(3) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 791.
(4) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 850.
(5) Elemental analyses were performed by Mr. P. Borda of this department.
(6) IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film.
(7) ^{1}H NMR spectra were recorded on a Varian Associates T60 spectrometer with Me_4Si being employed as an internal standard.
(8) Melting points were taken in capillaries and are uncorrected.
(9) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38.
(10) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Martinez, N. *J. Chem. Soc., Chem. Commun.* **1971**, 1476.
(11) Müller, J.; Schmitt, S. *Z. Anorg. Allg. Chem.* **1976**, *426*, 77.
(12) The thermal instability of transition-metal carbonyl nitrosyl halides has been previously discussed.[13]
(13) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173.
(14) Low-resolution mass spectra were obtained at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Mr. J. W. Nip.
(15) The assignments involve the most abundant naturally occurring isotopes in each fragment.

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Conformational Characterization of Nickel(II)-Tetraaza Macrocyclic Complexes through Isotropic Shift Studies

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Macrocyclic complexes provide stimulating examples for studying the conformational properties of the molecules, owing to the possible stable arrangements which the ligand can adopt around the metal ion.

The detection and the investigation of the different conformers for a given macrocyclic complex have been usually accomplished by means of X-ray diffractometric analysis[1-4] and/or proton magnetic resonance spectroscopy of solutions containing diamagnetic complexes.[4-7] The use of the latter technique, however, is limited by strong *J-J* coupling effects, which make difficult the interpretation and the assignment of the resonance signals of nonequivalent proton sets. If the complexes, however, are paramagnetic, the resulting large isotropic shifts can provide a powerful tool for the detection of the isomers and for obtaining conformational information. Indeed it has been shown that the contact shift contribution drastically depends on the conformational character, i.e., axial or equatorial, of the resonating proton.[8-10]

The results of an ^{1}H NMR investigation on some hexacoordinate selected complexes of general formula $NiLX_2$ (L = tetraamine macrocyclic ligand; X = Cl or NCS) are here reported and neatly show the conformational characterization of the nickel(II) macrocyclic moieties.

Experimental Section

The ligands 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4) and *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (Me_2[14]aneN_4) were prepared according to published methods.[11,12] Their paramagnetic derivatives Ni([14]aneN_4)Cl_2 and Ni(Me_2[14]aneN_4)Cl_2 were prepared by reaction of equimolar quantities of nickel(II) chloride and of the appropriate ligand in a minimum amount of methanol.

The diperchlorate derivatives of the isomers *β-meso-*, *β-rac-*, and *γ-rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) (Ni(Me_6[14]aneN_4)) were prepared by reduction of the parent 4,11-diene compound with $NaBH_4$ in basic solution and separated as described.[4,6] Isomers selectively deuterated on the 5,5,14,14-methyl groups were similarly obtained by using a parent 4,11-diene compound obtained by the reaction between the tris(ethylenediamine)nickel(II) ion and hexadeuterioacetone. The dithiocyanato derivatives of the three isomers were prepared by reaction between the appropriate diperchlorate derivative and sodium thiocyanate in dilute acidic solution, according to Warner and Busch.[6] The dichloro analogues of *β*-meso and *γ*-rac derivatives were prepared in a similar way by using acetonitrile as solvent and tetraethylammonium chloride. All the complexes were satisfactorily analyzed for C, H, and N.

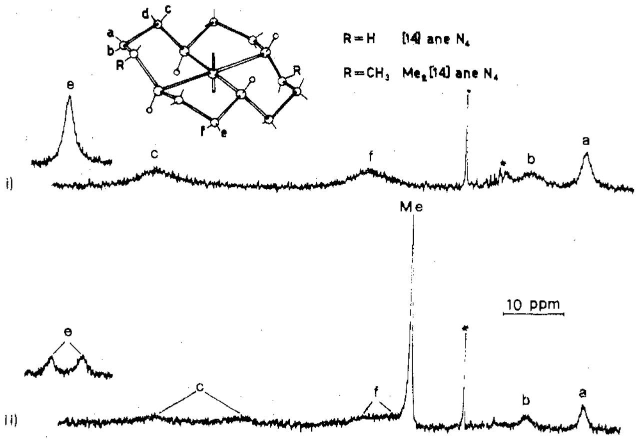

Figure 1. Proton magnetic resonance spectra at 34 °C of $CDCl_3$ solutions of (i) Ni([14]aneN_4)Cl_2 and (ii) Ni(Me_2[14]aneN_4)Cl_2. The resonance signals of protons labeled as d in the scheme are not shown. Signals labeled with * are due to solvent impurities.

^{1}H NMR Measurements. Proton magnetic resonance spectra were recorded on a Varian DA-60 IL spectrometer at 60 MHz and on a Varian EM 390 spectrometer at 90 MHz. Shifts were calibrated from internal tetramethylsilane (Me_4Si). The spectra were recorded both in HR mode (side-band technique used for calibration) and in HA mode in internal lock. Deuteriochloroform (Merck 99.8%) was used as solvent.

Results and Discussion

The ^{1}H NMR spectrum of the paramagnetic Ni([14]aneN_4)Cl_2 is reported in Figure 1 together with a scheme of the molecular structure of the complex.[1] The spectral data are reported in Table I. The conformation of the ligand in this compound is such that the six- and five-membered chelate rings are in a chair and gauche conformation, respectively, so that in the idealized C_{2h} symmetry there are six sets of nonequivalent protons, as labeled in Figure 1. Four of the six sets contain twice as many protons as compared to the remaining two sets. Accordingly, the ^{1}H NMR spectrum of this compound consists of six resonances, four located downfield and two upfield with respect to Me_4Si. The downfield resonances are two times stronger than those upfield. The correspondence between the observed signals and the sets of nonequivalent protons indicates that the conformation is fully retained in solution and no evidence exists of other species (either fast or slow on the ^{1}H NMR time scale) with the conformer shown in Figure 1. The resonance line pattern is completely different from those observed for complexes formed by simple symmetrical diamine ligands. As an example, ^{1}H NMR spectra of solutions containing 1:1 nickel(II) ethylenediamine[9] and nickel(II) 1,3-propanediamine[10] complexes show a single line at −93 ppm and two lines at −175 and +14 ppm, respectively, as a result of the averaging of axial and equatorial methylenic proton resonances by fast conformational interconversion. In contrast with this behavior, the high barrier of interconversion of the chelate ring system in the Ni([14]aneN_4) moiety (as well as in all the 14-membered macrocyclic systems here investigated) allows the observation of "frozen" resonance signals for axial and equatorial protons.

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Table I. Isotropic Shift Data (ppm)[a] and Spectral Assignments for Nickel(II) Tetraaza Macrocyclic Complexes in $CDCl_3$ at 34 °C

	five-membered chelate rings[b,c]		six-membered chelate rings[b,c]						
complex	CH_{ax} (f)	CH_{eq} (e)	α-CH_{ax} (c)	α-CH_{eq} (d)	β-CH_{ax} (b)	β-CH_{eq} (a)	Me_1[d]	Me_2[d]	Me_3
Ni([14]aneN_4)Cl_2	−20	−175	−56	−317	+4.5	+13.5			
Ni(Me_2[14]aneN_4)Cl_2	−19	−180, −175	−42, −55		+5.0	+13.7			−15.4
Ni(β-*meso*-Me_6[14]aneN_4)Cl_2	−30, −20	−189, −180	−55		+5[e]	+13.8	−20.1	+4.2	−13.7
Ni(β-*meso*-Me_6[14]aneN_4)$(NCS)_2$	−21	−177	−45		+5[e]	+14.9	−21.1	+3.5	−15.0
Ni(β-*rac*-Me_6[14]aneN_4)$(NCS)_2$	−33	−76, −125	−49		+6[e]	+15.5	−22.7	+4.7	−17.3
Ni(γ-*rac*-Me_6[14]aneN_4)Cl_2	−31, −29	−188, −185, −181 −160	−51		+6[e]	+12.3, 13.8	−19.7, −18.6	+4.0	+0.6 −13.9
Ni(γ-*rac*-Me_6[14]aneN_4)$(NCS)_2$	−23	−194, −163	−47		+7[e]	+15.4, 17.4	−19.8	+4	+0.7 −14.9

[a] The isotropic shifts are determined relative to the shifts of the free ligands or diamagnetic nickel(II) complexes: α-CH −2.8 ppm (average), β-CH −1.7 ppm (average), Me_{eq} −1.1 ppm, Me_{ax} −2.0 ppm. Estimated errors in isotropic shift data: shifts >−100 ppm, 1.5 ppm; shifts <−100 ppm, 1.0 ppm. [b] Key: ax = axial; eq = equatorial. [c] See Figures 1–4. [d] Resonances vanishing in deuterated samples. [e] From the spectra of deuterated samples because of the overlapping with Me_2 resonances.

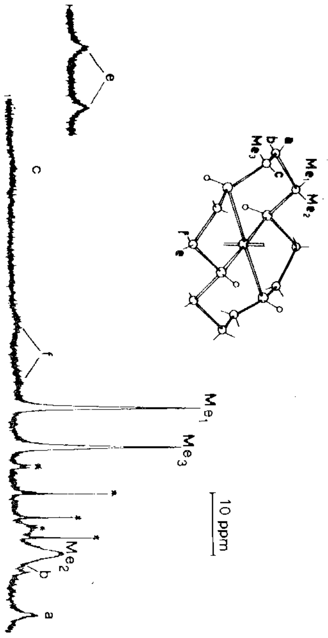

Figure 2. Proton magnetic resonance spectrum at 34 °C of Ni(β-*meso*-Me_6[14]aneN_4)Cl_2 in $CDCl_3$. Signals labeled with * are due to impurities.

The assignment of the resonances, as reported in Figure 1 and Table I, is based on: (i) the intensity ratios; (ii) the consideration that the β-methylenic protons of the propylenic chains shift upfield with respect to the diamagnetic position, probably because of spin polarization mechanisms;[10,13] (iii) the values of the isotropic shifts, whose average for each pair of geminal protons approaches the values observed for the corresponding methylenic protons in nickel(II)–ethylenediamine and nickel(II)–1,3-propanediamine complexes. As to the last point it is worth noting that the observed values of the isotropic shifts agree with those calculated by Reilley et al.[9,10] for "frozen" conformations of diamino chelate ligands in pseudooctahedral paramagnetic nickel(II) complexes.

The assignment of axial and equatorial protons is proposed on the basis that the former protons are expected to experience a smaller contact shift according to the well-known relationship

$$A_i = B_0 + B_2 \cos^2 \theta_i$$

where A_i is the hyperfine coupling constant and θ is the dihedral angle between the Ni–N and C–H bonds in the Ni–N–C–H moiety.[8,14] Furthermore the less shifted axial proton resonances are broader than those of the equatorial protons since the former protons are closer to the paramagnetic center and therefore are more affected by a dipolar relaxation mechanism.[15]

Similar considerations hold in order to assign the spectrum of the Ni(Me_2[14]aneN_4)Cl_2 complex (Figure 1), which can be considered as derived from Ni([14]aneN_4)Cl_2 by substitution of the equatorial protons of C(5) and C(12) carbons with two methyl groups. As a result of this substitution the molecule has a lower symmetry, i.e., C_i, than the parent Ni([14]aneN_4)Cl_2 molecule and therefore a larger number of resonance signals is expected, the sets of nonequivalent protons amounting to ten. The ^{1}H NMR spectrum of this compound, as compared with that of the Ni([14]aneN_4)Cl_2 complex, shows the splitting of the resonances attributed to the equatorial ethylene protons and to the axial α-propylenic protons; no splitting is observed for the resonances of the axial ethylenic protons, probably because of the large line width of the signals. The resonance attributed to the two equatorial α-propylenic protons has not been detected in this case, since it is expected to fall beyond −300 ppm from Me_4Si.

This type of spectral analysis can be useful also for systems known to give rise to a large variety of isomers. An example is given by the Ni(Me_6[14]aneN_4) system, whose three diastereoisomers labeled as β-meso, β-rac, and γ-rac have been characterized by means of X-ray diffraction analysis[4] and ^{1}H NMR spectroscopy of solutions containing the diamagnetic square-planar derivatives.[4,6] The spectral data of the fully paramagnetic dichloro- and dithiocyanato derivatives of these conformers are reported in Table I.

The Ni(β-*meso*-Me_6[14]aneN_4) diastereoisomer has the chelate ring skeleton similar to that of the above discussed

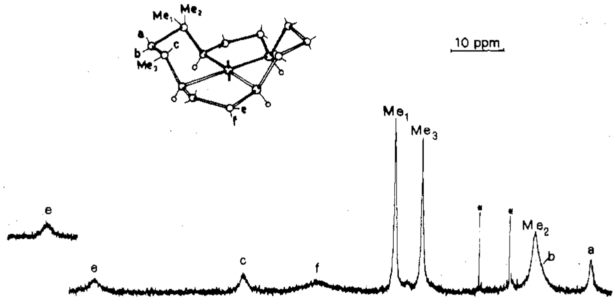

Figure 3. Proton magnetic resonance spectrum at 34 °C of Ni(β-*rac*-Me_6[14]aneN_4)$(NCS)_2$ in $CDCl_3$. Signals labeled with * are due to impurities.

Ni([14]aneN_4) and Ni(Me_2[14]aneN_4) complexes. The symmetry is C_i and the ^{1}H NMR spectrum (Figure 2) shows a pattern of resonances strictly relatable to those of the latter compounds. The eight resonance signals can be therefore assigned following the considerations discussed above. In this case also, the axial and equatorial geminal proton signals are well split; in particular the difference of ca. −180 ppm and ca. −20 ppm for the equatorial and axial ethylenic protons, respectively, indicates the existence of a quite regular gauche conformation of the five-membered chelate rings. The resonances at −22 and +2 ppm, with respect to the Me_4Si resonance, are assigned to the equatorial and axial geminal methyl groups, respectively, and the resonance at −16 ppm is assigned to the methyl groups attached to the asymmetric carbons. The latter assignment is supported by the spectra of samples containing selectively deuterated geminal methyl groups (see Table I). It should be noted that the different conformational character, i.e., axial or equatorial, of the methyl groups is well accounted for not only by the magnitude of the isotropic shift or by the line width of the signal but also by the sign of the hyperfine coupling constant, the axial and equatorial methyl groups experiencing upfield and downfield shifts, respectively. Similar conclusions fully agree with the analysis of the ^{1}H NMR data reported by Reilley et al. on the nickel(II) complexes with racemic and meso 2,3-butanediamine[16] and 2,4-pentanediamine,[10] which, however, display fast conformational interconversion on the ^{1}H NMR time scale.

The Ni(β-*rac*-Me_6[14]aneN_4) diastereoisomer has a C_2 axis orthogonal to the NiN_4 plane (Figure 3). The six-membered chelate rings adopt the same chair conformation as in the β-meso isomer; the five-membered rings, on the contrary, adopt a strongly distorted gauche conformation, because of the opposite configuration of the consecutive pair of nitrogens. As a consequence the methylenic protons of the ethylenic chains are intermediate between the axial equatorial limiting positions.[4]

This conformation clearly shows up in the spectrum of this compound (Figure 3). A pattern of resonances similar to that of the β-meso diastereoisomer is observed for the protons of the six-membered chelate rings, whereas the signals of the ethylenic protons are closer to each other than the proton resonances of the regular gauche conformation. If the conformation of the five-membered chelate rings was exactly eclipsed, a single signal in the range −80 to −90 ppm would have been expected. The splitting of the signal of the ethylenic protons, as compared to the splitting occurring in the spectrum of the β-meso isomer, can be taken as a measure of the degree of the distortion from the eclipsed conformation.

The Ni(γ-*rac*-Me_6[14]aneN_4) diastereoisomer has the same nitrogen configuration of the β-meso, but owing to the same configuration of the asymmetric carbons, the two six-membered chelate rings cannot be equivalent: one of them retains the regular chair conformation, whereas the other adopts a highly distorted conformation intermediate between the chair and the twist-boat. As a result of this inequivalence, the two five-membered chelate rings adopt unsymmetrical gauche conformations and therefore this diastereoisomer has C_1 symmetry.[4]

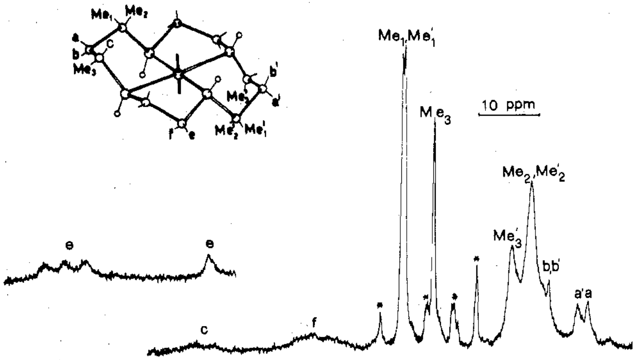

Figure 4. Proton magnetic resonance spectrum at 34 °C of Ni(γ-*rac*-Me_6[14]aneN_4)Cl_2 in $CDCl_3$. Signals labeled with * are due to impurities.

The pattern of the resonances, which appears in the spectrum of this compound (Figure 4), can be related to that of the β-meso isomer; however, the lack of symmetry causes the splitting of all the signals. Four resonance signals are detected for the equatorial protons of the ethylenic chains in the range −190 to −160 ppm, whereas the resonances assigned to the related axial protons are not well resolved because of the large line width. Again, two signals are observed for the two equatorial protons attached to the β carbons of the propylenic chains and for those of geminal groups occupying equatorial sites (labeled in Figure 4 as Me_1 and Me_1'). In the latter case the nonequivalence of the axial counterparts cannot be detected because of the small values of the isotropic shifts and the line width of the signals. However the most relevant feature of this spectrum is the shift difference between the resonances of the methyl substituents Me_3 and Me_3' of the asymmetric carbons: the former resonates at −15 ppm in a spectral region typical, as seen above, of equatorial methyl substituents and the other at −1.4 ppm, in a region expected for axial substituents.

The results here reported show how powerful the isotropic shift technique can be in detecting and assigning different conformers of the macrocyclic complexes. As a matter of fact, both the resonance position and the line width are strictly related to the conformational character of each resonating proton. Despite the full paramagnetism of the complexes, the signals are spread over a large spectral range and therefore the sensitivity of the ^{1}H NMR technique is highly improved.

Acknowledgment. I thank Professor L. Sacconi for constant encouragement. Thanks are also due to Professor I. Bertini for helpful discussion. I am indebted to Mr. G. C. Vignozzi for microanalyses and to Mr. D. Masi for technical assistance in ^{1}H NMR measurements.

Registry No. Ni([14]aneN_4)Cl_2, 15333-47-8; Ni(Me_2[14]aneN_4)Cl_2, 66059-77-6; Ni(β-*meso*-Me_6[14]aneN_4)Cl_2, 62939-49-5; Ni(β-*meso*-Me_6[14]aneN_4)$(NCS)_2$, 14409-17-7; Ni(β-*rac*-Me_6[14]aneN_4)$(NCS)_2$, 26029-90-3; Ni(γ-*rac*-Me_6[14]aneN_4)Cl_2, 68779-96-4; Ni(γ-*rac*-Me_6[14]aneN_4)$(NCS)_2$, 15557-17-2.

References and Notes

(1) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(2) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).

(3) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1403 (1973).

(4) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1963 (1973).

(5) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, **90**, 6938 (1968).

(6) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).
(7) R. A. Kolinsky and B. Korybut-Daskiewicz, *Inorg. Chim. Acta*, **14**, 237 (1975).
(8) R. H. Holm and C. J. Hawkins "NMR of Paramagnetic Molecules", Academic Press, New York, 1973, p 243.
(9) F. F. L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969).
(10) J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, **13**, 977 (1974).
(11) E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972).
(12) R. A. Kolinsky and B. Korybut-Daskiewicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **17**, 13 (1969).
(13) M. J. Scarlett, A. T. Casey, and R. A. Craig, *Aust. J. Chem.*, **23**, 1333 (1970).
(14) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
(15) D. R. Eaton and W. D. Phillips, *Adv. Magn. Reson.*, **1**, 103 (1965).
(16) R. F. Evilia, D. C. Young, and C. N. Reilley, *Inorg. Chem.*, **10**, 433 (1971).

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Structure and Chemistry of $[RhX(ttp)]^{n+}$ Complexes: Trans Influence and Steric Distortion Effects on Rhodium–Phosphorus Coupling Constants and Bond Distances

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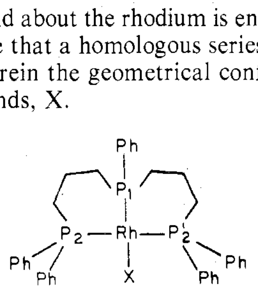
Polyphosphine ligands have been synthesized with two primary aims:[1] First, the chelate effect has been used to reduce complications in studies of catalytic properties of the metal complexes by eliminating substitution equilibria of labile monodentate phosphine ligands.[2] Second, linking the phosphines in an open chain arrangement would eliminate steric interactions of the attendant R groups in otherwise bulky phosphines and permit the metal atom to assume an undistorted but defined coordination geometry. Complexes of Rh(I) and other metals with the linear tridentate triphosphine ligand $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) should provide excellent probes with which to study catalytic hydrogenation, substrate displacement reactions, and metal-induced activation of small molecules (e.g., O_2, SO_2, H_2). Since the intramolecular steric forces are expected to be small, this system should also serve well to probe the trans influence of a variety of ligands upon the central phosphorus–metal bond. As the ttp chelate ensures that the ligand field about the rhodium is enforced, this system has the advantage that a homologous series RhX(ttp), I, can be prepared, wherein the geometrical configuration is fixed for differing ligands, X.



I

The ttp ligand has been found, however, to endow its Rh(I) complexes with somewhat different reactivity than its tris(triarylphosphine) monodentate counterparts. For example, the rhodium atom in RhCl(ttp) is a much stronger nucleophile than that in the $RhCl(PPh_3)_3$ analogue, reacting readily with neutral and cationic acids (SO_2, BF_3, CO, Cl_2, CH_3I, NO^+, N_2Ph^+, CH_3^+, CH_3CO^+, and H^+) to yield stable five-coordinate complexes.[1,3] The apparent basicity of the metal center is in fact more akin in its behavior to that of $IrCl(PPh_3)_3$ complexes.[4] Studies on the five-coordinate SO_2 adducts of $[RhX(ttp)]^{n+}$ ($n = 0$, $X^- = Cl^-$, N_3^-, CN^-; $n = 1$, X = CH_3CN, $PPhMe_2$, CO, and PEt_3)[5] suggest that the environment at the fourth coordination site of the parent $[RhX(ttp)]^{n+}$ may actually be somewhat sterically hindered and thus may contribute to that site's reactivity. In $[Rh(ttp)(PEt_3)(SO_2)]$, it is the equatorial PEt_3 group rather than the normally more weakly bound SO_2 that is the more labile.[5b]

Table I. ^{31}P NMR Data for $[Rh(ttp)X]^{n+}$ Complexes

complex[a]	J_{Rh-P_1}, Hz	J_{Rh-P_2}, Hz	cone angle,[b] deg	PA(X)[i]
Rh(OH)(ttp)	166.5	127.7	90	390[c]
RhCl(ttp)	162.5	128.7	102	333[d]
$Rh(N_3)(ttp)$	152.2	131.6	95–110	
$[Rh(ttp)(CH_3CN)]PF_6$	151.5	123.0	95	186[e]
Rh(NCS)(ttp)	149.3	127.4		
$[Rh(ttp)(py)]BF_4$	139.7	129.7	119	225[f]
Rh(CN)(ttp)	122.6	134.5	95	349[d]
$Rh(CH_3)(ttp)$	113.3	152.8	90	405[e]
$[Rh(ttp)(CO)]PF_6$	113.3	114.3	95	143[f]
$[Rh(ttp)(PEt_3)]AsF_6$	113.2	137.9	132	~220[g]
$[Rh(ttp)P(OMe)_3]AsF_6$	111.6	124.7	107	218[h]

[a] P_1 is the central, P_2 the terminal phosphorus atom. [b] From ref 15; some values for the smaller ligands (e.g., CH_3CN) have been estimated from models. [c] S. A. Sullivan and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5017 (1977). [d] S. A. Sullivan and J. L. Beauchamp, *ibid.*, **98**, 1160 (1976). [e] J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [f] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972). [g] Estimated from values of other phosphines. [h] R. V. Hodges, T. J. McDonnell, and J. L. Beauchamp, *J. Am. Chem. Soc.*, in press. [i] Gas-phase proton affinity in kcal/mol.

In order to explain this behavior and to gather data for trans influence studies, we have synthesized and characterized an extended series of $[RhX(ttp)]^{n+}$ complexes, examined their ^{31}P NMR spectra, and determined the structures of the X = py and X = PEt_3 derivatives.[6]

In Table I we have assembled some of the ^{31}P NMR results for a number of the neutral and cationic four-coordinate complexes $[RhX(ttp)]^{n+}$, arranged in the order of decreasing rhodium–phosphorus coupling constant, J_{Rh-P_1}.[7] We find, as has been found for Pt(II) complexes,[8] that the neutral and cationic complexes can be considered together; the range of rhodium–phosphorus coupling constant values, particularly of J_{Rh-P_2}, are indistinguishable. As for the platinum complexes, the rhodium–phosphorus coupling constants (J_{Rh-P_1}) can be used similarly to establish a trans influence series for the ligands. Our observed ordering, in part, is $OH^- < Cl^- < N_3^- \sim CH_3CN \sim NCS^- < py < CN^- < CH_3^- \sim CO \sim PEt_3 \sim P(OMe)_3$, which is considerably different from that found (using J_{Pt-P}) for Pt(II):[8,9] $CH_3CN < Cl^- < py < SCN^- < OH^- < PhS^- < CO < CN^- < P(OPh)_3 \sim PPh_3 \sim CH_3$. That the ordering of the ligands is different is not surprising, because the trans influence of a ligand depends not only upon the nature and properties of the ligand itself but as well on the particular metal, its oxidation state, the other ligands, and the degree of coordination of the metal.[10] We do, however, find the placement of some of the ligands in this series inconsistent with bonding arguments which should hold a priori for these complexes and which have well rationalized the trans influence series observed for some other metal systems.[10,11]

Equation 1 is appropriate for discussion of the rhodium–phosphorus coupling constants:[12]

$$J_{Rh-P} \propto \gamma_{Rh}\gamma_P\alpha_{Rh}^2|\psi_{Rh(5s)}(0)|^2\alpha_P^2|\psi_{P(3s)}(0)|^2(^3\Delta E)^{-1} \quad (1)$$

γ_A is the appropriate gy-

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