NH$_2$)
		980 w	980 m	
		950 w	950 m	
925 m	930 vw	925 m		ν(C–N)
885 w	885 w	885 m	885 m	ρ(CH$_2$)
860 vw		860 vw		ρ(CH$_2$)
845 w	840 w	845 w	855 vw	ν(C–N)
763 vw		778 m	772 vs	ρ(NH$_2$)
710 vw		735 w	730 s	ρ(NH$_2$)
		610 w	610 m	
585 w		585 vw		ν(N′–Pt–N′)
		545 w	543 w	
520 w		520 w	515 w	ν(Pt–N″)
500 vw				
480 vw		475 w	475 w	δ(NCC)
393 w		393 vw		δ(NCC)
273 s		272 w		δ(N′–Pt–N′)
263 s		262 w	265 vw	δ(N′–Pt–N′)
230 s				

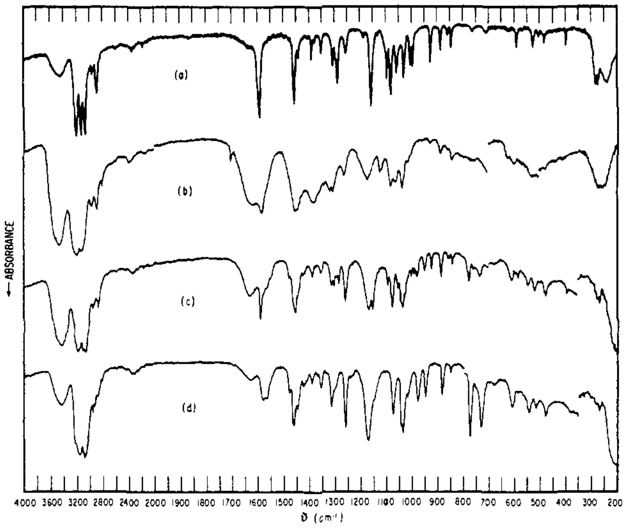

Figure 1. The infrared spectra of (a) [Pt(dien)I]I, (b) [Pt(dien-H)I], (c) [Pt(n-mdien)I]I, and (d) [Pt(1-mdien)I]I.

broadening of the δ(CH$_2$) band at 1450 cm^{-1}. Having failed to obtain clear physical evidence of the deprotonation site, [Pt(dien-H)I] was treated with CH$_3$I as described below to produce [Pt(n-mdien)I]I. Again, as can be seen from Figure 1c, the infrared spectrum failed to indicate clearly the position of the added –CH$_3$ group. An nmr spectrum was obtained for the methylated compound in an acid solution of D$_2$O, and a single peak was recorded which could be interpreted as due to a –CH$_3$ group bonded to an N atom not also bonded to H. However, owing to the low solubility of [Pt(n-mdien)I]I, the signal strength was not far enough above the noise level to rule out completely any splitting of the –CH$_3$ signal which would exist had H been bound to the same N atom. As a last resort, [Pt(1-mdien)I]I was synthesized independently and its infrared spectrum (Figure 1 d) compared with that of [Pt(n-mdien)I]I. Thus, conclusive evidence was obtained that the latter compound is in fact [Pt(2-mdien)I]I; *i.e.*, the –CH$_3$ group is on the center nitrogen of dien and deprotonation did therefore occur *trans* to the coordinated iodide ion. One has only to note the moderate δ(NH) peak at 1445 cm^{-1} and the split nature of the δ(NH$_2$) peak at 1565–1580 cm^{-1} in the spectrum of [Pt(1-mdien)I]I and compare these features with the corresponding features of the spectra of both the starting compound and the compound prepared by deprotonation and subsequent methylation to conclude that the methyl group of the latter is not attached to what was a primary amino group of dien. As indicated in Table I, it was reasoned that the δ (NHCH$_3$) vibrational mode at 1565 cm^{-1} was changed from the normal 1590 cm^{-1} for δ(NH$_2$) owing to the inertial effects of the added mass of the methyl group. In this connection, it may be noted that the remaining δ-(NH$_2$) mode was lowered also by some 10 cm^{-1} and broadened, which is attributable to some *trans*-coupling effect.

The secondary *trans* effect as suggested by the work of Palmer and Basolo[2] and confirmed here appears to be chemically significant. Because deprotonation of the center nitrogen of NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$ has only a 20% statistical chance of occurring and because the acidity of primary amines is some five to ten times that of secondary amines,[5] the selective deprotonation of the *trans* nitrogen as described herein is significant enough to indicate a major change in the bonding of coordinated dien as compared with that expected of the free ligand.

In addition to the finding which shows that a N–H bond has been weakened through the secondary *trans* effect, the experimental data below also indicate that the resultant Lewis base [Pt(dien-H)X] varies in strength depending in the ligand X. It was qualitatively determined that the rate of reaction with the Lewis acid, CH$_3^+$, was I$^-$ > SCN$^-$ > NO$_2^-$. It is of interest to note that this is identical with the order for the rates of reactions found when the same ligands are replaced from [Pt(dien)X]$^+$ by pyridine.[6] It may reasonably be presumed that [Pt(dien-H)I] is a stronger base than [Pt-(dien-H)SCN], etc., owing to the higher rate of reaction with CH$_3$I, but the correlation between base strength and the relative *trans* effect of I$^-$, SCN$^-$, and NO$_2^-$ is more difficult to deduce. Simple polarization arguments lead to the conclusion that I$^-$ has less over-all *trans* effect than the other two ligands, but it is by no

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(5) C. R. Noller, "Chemistry of Organic Compounds," 3rd ed, W. B. Saunders Co., Philadelphia, Pa., 1965, pp 258, 989.

(6) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82,** 4200 (1960).

means clear that this is so. If a consistent correlation is found between the secondary *trans* effect as observed here and the over-all *trans* effect with other, more extreme examples of ligands, the secondary effect may provide a means to estimate the relative magnitudes of the σ and π contributions to the over-all *trans* effect for those ligands which owe their *trans*-labilizing ability to a combination of these effects.

Experimental Section

A part of the synthetic procedures used is reported below; other procedures related to this investigation have been described elsewhere.[7]

Materials and Methods. With the exceptions that are noted below or previously described,[3] all materials used were reagent grade chemicals that were used without further purification. Experimental methods for carrying out reactions in liquid ammonia, purification, and handling of the resulting air-sensitive products and physical measurements thereon were the same as those described or referred to earlier.[8] The most intense lines in the X-ray diffraction patterns of both starting materials and products are listed (*d* spacings in ångström units) with relative intensities (in parentheses) immediately following analytical data.

Iodo(N^1-methyldiethylenetriamine)platinum(II) iodide was prepared in the same fashion as described previously[3] for the preparation of [Pt(dien)I]I. The ligand N^1-methyldiethylenetriamine (1-mdien) was obtained by custom synthesis from K & K Rare and Fine Chemicals, Plainview, N. Y., and was used without further purification. To 10 mmoles (4.67 g) of $PtI_2 \cdot H_2O$ was added 10 mmoles (estimated 1.2 ml) of N^1-methyldiethylenetriamine and the resultant mixture baked to dryness. Extraction of the product with hot water gave a yield of 4.85 mmoles.

Anal. Calcd for [Pt(1-mdien)I]I: Pt, 34.46; I, 44.83. Found: Pt, 34.30; I, 44.00. X-Ray diffraction data were 7.08 (0.7), 4.87 (0.5), 2.32 (1.0).

Bromo(diethylenetriamine)platinum(II) bromide was prepared both as described previously[9] and by addition of 8.0 mmoles (1.0 g) of KBr to a solution of 4.0 mmoles (1.48 g) of [Pt(dien)Cl]Cl in 10 ml of water.[3] A fine, crystalline solid precipitated immediately but proved to be impure. Purification was accomplished by redissolving it in 50 ml of warm (50°) water containing 1 g of KBr and evaporating at 50° until crystals appeared. Chilling to 5° produced long, yellow, needle crystals which were filtered, washed with ice water, and dried in air. Evaporation of the filtrate produced additional product for a total yield of 3.22 mmoles (1.47 g) or 80% based on Pt. This product had an infrared spectrum and X-ray diffraction pattern identical with those for the product produced by the method of Mann.[5] *Anal.* Calcd for [Pt(dien)Br]Br: Pt, 42.59. Found: Pt, 42.82. X-Ray diffraction data were 6.68 (0.3), 6.21 (0.3), 4.75 (0.3), 4.64 (0.3), 4.38 (0.3), 3.81 (1.0), 3.44 (0.3), 3.24 (0.3), 2.74 (0.6), 2.15 (0.6).

Thiocyanato(diethylenetriamine)platinum(II) thiocyanate was synthesized by adding an excess (12.0 mmoles, 1.2 g) of KSCN to a solution of 4.0 mmoles (1.48 g) of [Pt(dien)Cl]Cl in 10 ml of water and evaporating to 7 ml which caused the appearance of a few crystals. Chilling to 5° overnight, filtering, and washing with two 5-ml portions of ice water produced 1.02 g of yellow crystals for a total yield of 62% based on Pt. *Anal.* Calcd for [Pt(dien)SCN]SCN: Pt, 47.08. Found: Pt, 47.06. X-Ray diffraction data were 8.00 (0.7), 7.53 (0.7), 6.51 (0.5), 5.90 (1.0), 5.55 (0.5), 5.26 (0.5), 4.65 (0.8), 4.44 (0.5), 4.08 (0.7), 3.57 (0.5), 3.32 (0.8), 3.08 (0.6).

Thiocyanato(diethylenetriamine)platinum(II) iodide was prepared by stirring 4.0 mmoles (2.21 g) of [Pt(dien)I]I in 100 ml of water at 90° and then adding 8.0 mmoles (0.8 g) of KSCN. Addition of the KSCN caused a few remaining crystals of the iodide to dissolve and intensified the color of the solution to a darker yellow. Evaporation of the hot solution to 25 ml caused crystals to appear and chilling to 5° for 6 hr produced yellow-orange needle crystals which were filtered and washed with ice water; the filtrate and washings were evaporated again to produce additional crystals. The total yield after drying *in vacuo* was 1.74 g (3.6 mmoles) or 90% based on Pt. *Anal.* Calcd for [Pt(dien)SCN]I: Pt, 40.37. Found: Pt, 40.49. X-Ray diffraction data were 7.25 (1.0), 5.71 (1.0), 4.63 (1.0), 4.50 (1.0), 4.33 (1.0), 3.77 (0.5), 3.68 (0.5), 3.50 (0.5), 3.34 (1.0), 3.15 (1.0), 2.25 (0.5), 2.18 (0.5), 2.15 (0.5).

Nitro(diethylenetriamine)platinum(II) iodide was prepared almost as above by adding an excess (12 mmoles, 0.83 g) of $NaNO_2$ to 4.0 mmoles (2.21 g) of [Pt(dien)I]I in 100 ml of hot water. In this case the color of the solution changed from a medium to a very pale yellow and long (up to 3 cm), golden-yellow, needle crystals were produced. After washing with ice water and drying *in vacuo*, 1.70 g (3.61 mmoles) of product was obtained for a total yield of 90.5% based on Pt. *Anal.* Calcd for $[Pt(dien)NO_2]I$: Pt, 41.41; C, 10.20; H, 2.78. Found: Pt, 41.14; C, 10.20; H, 2.94. X-Ray diffraction data were 9.93 (0.4), 8.15 (0.5), 5.34 (0.4), 4.69 (0.8), 4.48 (1.0), 3.64 (0.4), 3.45 (0.5), 3.01 (0.4), 2.86 (0.5), 2.76 (0.4), 2.57 (0.4), 2.08 (0.4).

Deprotonation and Methylation. To determine whether the dien complexes were altered upon exposure to liquid ammonia, samples of [Pt(dien)I]I, [Pt(dien)SCN]SCN, [Pt(dien)SCN]I, and $[Pt(dien)NO_2]I$ were dissolved in liquid ammonia at −70° (*ca.* 1 g of complex in 5 ml of solvent) to form yellow solutions. In all cases, solubility of the compounds in NH_3 exceeded their solubility in H_2O. Upon evaporation of the solvent all four complexes were recovered unchanged as evidence by their infrared spectra and X-ray diffraction patterns. When, however, yellow [Pt(dien)Cl]Cl and [Pt(dien)Br]Br were dissolved in ammonia, the solutions were colorless and the solids recovered upon evaporation of the solvent were white. *Anal.* Calcd for $[Pt(dien)NH_3]Cl_2$: Pt, 50.52. Found: Pt, 50.77. X-Ray diffraction data were 6.96 (1.0), 4.19 (0.6), 3.70 (0.6), 3.43 (0.5). Calcd for $[Pt(dien)NH_3]Br_2$: Pt, 42.59. Found: Pt, 42.82. X-Ray diffraction data were 7.05 (1.0), 4.32 (0.8), 3.80 (0.8), 3.50 (0.8).

Deprotonation of [Pt(dien)I]I, $[Pt(dien)NO_2]I$, and [Pt(dien)SCN]I was accomplished by dissolving 10 mmoles (4.71–5.52 g) of the compound in 20–25 ml of anhydrous liquid ammonia at −33° and then adding 10 mmoles of KNH_2 dissolved in 20 ml of NH_3. Addition of the amide immediately produced pale yellow precipitates. The solvent was separated by filtration and the solid washed with two 10-ml portions of liquid NH_3 to remove any traces of KI. *Anal.* Calcd for [Pt(dien-H)I]: Pt, 46.00. Found: Pt, 45.62. Calcd for $[Pt(dien\text{-}H)NO_2]$: Pt, 56.84. Found: Pt, 56.39. Calcd for [Pt(dien-H)SCN]: Pt, 54.93. Found: Pt, 54.32.

Methylation of [Pt(dien-H)I] was accomplished by condensing 15 ml of CH_3I into a cold (−50°), evacuated reactor containing *ca.* 5 mmoles (2.1 g) of the deprotonated species, allowing the system to warm to 25°, and stirring the mixture continuously. After 24 hr, the excess CH_3I was removed by filtration and the product dried *in vacuo*. *Anal.* Calcd for [Pt(n-mdien)I]I: Pt, 34.46; C, 10.61; H, 2.67. Found: Pt, 34.11; C, 10.48; H, 2.88. X-Ray diffraction data were 4.73 (1.0), 3.58 (0.5).

Methylation of $[Pt(dien\text{-}H)NO_2]$ and [Pt(dien-H)SCN] was done in much the same fashion as described above except that the reaction proceeded more slowly and equilibrium mixtures of the deprotonated and methylated species appeared to have been produced. A satisfactory platinum analysis was obtained only after purification by recrystallization of the product from methanol. *Anal.* Calcd for $[Pt(n\text{-}mdien)NO_2]I$: Pt, 40.21. Found: Pt, after 1 day, 50.64; after 2 days, 46.33; after 1 week, 44.40; after 1 week and recrystallization, 40.31. X-Ray diffraction data were 6.80 (1.0), 5.75 (0.5), 4.46 (1.0), 4.11 (0.8). Calcd for [Pt(n-mdien)SCN]I: Pt, 39.23. Found: Pt, after 1 day, 41.48; after 3 days, 40.18; after 3 days and recrystallization, 38.60. X-Ray diffraction data were 6.17 (1.0), 6.00 (0.5), 3.08 (0.5), 2.32 (0.5).

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