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Use of Nuclear Magnetic Resonance Contact Shifts to Study the Stability of Paramagnetic Coordination Complexes. Bis(2,4-pentanedionato)nickel(II) Complexes of Substituted Anilines[1]

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The use of nuclear magnetic resonance contact shifts of ligands in paramagnetic coordination complexes to measure relative stability constants for the complexes is demonstrated. Bis(2,4-pentanedionato)nickel(II) complexes of *meta-*, *para-*, and N-substituted anilines are investigated. The effects of *meta* and *para* substituents on the stability constants are well described by a blend of the inductive and resonance effect parameters σ_I and σ_R. N-Methylation decreases the stability of the complex. N-Methyl contact shifts are strongly dependent on the *meta* or *para* substituents and linearly related to the stability of the complex.

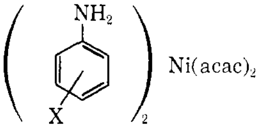
Introduction

The effects of structure variation within a family of ligands on the stability of their coordination complexes have long been of interest.[2] Accurate measurement of these effects has been difficult, however, since the difference methods generally employed have low sensitivity and methods allowing direct measurement have not been reported. This paper describes a direct method for measuring relative stability constants of paramagnetic coordination complexes which undergo facile ligand exchange, using the nuclear magnetic resonance contact shifts[3] of coordinated ligands.[4] Relative stability constants for a family of ligands coordinated to metal ion M are defined by eq 1, where L_0 is an arbitrarily selected reference ligand. When

$$n\mathrm{L}_0 + (\mathrm{L})_n\mathrm{M} \overset{K_m}{\rightleftharpoons} (\mathrm{L}_0)_n\mathrm{M} + n\mathrm{L} \qquad (1)$$

exchange rates for eq 1 are fast on the nmr time scale, chemical shifts for magnetic nuclei in L or L_0 are observed as the weighted average of their values in the free ligand, $\Delta\nu_f$, and the coordinated ligand, $\Delta\nu_c$. For diamagnetic complexes $\Delta\nu_f$ and $\Delta\nu_c$ are not very different and consequently the observed nmr spectra are only weakly dependent on the equilibrium position of eq 1. When the complexes are paramagnetic, however, electron–nuclear spin interactions cause large chemical shifts in $\Delta\nu_c$[3] with the result that the exchange-averaged chemical shifts are strongly dependent on and a sensitive measure of the equilibrium position.

Bis(2,4-pentanedionato)nickel(II) (hereafter $\mathrm{Ni(acac)_2}$) complexes of *meta-* and *para-*substituted anilines (1) and N-methylanilines (2) were selected to demonstrate this technique since the stability constants should vary systematically over a small range within the family and the stability of transition metal ion complexes of anilines has received little attention.[5] Additionally, the possible existence of precise contact shift–stability relationships for select ligand nuclei was of interest and the contact shifts for 1 and 2 were studied in this regard.



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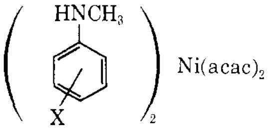

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Results

The nmr method requires knowledge of the limiting chemical shifts $\Delta\nu_f$ and $\Delta\nu_c$ for the substituted anilines in 1 and 2. If the free ligand resonance is taken as the chemical shift reference for each nucleus, then $\Delta\nu_f$ equals zero and $\Delta\nu_c$ is the nuclear contact shift. Contact shifts for 1 and 2 cannot be measured directly since the complexes dissociate in solution to give spectra which are exchange averaged between the free and coordinated ligand, but can be calculated from an analysis of the concentration dependence of the exchange-averaged chemical shifts of partially coordinated ligand.[6] $\mathrm{Ni(acac)_2}$ is trimeric in noncoordinating solvents[7] and forms 2:1 and 1:2 complexes with coordinating ligands.[8] In the presence of a large excess of ligand, however, the 2:1 pseudooctahedral complex should predominate, as in equilibrium

$${}^{1}/{}_{3}(\mathrm{Ni(acac)_2})_3 + 2\mathrm{L} \rightleftharpoons \mathrm{L_2Ni(acac)_2} \qquad (2)$$

2. Accordingly, when the $[\mathrm{Ni(acac)_2}]/[\text{aniline}]$ ratio is small enough and the equilibrium constant for eq 2 is large enough that essentially all of the $\mathrm{Ni(acac)_2}$ is coordinated as the 2:1 complex, the exchange-

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968; see Abstracts, No. PHYS 155.

[2] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, Inc., New York, N. Y., 1953, Chapter 4.

[3] For excellent discussions of the application of nmr to paramagnetic compounds see D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); E. deBoer and H. van Willigen in "Nuclear Magnetic Resonance Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Vol. 2, Pergamon Press, Ltd., London, 1967.

[4] D. Forster, K. Moedritzer, and J. R. Van Wazer, *Inorg. Chem.*, **7**, 1138 (1968), have obtained qualitative measures of ligand preferences using nmr contact shifts.

[5] W. S. Fyfe, *J. Chem. Soc.*, 2018 (1952); L. Armeanu and C. Luca, *Z. Physik. Chem.*, **214**, 81 (1960).

[6] R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965); **88**, 1399 (1966).

[7] F. A. Cotton and J. P. Fackler, *ibid.*, **83**, 2818 (1961).

[8] J. P. Fackler, *ibid.*, **84**, 24 (1962).

averaged chemical shift for any ligand nucleus, $\Delta\nu_n$, is related to the total $Ni(acac)_2$ trimer concentration in solution by eq 3, where $[L]_0$ is the initial ligand concentration.

$$\Delta\nu_n = \frac{6\Delta\nu_c}{[L]_0}[(Ni(acac)_2)_3] \qquad (3)$$

centration. Therefore, subject to these conditions, a plot of $\Delta\nu_n$ *vs.* the total concentration of $Ni(acac)_2$ trimer will be linear and pass through the origin, and the contact shift for ligand nuclei in the 2:1 complex, $\Delta\nu_c$, equals the slope divided by $6/[L]_0$.

Nmr spectra were obtained for 1.0 *M* CCl_4 or CH_2Cl_2 solutions of substituted anilines to which increments of $Ni(acac)_2$ were added so that the Ni:aniline mole ratio varied from 0 to 0.05. Plots of observed $\Delta\nu_n$ *vs.* $[(Ni(acac)_2)_3]$ were linear, as evidenced by the typical data plotted in Figure 1. The observation of linearity for these plots is most significant. First, it demonstrates that within the concentration range studied only one complex (most likely the 2:1 complex[9]) forms in significant amounts. An equilibrium involving simultaneous formation of both 2:1 and 1:2 complexes, which probably is important at larger $Ni(acac)_2$: aniline concentration ratios, would result in curved plots. Second, it confirms the applicability of eq 3. Therefore, limiting contact shifts (Tables I and II) can be calculated from the least-squares slopes. Identifying shifts calculated by eq 3 as pure contact shifts assumes the diamagnetic contribution to chemical shifts of nuclei in L is not changed significantly by coordination. Support for this assumption is provided by the finding that addition of $Zn(acac)_2$ to solutions of anilines to form diamagnetic coordination complexes, $L_2Zn(acac)_2$, does not significantly alter the ligand chemical shifts.

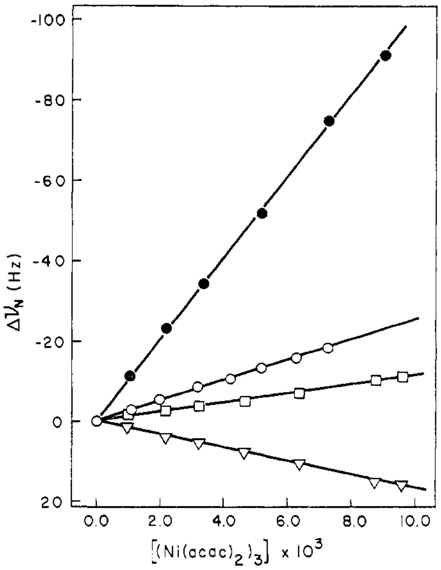

Figure 1.—Time-averaged chemical shifts of partially coordinated N-methyl-*p*-toluidine, 1.0 *M* in CCl_4, relative to the free ligand resonance, plotted *vs.* the bis(2,4-pentanedionato)nickel(II) trimer concentration: ●, N-methyl; ○, *p*-methyl; □, *meta*; ▽, *ortho*.

Table I

Limiting Contact Shifts for *meta*- and *para*-Substituted $HNCH_3C_6H_5$–$Ni(acac)_2$ Complexes (**2**)

	$\Delta\nu_c$,[a] Hz			
Substituent	N-CH_3[b]	*ortho*[c]	*meta*[c]	Substituent[b]
p-OCH_3	−1990	380	−200	. . .
p-CH_3	−1690	290	−180	−410
p-F	−1670	300	−180	−980
m-CH_3	−1670	. . .	. . .	140
H	−1530	. . .	−150	. . .
p-Cl	−1430	290	−170	. . .
m-OCH_3	−1320	. . .	. . .	. . .
m-Cl	−1320	. . .	. . .	. . .
m-NO_2	−860[d]	. . .	. . .	. . .
p-CO_2CH_3	−580[d]	*e*	*e*	. . .
p-CN	−150[d]	*e*	*e*	. . .

[a] Large positive shifts were also observed for N–H but not recorded. Contact shifts for individual aromatic protons in the *meta*-substituted compounds could not be resolved from the complex multiplet. [b] Uncertainty is 2%. [c] Uncertainty is 5%. [d] Estimate, uncertainty >5%. [e] Less than 50 Hz.

Table II

Limiting Contact Shifts for *para*-Substituted $NH_2C_6H_5$–$Ni(acac)_2$ Complexes (**1**)

	$\Delta\nu_c$, Hz		
Substituent	*ortho*[a]	*meta*[a]	Substituent[b]
p-OCH_3	990	−430	−90
p-CH_3	880	−420	−1040
p-F	1010	−400	. . .
H	. . .	−340	. . .
p-Cl	900	−390	. . .
p-CO_2CH_3	600	−250	. . .

[a] Uncertainty is 5%. [b] Uncertainty is 2%.

Slopes calculated for CH_3 resonances are in most cases uncertain to less than 2%, based on least-squares analysis, and are reproducible within this range. Slopes for the aromatic protons are more uncertain (~5%) owing to the difficulty of assigning resonance positions within the aromatic multiplet. Contact shifts calculated from these slopes are assumed to have the same level of uncertainty.

In experiments designed to measure relative stability constants, solutions of two ligands L and L_0 were treated with small amounts of $Ni(acac)_2$ and the concentration dependence of some appropriate probe nuclei in L_0 followed as before. Probe groups with distinct nuclear resonances are required; typically groups such as *p*-methyl or N-methyl were employed. The $Ni(acac)_2$ is partitioned between L and L_0 as described by equilibria 4 and 5, and the positions of the equilibria are determined from the ratio $\Delta\nu'/\Delta\nu_c$

$$L_0 + L_2Ni(acac)_2 \xrightleftharpoons{K_1} LL_0Ni(acac)_2 + L \qquad (4)$$

$$L_0 + LL_0Ni(acac)_2 \xrightleftharpoons{K_2} (L_0)_2Ni(acac)_2 + L \qquad (5)$$

observed for the probe nuclei. $\Delta\nu'$ is the limiting chemical shift calculated in this experiment using eq 3

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(9) A reviewer has questioned this assumption that only 2:1 complexes form significantly for all ligands in the concentration range studied. Results in Table III demonstrate, however, that for *p*-methyl- and *p*-methoxyaniline the complex is in fact of 2:1 stoichiometry and unreported experiments in which identical values of K_m for the competition between N-methylaniline and *p*-methylaniline are calculated from eq 7 using either *p*-methyl or N-methyl contact shifts demonstrate 2:1 stoichiometry for the ligand N-methylaniline. Therefore the only alternative to our assumption is the very unlikely situation that within the closely related family of ligands (*meta*- or *para*-substituted anilines or N-methylanilines) some members form exclusively 2:1 complexes while others form exclusively 1:2 complexes.

and $\Delta\nu_c$ is taken from Table I or II. The relationship between $\Delta\nu'/\Delta\nu_c$ and K_1 and K_2 given by eq 6 is derived using the reasonable approximation that the

$$\frac{\Delta\nu'}{\Delta\nu_c} = R = \frac{K_1K_2X^2 + (1/2)K_2X}{K_1K_2X^2 + K_1X + 1} \qquad (6)$$

concentration ratio $[L_0]/[L]$ remains essentially constant at its initial value, X. Therefore, measurement of R for two different values of X yields two equations which can be solved simultaneously for K_1 and K_2. The product K_1K_2 equals K_m, the relative stability constant for the net exchange equation, eq 1.

Simultaneous solution of eq 6 is not always possible in practice and it becomes desirable to calculate K_m from a single experiment. For instance, when L and L_0 are such that K_m is either much greater or less than unity, variations in X over the experimentally feasible range effect changes in R which are too small for accurate simultaneous solution of eq 6. When L and L_0 have similar structures, it is reasonable to expect that the propensity for L to replace L_0 is the same in both steps 4 and 5, and accordingly K_1 and K_2 differ only by the statistical factor 4 ($K_1 = 4K_2$). With this approximation eq 6 reduces to eq 7, which can be solved for K_2, and thus also K_1, with a single set of X and R. The

$$K_2^2(4X^2(1 - R)) + K_2(2X(1 - R)) - R = 0 \qquad (7)$$

correctness of this approximation was tested by considering p-methyl- and p-methoxyaniline as a typical pair of ligands and the results are shown in Table III.

TABLE III
STABILITY CONSTANTS FOR $Ni(acac)_2$ COMPLEXES OF p-METHOXYANILINE (L) RELATIVE TO p-METHYLANILINE (L_0)

X^a	R^b	K_1	K_2	K_m
1.0	0.349	1.07	0.27	0.29
2.0	0.523	1.09	0.27	0.30
3.0	0.610	1.04	0.26	0.27
...	...	1.11^c	0.25^c	0.28^c
...	...	1.02^d	0.29^d	0.30^d

[a] $X = [p\text{-methylaniline}]_0/[p\text{-methoxyaniline}]_0$. [b] R is defined in eq 6. [c] Calculated using eq 6 with $X = 1.0$ and $X = 3.0$. [d] Calculated using eq 6 with $X = 1.0$ and $X = 2.0$.

Two observations should be made. Data in the top three rows calculated using eq 7 are independent of the initial ligand concentrations and compare closely with the results in the bottom two rows which were calculated using the exact eq 6; and the ratio K_1/K_2 calculated by eq 6 is approximately 4. Therefore, the use of eq 7 is apparently justified for substituted anilines.[10] It should be noted that this finding supports the initial assumption that the complexes studied are of 2:1 stoichiometry. Relative stability constants for **1** and **2** were calculated with eq 7 and are tabulated in Table IV. R was calculated using the CH_3 resonance of p- or m-toluidine or N-methylaniline as probe. The data were then referenced to unsubstituted aniline.

TABLE IV
RELATIVE STABILITY CONSTANTS FOR (substituted aniline)$_2$Ni(acac)$_2$ COMPLEXES[a]

Substituent	Log K_m	Substituent	Log K_m
p-CH_3O	0.69	m-CH_3	0.14
p-F	0.27	m-CO_2CH_3	−0.35
p-CH_3	0.15	m-CH_3O	−0.38
H	(0.00)	m-Cl	−0.43
p-Cl	−0.20	m-F	−0.52
p-CO_2CH_3	−1.24	m-NO_2	−0.69
N-CH_3	−1.5		

[a] Uncertainty is less than 5%. Positive log K_m value indicates complex with substituted aniline is favored.

Discussion

The results of the test experiment recorded in Table III indicate that at least for these systems reliable relative stability constants can be obtained by the nmr technique. It is likely this technique will also be applicable to other paramagnetic transition metal ion complexes and in general to equilibria in which diamagnetic reactants are converted to paramagnetic products and the exchange rate between reactants and products is fast on the nmr time scale.[11] The technique is very sensitive when K_m is near unity since the contact shifts involved are large but becomes rapidly insensitive when $|RT \ln K_m|$ is large and R approaches zero or unity. Consequently, free energy differences can be reliably measured only in the range ±2 kcal/mol, although data outside this range can be accumulated in a stepwise fashion. Quantitative use of the nmr method requires derivation of an equation such as (6) relating K_m to the chemical shifts observed. This is simple for the complexes which contain only two labile ligands, but in general will be more difficult, although feasible, since complexes with n labile ligands require n equations analogous to (4) and (5) and an equation in n unknowns analogous to eq 6. Simplified equations similar to eq 7 can be derived, however, when the equilibrium constants K_1 through K_n can be demonstrated to differ only by statistical factors.

Results in Table IV demonstrate the effect of N-methylation and ring substitution on the stability of the complexes. The lower stability of the N-methyl complex likely results from strain due to the bulk of the methyl group. The effects of ring substituents are generally consistent with the role of aniline as a donor ligand; electron-donor groups stabilize and electron-withdrawing groups destabilize the complex. An attempted quantitative correlation of the data with the Hammett substituent parameters gave poor results, however.[12,13] Poor Hammett plots obtained for stability constants in other systems have been attributed

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(10) These findings also support an additional approximation used to derive eq 6 and 7 that contact shifts for the probe nuclei in the pure and mixed complexes of eq 4 and 5 are equal. Further support is provided by the low-temperature nmr of several analogous substituted pyridine complexes where exchange between pure and mixed complexes is slow and only one set of resonances is observed for the coordinated ligands.

(11) The studies of the equilibria between paramagnetic tetrahedral and diamagnetic planar nickel complexes (*e.g.*, D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963)) are another example.

(12) A value of 49 was found for the function of the standard deviation over the root mean square of the data as a percentage (sd/rms) while a value of 15 or less is generally considered indicative of a good fit.[13]

(13) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

to π bonding,[14] but π bonding in these complexes between nickel and quatenary nitrogen is not likely. The π-bond arguments have also been criticized on general grounds.[15] In an attempt to understand the poor Hammett correlation the notion[13,16] that the Hammett parameters are not an intrinsic measure of electronic substituent effects but rather a special composite of the more fundamental inductive and resonance effect parameters σ_I and σ_R was considered; possibly different blends of σ_I and σ_R apply for coordination complexes in aprotic solvents. The extended equation

$$^1/_2 \log K_m = \sigma_I \rho_I + \sigma_R \rho_R \qquad (8)$$

allows independent variation of the importance of inductive and resonance effects, as determined by ρ_I and ρ_R. ρ_I and ρ_R are determined separately for *meta* and *para* substituents, and the normalizing factor of $^1/_2$ is included because log K_m results from the effects of two substituents. A good correlation of log K_m is found with eq 8;[17] *meta* substituents exert nearly a pure inductive effect on log K_m while resonance interactions are most important for *para* substituents. While the reasons for these findings are not clear, they suggest a way of handling data which might lead to understanding as other systems are studied and trends become apparent.

Since nmr chemical shift–reactivity relationships have been reported for many diamagnetic reaction series, it was of interest to investigate whether ligand contact shifts paralleled the complex stability. The existence of such a relationship can be predicted. Nmr contact shifts are directly proportional to the unpaired spin density at the nucleus resulting from covalency in the metal–ligand bond.[3] Substituent effects of electronic origin which alter the bond stability should induce proportional changes in the bond covalency and consequently in the ligand contact shifts. However, contributions to the contact shift substituent effects arising from other mechanisms could ruin the simple relationship.[18] The contact shifts for **1** and **2** listed in Tables I and II are consistent with the shift ratios reported earlier for some of these compounds.[19] Substituent effects are observed for both aromatic and N-methyl nuclei, somewhat small for the aromatic protons but large for N-methyl, and the trend is as expected: the contact shifts are increased (in absolute value) by substituents which stabilize the complex and decreased by destabilizing substituents. The smaller aromatic shifts for **2** are also consistent with the destabilization caused by N-methylation. The N-methyl contact shifts are plotted *vs.* log K_m in Figure 2 and a single, good correlation is obtained for both *meta* and *para* substituents. Apparently for suitably designed systems ligand contact shifts obtained from simple nmr measurements reliably depict the effects of ligand structure variation on metal–ligand bond stabilities and should be considered as a technique for obtaining such information.

While this work was in progress there appeared a report[20] concerning substituent effects on exchange-averaged contact shifts of the formyl proton in Ni(acac)$_2$ complexes of *meta*- and *para*-substituted benzaldehydes. The substituent effect was interpreted as arising from differences in the stability constants of the complexes, the assumption being made that the limiting contact shift of the formyl proton was substituent independent. Our results suggest that this assumption may be incorrect and that both changes in the stability constant and the limiting shift contribute to the observed substituent effect.

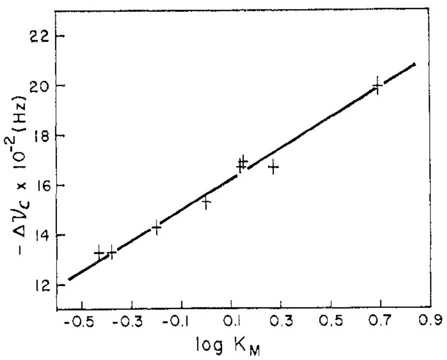

Figure 2.—N-Methyl contact shifts for *meta*- and *para*-substituted N-methylaniline complexes of Ni(acac)$_2$ plotted *vs.* log K_m of the corresponding aniline complex.

Experimental Section

Materials.—The majority of the anilines and several of the N-methylanilines were commercially available. *m*-Carbomethoxyaniline, mp 38–38.5, and *p*-carbomethoxy-N-methylaniline, mp 93–95° (lit.[21] mp 95.5°) were prepared by esterifying the corresponding benzoic acids with methanol and HCl. *p*-Chloro-N-methylaniline, bp 58° (0.4 mm) (lit.[22] bp 141–142° (40 mm)), *m*-chloro-N-methylaniline, bp 83–84° (2.3 mm) (lit.[23] bp 105° (10 mm)), and *p*-fluoro-N-methylaniline, bp 104° (14 mm), were prepared by the method of Roberts and Vogt.[22] *p*-N-Methylanisidine, bp 80–81° (1.0 mm) (lit.[24] bp 80–84° (0.2 mm)), and *m*-N-methylanisidine, bp 84° (1.2 mm) (lit.[25] bp 131° (17 mm)) were prepared by formylating the corresponding aniline and reducing the resulting formanilide with lithium aluminum hydride. *p*-Cyano-N-methylaniline, mp 78–81° (lit.[26] mp 89–91°), was prepared by formylating and methylating *p*-aminobenzonitrile and hydrolyzing the resulting N-methylformanilide. *Anal.* Calcd for $C_8H_8N_2$: C, 72.7; H, 6.1; N, 21.2. Found: C, 72.71; H, 6.14; N, 21.18.

Procedures.—Nmr spectra were obtained on a Varian A56-60

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[14] J. J. R. F. da Silva and J. G. Caldo, *J. Inorg. Nucl. Chem.*, **28**, 125 (1966), and references therein.

[15] A. Yingst and D. H. McDaniel, *ibid.*, **28**, 2919 (1966).

[16] C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

[17] *para:* ρ_I = 0.71, ρ_R = −1.02, sd/rms = 11. *meta:* ρ_I = 0.55, ρ_R = −0.03, sd/rms = 15.

[18] R. S. Drago and B. B. Wayland, *Inorg. Chem.*, **7**, 628 (1968).

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[24] M. Cais and D. Ginsburg, *J. Org. Chem.*, **23**, 23 (1958).

[25] M. F. Millson and R. Robinson, *J. Chem. Soc.*, 3362 (1955).

[26] J. N. Ashley and S. S. Berg., *ibid.*, 3092 (1957).

spectrometer at a probe temperature of ~36°. TMS was used as an internal reference, and chemical shifts were calibrated by the side-band method.

Nmr samples for contact shift measurements were prepared from a 1.0 *M* solution of the appropriate aniline in CCl_4 or CH_2Cl_2 with a trace of TMS by treating 1–5-ml portions of this solution with enough $Ni(acac)_2$ to give the desired concentration. The volume change resulting from the addition was assumed to be insignificant. For relative stability constant measurements, a solution containing both anilines at concentrations varying from 0.3 to 1.2 *M* was prepared and treated in a similar fashion.

Spectrograde solvents were distilled from CaH_2 before use. All anilines were freshly vacuum distilled or sublimed and the spectra were recorded immediately. Transfer of liquid anilines was made by syringe through rubber septa to minimize air oxidation, and solids were weighed under a stream of nitrogen. $Ni(acac)_2$ (J. T. Baker Chemical Co.) was dried in a vacuum oven just prior to use. Use of $Ni(acac)_2$ which was exposed to moist laboratory air for 1 day gave contact shifts which were nonreproducible and generally smaller than those obtained with freshly dried material.

A linear multiple regression analysis computer program provided in the IBM-1130 Scientific Subroutines Package was used for analysis of substituent effects.

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Kinetics and Mechanism of Substitution Reactions of *trans*-$Pt(P(C_2H_5)_3)_2RCl$

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The kinetic behavior of the complexes *trans*-$Pt(P(C_2H_5)_3)_2RCl$ (R = phenyl or *o*-tolyl) in substitution reactions with different entering groups in methanol and in dimethyl sulfoxide is examined. The substrates with *ortho*-substituted phenyl ligands show a discriminating ability toward the various entering groups, which distinguishes the biphilic reagents from the simple nucleophiles with respect to the possibility of associative attack. The influence of increasing steric hindrance on the central metal atom is estimated by comparing the kinetic data for the complexes with R = phenyl, *o*-tolyl, or mesityl.

Introduction

In a recent paper[1] we have reported the rates of substitution reactions of *trans*-$Pt(P(C_2H_5)_3)_2(ms)Cl$ (ms = mesityl) with various entering groups. The suggestion was made that in this sterically hindered complex the substitution proceeds by means of two competing paths, an associative one and a solvolytic one. When the latter is operative, the steric hindrance of two methyl groups on the metal atom seems sufficient to prevent a direct bimolecular attack by poor nucleophiles, especially in protic solvents which are very effective in assisting bond breakage in the rate-determining step. On the other hand an associative path is favored in dipolar aprotic solvents and in the reactions with good nucleophiles.

The analogous *o*-tolyl complex presents only one coordination position blocked by the *o*-methyl group of the aromatic ring, while the other is open to nucleophilic attack on the vacant p_z orbital of the metal.

In the present work kinetics data for substitution reactions of *trans*-$Pt(P(C_2H_5)_3)_2RCl$ (where R = phenyl, *o*-tolyl or mesityl) are reported. The object was to study the dependence of the reactivity and the reaction mechanism on an increasing steric hindrance at the reaction center.

Experimental Section

Materials.—The complexes used in this investigation, *trans*-$Pt(P(C_2H_5)_3)_2C_6H_5Cl$, *trans*-$Pt(P(C_2H_5)_3)_2(o\text{-tol})Cl$ (*o*-tol = *o*-tolyl), and *trans*-$Pt(P(C_2H_5)_3)_2(ms)Cl$, are all known compounds and were prepared by the methods reported in the literature.[2,3] Each one was characterized by elemental analysis and molecular weight determination.

Methanol was purified by distillation after refluxing over $Mg(OCH_3)_2$ to remove water.[4] Dimethyl sulfoxide was fractionated under reduced nitrogen pressure.[5] Other chemical products were all reagent grade commercial materials and were used without further purification.

Kinetics.—The rates of reaction were followed spectrophotometrically by measuring from time to time the changes in the optical density of the reaction mixture at some selected wavelength in the ultraviolet region. The instruments used were either a Beckman DU or an OPTICA CF 4 recording apparatus, with a cell compartment thermostated at the desired temperature.

All the reactions were carried out by using an excess of reagent with respect to the complex, in order to provide pseudo-first-order conditions. The substrate concentration in the reaction mixture was about 5×10^{-4} *M* and the reagent concentration varied from 5×10^{-3} to 10^{-1} *M*. The completeness of the reaction was checked by comparing the final spectra obtained at various reagent concentrations with those of the products independently prepared. In many cases the spectral changes during the reactions showed well-defined isosbestic points, indicating that only the substrate and the product are the absorbing species.

No significant ionic strength effect was found.

The pseudo-first-order constants were obtained graphically by means of the usual first-order plots. The experimental uncertainty in k_{obsd} values is about 10%.

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