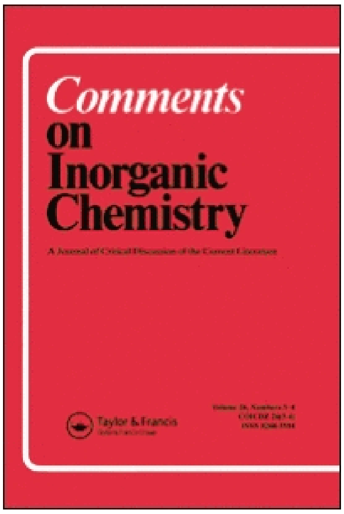

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The Correlation Between Transition Metal NMR Chemical Shifts and the Stability of Coordination Compounds

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The Correlation Between Transition Metal NMR Chemical Shifts and the Stability of Coordination Compounds

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Linear correlations of transition metal NMR chemical shifts with the logarithm of overall stability constants for six different series of complexes of Co(III), Rh(III), Rh(I) and Pt(II) have been found. Each case is presented and discussed. The relation is interpreted with a simplified version of Ramsey's equation for the chemical shift. A derivation of a relation of the type $\delta = m - k \log K$ using ligand field theory is proposed.

Key Words: *^{59}Co NMR spectroscopy, ^{103}Rh NMR spectroscopy, ^{195}Pt NMR spectroscopy, stability constants, Ramsey's equation, ligand field theory, Co(III), Rh(III), Rh(I), Pt(II), halide complexes, amine complexes, alkene complexes*

Transition metal NMR spectroscopy offers a method to probe directly the metal center in coordination compounds. Consequently it has been recognized as having a large potential in coordination chemistry, organometallic chemistry and related areas.[1,2] Furthermore, inverse 2D detection techniques have greatly increased the sensitivity of nuclei ear-

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lier considered as difficult, as for example ^{57}Fe, ^{103}Rh, ^{107}Ag, ^{109}Ag, ^{183}W and ^{187}Os.[3]

However, inasmuch as numerous applications depend only on the observation of a signal or a correlation, the promises of deeper insight into the nature of the electronic state of the metal and the metal-ligand bond from the *value* of the chemical shift have only partly been fulfilled. The reason is the large number of parameters that determine the transition metal NMR chemical shift. Not only do we have to consider the diamagnetic term in Ramsey's equation, even more important is the paramagnetic term, whose description requires the mixing of excited states into the electronic ground state of the metal ion.[4] Nevertheless, in a thorough review Mason shows how a simplification of Ramsey's equation of the following type can be used to explain trends of transition metal chemical shifts:[5]

$$\delta = \delta_{dia} + B\frac{\langle r^{-3}\rangle_d \Sigma Q_N}{\Delta E_{d-d}} . \qquad (1)$$

Here δ_{dia} is the diamagnetic shift which we usually think of in terms of electron density closest to the nuclei. The second term is the paramagnetic contribution where $\Delta E_{d\text{-}d}$ can be approximated with the ligand field splitting or a weighted average for lower symmetries, $\langle r^{-3}\rangle_d$ is the inverse of the mean value of the cube of the *d*-orbital radii, ΣQ_N is the imbalance of the *d*-orbital electron population or more correctly, the angular imbalance of charge, and B is a constant.

Equation (1), in any of its forms, can be considered at least as a good working model for the transition metal chemical shifts. Since Mason's review, more examples have appeared that show excellent agreement with this model.[6–8]

On the basis of similar equations it was also suggested that there should be a correlation of complex stability and the corresponding metal chemical shift.[9,10] In this study I will show that such a relation indeed exists for a number of classes of compounds.

In the following I will first give a very brief theoretical background, then present data for classical coordination complexes of Co(III), Rh(III) and Pt(II), go on to alkene complexes of Rh(I) and Pt(II) and finally mention Rh(III) compounds with σ-bound organic groups. Finally I will derive a linear relationship $\delta = m - k \log K$ using ligand field arguments.

$\Delta E_{d\text{-}d}$, $\langle r^{-3}\rangle_d$, ΣQ_N AND THEIR CONNECTIONS TO METAL–LIGAND BONDING

Of the four parameters in Eq. (1) we will start by neglecting the diamagnetic term, δ_{dia}.[11] Quantitatively we can understand this by considering that: (1) The electrons closer to the nucleus contribute more to the diamagnetic shift than the valence electrons. (2) The valence electrons make up only a small part of the total electron density of a transition metal, and thus changes in this parameter will be a diminishing contribution.

Next, we consider the $\Delta E_{d\text{-}d}$ factor. Ligand field theory directly connects the d-orbital splitting to the stability of the complex. For example, a low spin d^6-metal ion in an octahedral field gains a ligand field stabilization energy of $12\Delta E_{d\text{-}d}/5$.[12] If we disregard entropy effects this energy can be directly related to the complex stability.

The usual interpretation of the radial factor $\langle r^{-3}\rangle_d$ is as the covalency or delocalization factor. Thus, in a more covalent M-L bond there will be more mixing of metal and ligand orbitals and, consequently, the effective radii of the d-orbitals will increase. The effect of this expansion of the d-electron shell (the nephelauxetic effect) is to reduce the d-d-electron repulsion and thereby decrease the total energy of the complex. A larger r_d and consequently a lower $\langle r^{-3}\rangle_d$ should therefore give a more stable complex.

Mason states that in general the $\Delta E_{d\text{-}d}$ factor is more important for higher oxidation states and $\langle r^{-3}\rangle_d$ for lower oxidation states.[5]

Finally we have the imbalance of charge, ΣQ_N. For free ions or core electrons this factor is zero, but may take values up to 12, for example, in low spin d^6-metal ions.[5] Within a series of complexes with only small changes in coordination geometry around the metal, this parameter can be taken as constant. However, care has to be taken when discussing cases where a serious deviation from ideal geometry may be envisaged, i.e., chelating ligands or extra bulky ligands.

We conclude that the stability of a complex should increase with increasing $\Delta E_{d\text{-}d}$ and decreasing $\langle r^{-3}\rangle_d$. If we then consider Eq. (1) we would predict a higher chemical shift for a less stable species in a series of complexes of the same metal ion and the same coordination geometry.

As for the form of such a correlation we note that a straight line relationship, $\delta = m - k \log K$, has been observed in all cases reported below. Within the ligand field approximation where the $\Delta E_{d\text{-}d}$ factor will determine both shift and stability constant, such a relation can be derived theoretically as will be shown later.

Rh(III) AND Co(III) COMPLEXES WITH HALOGENIDES AND OTHER LIGANDS

Read and co-workers found correlations for Rh(III) and Co(III) complexes.[8] In Fig. 1 I present the ^{103}Rh-NMR chemical shifts and overall equilibrium constants for the formation of $Rh(H_2O)_n(X)_m^{3-m}$ complexes in H_2O and in Fig. 2 I have made a corresponding plot for some $Co(III)L_6$ compounds.

$$M(III)(H_2O)_6^{+3} + nX^- \rightleftarrows M(III)(H_2O)_{6-n}(X)_n^{3-n} + nH_2O, \quad (2)$$

$$K = \frac{[M(III)(H_2O)_{6-n}(X)_n^{3-n}]}{[M(III)(H_2O)_6^{+3}][X^-]^n}. \quad (3)$$

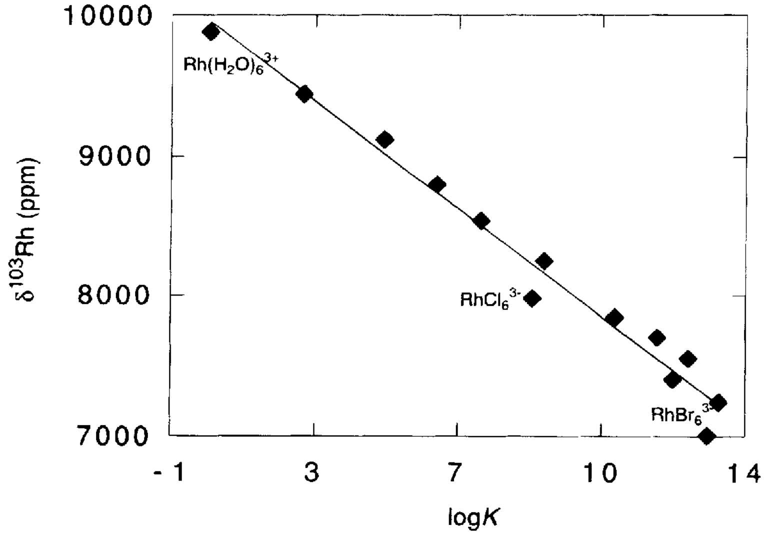


FIGURE 1 The ^{103}Rh-NMR chemical shifts and overall stability constants for the formation of $Rh(H_2O)_n(X)_m^{3-m}$ complexes in H_2O [Eqs. (2) and (3)].

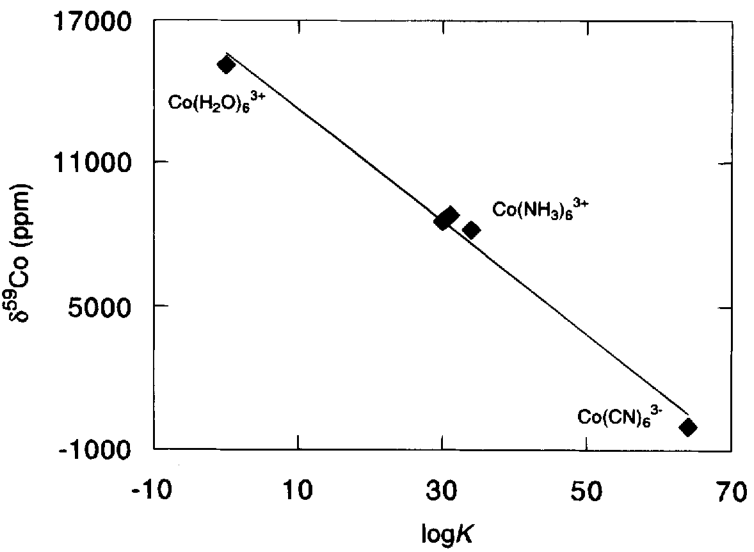
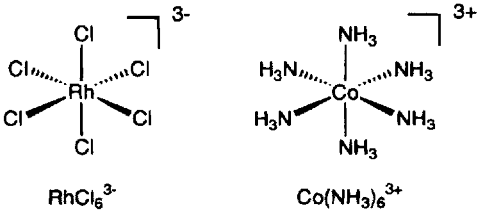


FIGURE 2 The ^{59}Co-NMR chemical shifts and overall stability constants for the formation of Co(III)L_6^q complexes in H_2O [Eqs. (2) and (3)].

A detailed discussion of these data is fond in Ref. 8. Here I would only like to point out the main features.

In this system the rhodium NMR chemical shifts have been shown to follow a simplified Ramsey's equation where both ΔE and $\langle r^{-3}\rangle_d$ were taken into account. It is interesting to see the large span of chemical shifts and equilibrium constants: for Rh(III) 3000 ppm (if we extrapolate to the cyanide complex 9000 ppm)[8] and for Co(III) 16,000 ppm with the corresponding log$K$ values ranging from 0 to 60. Considering the limits



SCHEME 1

of chemical shift values for the two metals, the complexes from hexa-aqua to hexa-cyano cover about the same parts of the total spectral ranges. Furthermore, the fitted lines for these two metal ions have similar slopes. The displacement may be related to the larger $\Delta E_{d\text{-}d}$ splitting for the second transition series, reducing the chemical shift.

A small peculiarity may also be mentioned. When going from $Rh(Cl)_5(H_2O)^{2-}$ to $Rh(Cl)_6^{3-}$ and from $Rh(Br)_5(Cl)^{3-}$ to $Rh(Br)_6^{3-}$ the shift actually increases with increasing stability, contradictory to the general trend. A speculative suggestion is that the increasing symmetry, through the term $\sum Q_N$, is at play here.

Since ligand exchange in Rh(III) complexes is extraordinarily slow, the measurement of equilibrium constants is sometimes impossible or extremely tedious. Note also that the observation of peaks in a ^{103}Rh-NMR spectra does not usually permit their direct quantification by integration since the relaxation times may vary by a factor of 60 and be up to a minute long.[13,14] Similar correlations may then give helpful estimates of the stability of complexes. In this special case the equilibrium constant for $Rh(CN)_6^{3-}$ and $Rh(SCN)_6^{3-}$ were estimated and used in a discussion of the thermodynamic basis for leaching of rhodium from spent catalytic exhaust converters for cars.[8] The existence of RhF_6^{3-} in solution was also discussed.

Pt(II) COMPLEXES WITH HALOGENIDES AND RELATED LIGANDS

In order to investigate if a similar correlation existed for four coordinated square planar platinum(II) complexes a comprehensive search of the literature was performed. Correlations were found for halogenide compounds[15–21] and also for amine complexes[22–25] with water as a solvent. The data are presented in Table I and Figs. 3 and 4.

$$\mathrm{Pt(II)(H_2O)_4^{+2}} + n\mathrm{X^-} \rightleftarrows \mathrm{Pt(II)(H_2O)_{4-n}(X)_n^{2-n}} + n\mathrm{H_2O} \qquad (4)$$

$$K = \frac{[\mathrm{Pt(II)(H_2O)_{4-n}(X)_n^{2-n}}]}{[\mathrm{Pt(II)(H_2O)_4^{+2}}][\mathrm{X^-}]^n}. \qquad (5)$$

$$\mathrm{Pt(II)(diamine)(Cl)_2} + n\mathrm{H_2O} \rightleftarrows \mathrm{Pt(II)(diamine)(Cl)_{2-n}(H_2O)_n^{\,n}} + n\mathrm{Cl^-} \qquad (6)$$

TABLE I

^{195}Pt-NMR Chemical Shifts and Stability Constants for Reactions 4 and 6.

Complex	Chemical Shift (ppm)	log *K*	Reference	
			δ	log *K*
Equilibrium Eq. 4				
$Pt(H_2O)_4^{2+}$	30	0	16	
$Pt(H_2O)_3Cl^+$	–350	5.0	16	19
$Pt(H_2O)_2Cl_2$ *trans*	–644	8.66	16	19
$Pt(H_2O)_2Cl_2$ *cis*	–811	8.74	16	19
$Pt(H_2O)Cl_3^-$	–1185	11.9	16	19
$PtCl_4^{2-}$	–1625	14.0	16	19
$PtCl_4^{2-}$	–1614	16.6	15	17
$PtBr_4^{2-}$	–2690	16.1	15	19
$PtBr_4^{2-}$		20.4		17
PtI_4^{2-}	–5490	48[a]	15	17[a]
$Pt(NH_3)_4^{2+}$	–2610	35.3	15	17
$Pt(CN)_4^{2-}$	–4713	41	15	17
Equilibrium Eq.6				
$Pt(en)_2Cl_2$	–711[b]	0.00	23,24	
$Pt(en)_2Cl(H_2O)^+$	–506[b]	–2.66	23,24	21
$Pt(en)_2Cl(H_2O)^+$		– 2.82		22
$Pt(en)_2(H_2O)_2^{2+}$	–284[b]	–6.51	23,24	21
$Pt(en)_2(H_2O)_2^{2+}$		–6.68		21,22
$Pt(R1\text{-}en)_2Cl_2$	–722[b]	0.00	23	
$Pt(Rl\text{-}en)_2Cl(H_2O)^+$	–447[b].	–3.14	23	23
$Pt(Rl\text{-}en)_2(H_2O)_2^{2+}$	–227[b]	–7.06	23	23

[a] Estimated from the log*K*(ML_4)/log*K*(ML_2) ratios for Cl^- and Br^- (1.6 ± 0.05) in Ref. 20 and the log*K*(ML_2) value for I^- in Ref. 18.

[b] Reference $PtCl_4^{2-}$: 0 ppm.

$$K = \frac{[Pt\,(II)(diamine)(Cl)_{2-n}(H_2O)_n{}^{n}][Cl^-]^n}{[Pt\,(II)(diamine)(Cl)_2]}. \tag{7}$$

Here, too, we see a large span of shifts and equilibrium constants, but we also observe a relatively large deviation from the trend by the ammonia compound (Fig. 3). For this ligand no rhodium data are available, but for Co(III) the hexammine complex falls well on the line.

The sometimes large discrepancy between different equilibrium studies is illustrated by the values for $PtCl_4^{2-}$ and $PtBr_4^{2-}$. In general, constants taken from Refs. 19 and 20 should be preferred since these are critical evaluations of the literature. Note also that the stability constant for PtI_4^{2-}

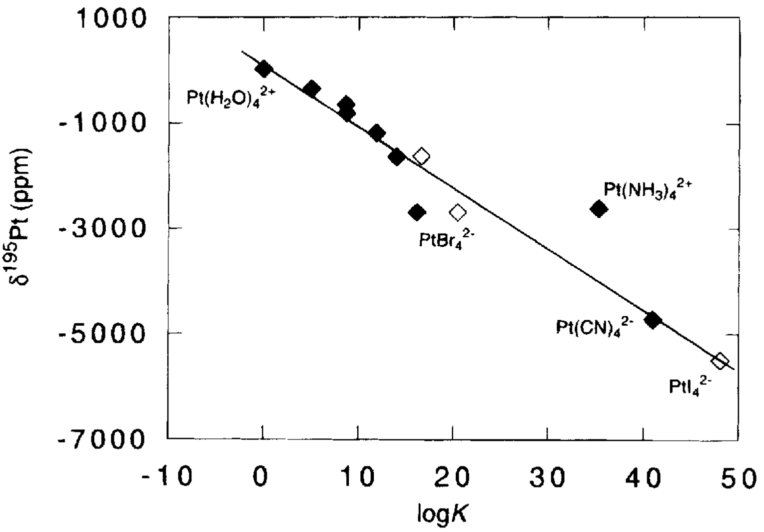


FIGURE 3 The ^{195}Pt-NMR chemical shifts and overall stability constants for the formation of square planar $Pt(H_2O)_n(X)_m{}^q$ complexes in H_2O [Eqs. (4) and (5)]. Outlined symbols refer to a second measurement of the stability constant, or, for $PtI_4{}^{2-}$, to an estimated constant.

is estimated from the stability of the diiodide complex and the corresponding chloride and bromide compounds (see footnote in Table I).

Pesek and Mason deduced that there are anomalies in the ^{195}Pt-NMR shifts for the iodide in their original study of $PtX_4{}^{2-}$ and $PtX_6{}^{2-}$ complexes and tentatively attributed this to relativistic effects of I^-.[16] Given the large ionic radius of I^- one may also be tempted to classify it as a bulky ligand and therefore distortions of the coordination geometry may be possible. Nevertheless, the log*K* values estimated from the shift-log*K* correlation and the extrapolation from known thermodynamic constants agree well.

The diamine complexes are spread out over a rather limited range of shift and log *K* values (Fig. 4.). It is also clear that any quantitative predictions here will be very uncertain; however, it is undeniable that the trend is the same. Furthermore, we get a somewhat less steep slope compared to the halogenide complexes, –70 ppm/log*K* versus –110 ppm/log*K*.

Since a great deal of research in this domain is related to the metabolism and mechanism of action and the design of new platinum anticancer

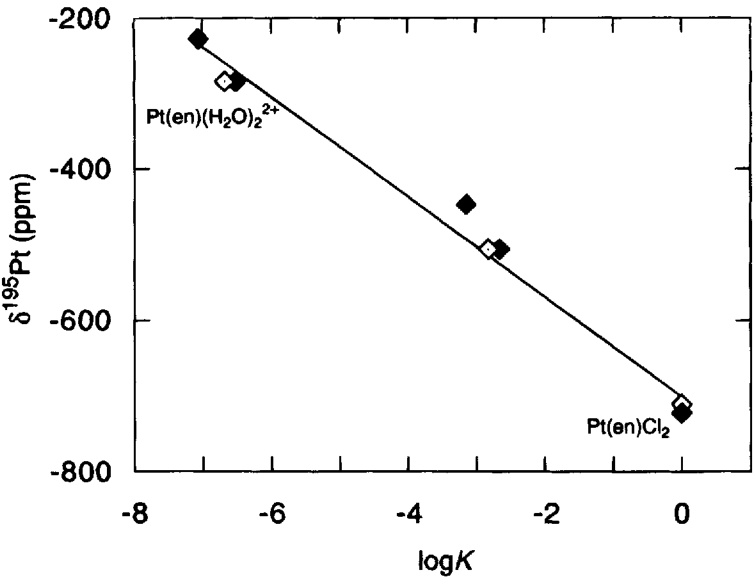
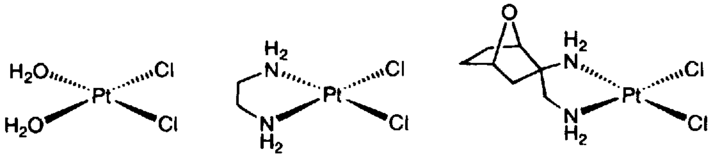


FIGURE 4 The ^{195}Pt-NMR chemical shifts and overall stability constants for the aquation of dichloride Pt(diamine)Cl_2 complexes in H_2O [Eqs. (6) and (7)]. Open symbols refer to a second measurement of the stability constant.

drugs,[26,27] one might want to envisage applications in this area. However, it is known that the binding of *cis*-$Pt(NH_3)_2(Cl)_2$, one of the most commonly used platinum anticancer drugs, to DNA is *kinetically* controlled,[28] and the thermodynamics may thus only be of secondary importance in this respect.

Still, Pt-NMR is an important method in this area,[29] and an increased knowledge of the parameters that determine the shifts may be valuable.



cis-$Pt(H_2O)Cl_2$ $Pt(en)Cl_2$ $Pt(R1\text{-}en)Cl_2$

SCHEME 2

Åkermark *et al.* studied Rh(acetylacetonato)(alkene)$_2$ complexes and found the trend in Fig. 5.[30] Here, the shifts are measured in $CDCl_3$ and the stability constants[31] in toluene. A related phenomenon is the observation of a pair-wise preference of the minor epimer of Rh(chiraldiphosphine)(S-enamide)$^+$ for the higher chemical shift (Table II).[32] SS-chiraphos and SS-diamp were used as chiral phosphines; the solvent was methanol-d_4.

$$\begin{aligned}&\mathrm{Rh(acac)(ethylene)_2 + alkene} \rightleftarrows \\ &\qquad\qquad \mathrm{Rh(acac)(ethylene)(alkene) + ethylene},\end{aligned} \tag{8}$$

$$K = \frac{[\mathrm{Rh(acac)(ethylene)(alkene)}][\mathrm{ethylene}]}{[\mathrm{Rh(acac)(ethylene)_2}][\mathrm{alkene}]} \tag{9}$$

Worth noting here is the deviation of the tetrafluoroethylene, TFE, complex, 150 ppm from the expected value. This is about the same order as the

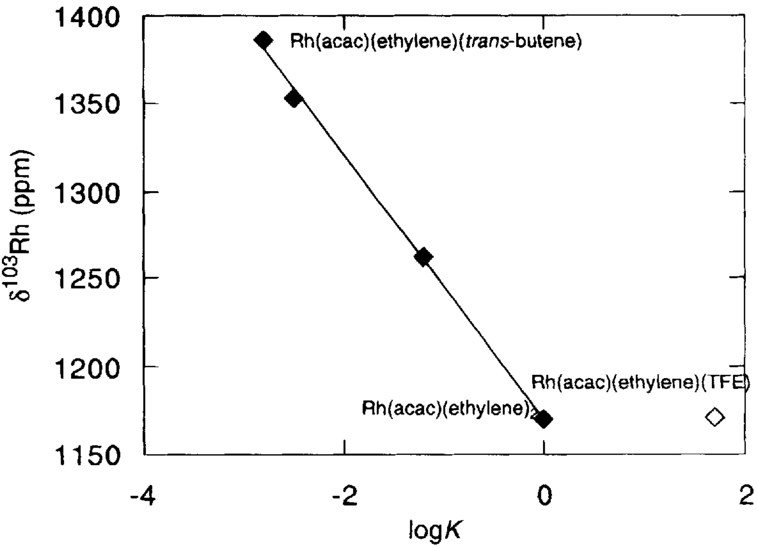
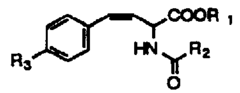


FIGURE 5 The ^{103}Rh-NMR chemical shifts and the stability constants for the replacement of one ethylene in Rh(acac)(ethylene)$_2$ by propene, tetrafluoroethylene *cis*- and *trans*-butene [Eqs. (8) and (9)].

TABLE II

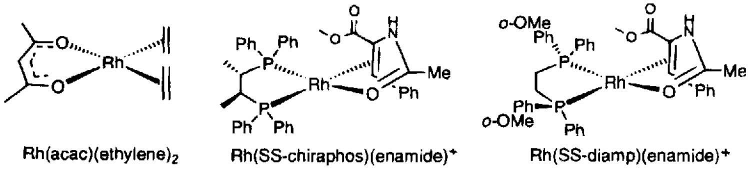
^{103}Rh-NMR Chemical Shift Differences for Major and Minor Isomers of Rh(chiraldiphosphine)(enamide).[32]

			Δ, minor-major isomer difference in δ^{103}Rh chemical shifts (ppm)	
R_1	R_2	R_3	SS-chiraphos	SS-diamp
CH3	CH_3	H	178	97
$C(CH_3)_3$	CH_3	H	33	290
H	CH_3	H	160	85
H	C_6H_5	H	136	108
H	C_6H_5	OH	134	47
H	C_6H_5	NO_2	245	247

deviation of the symmetric $Rh(Cl)_6^{3-}$ and $Rh(Br)_6^{3-}$ complexes, but much smaller than the difference between prediction and experiment for $Pt(NH_3)_4^{2+}$. In this case there is a convenient explanation in the different electronic properties of the fluorosubstituted alkene. The TFE ligand can be expected to form a bond much closer to the metalacyclopropane model,[33] thus with a formal Rh(III) center, than the aliphatic olefins that normally show a classical σ-donation–π-back-donation pattern. This interpretation was supported by *ab initio* quantum chemical calculations.[30]

Unfortunately, no equilibrium data are available for the complexes with the chiral phosphine. That should have provided results of a slightly different character since here we have independent sets of equilibrium constants and chemical shifts for two series of similar compounds. It is not evident, but in the light of the earlier results it seems probable, that the difference in chemical shift reflects the isomer ratio.

We can, however, estimate the equilibrium constant for the methyl (Z)–α-*N*-acetamidocinnamate chiraphos complexes (entry 1, Table II)



Rh(acac)(ethylene)$_2$ Rh(SS-chiraphos)(enamide)$^+$ Rh(SS-diamp)(enamide)$^+$

SCHEME 3

from the spectra reproduced in Ref. 32. This gives an isomer relation of 30/1 and log$K$ = 1.5 which is in good agreement with the value obtained using the equation for the straight line in Fig. 4 and the shift difference 178 ppm, log$K$ = 1.3.

Undoubtedly the Rh-NMR chemical shift difference of the major and minor stereoisomer reflects two electronically different rhodium atoms.[32,34] However, the connection of this difference to the reactivity of the isomers, vis-à-vis, for example, H_2 oxidative addition, is not completely clear. Since the isotropic chemical shift is an average of the chemical shift tensors and the stability constant can be seen as an average of bonding energies, their correspondence is intuitive. Chemical reactions and their rate constants, on the other hand, are usually very stereospecific and individual chemical shift tensors may therefore be more relevant. Nevertheless, reactivity and isotropic chemical shifts have been shown to correlate in many cases.[35]

Pt(II) COMPLEXES WITH ALKENES

Erickson and co-workers have done some extensive work on Pt(II)-alkene complexes. For the system $PtCl_3(alkene)^-$ in D_2O, Pt-NMR measurements were employed to determine the equilibrium concentration ratios and to obtain the correlation shown in Fig. 6.[36]

$$\begin{aligned}&\mathrm{PtCl_3(2\text{-}methyl\text{-}3\text{-}butene\text{-}2\text{-}ol)^-} + \mathrm{alkene} \rightleftarrows \\ &\qquad \mathrm{PtCl_3(alkene)^-} + \mathrm{2\text{-}\ methyl\text{-}3\text{-}butene\text{-}2\text{-}ol},\end{aligned} \tag{10}$$

$$K = \frac{[\mathrm{PtCl_3(alkene)^-}][\mathrm{2\text{-}methyl\text{-}3\text{-}butene\text{-}2\text{-}ol}]}{[\mathrm{PtCl_3(2\text{-}methyl\text{-}3\text{-}butene\text{-}2\text{-}ol)^-}][\mathrm{alkene}]} \tag{11}$$

The spread in shift and log$K$ values is comparable to that noted for the Rh(acac)(alkene)$_2$ system. The largest deviations from the linear regression line, whose slope is –44 ppm/log$K$, is of the same order as in Fig. 3, 30–40 ppm or 0.5–1 log$K$ units. Most alkenes in the study have polar groups of different kinds, and it seems likely that differences in solvation of the alkenes also may influence the stability constant. Still, the correlation is reasonable.

Even small differences in stereochemistry of these olefin complexes can have significant effects on platinum shifts. The two diastereomers,

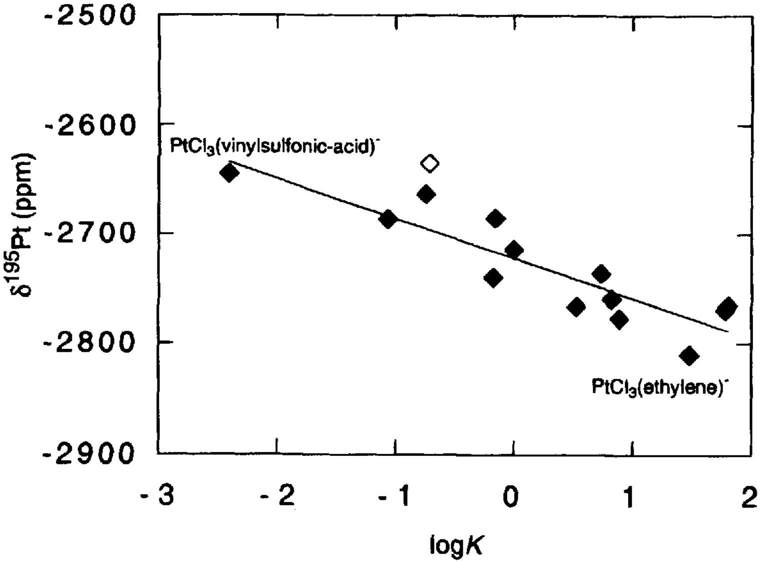
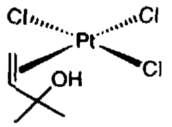


FIGURE 6 The ^{195}Pt-NMR chemical shifts plotted versus the stability constants in D_2O for the replacement of 2-methyl-3-butene-2-ol in Pt(sarcosine)Cl(2-methyl-3-butene-2-ol) by other alkenes [Eqs. (10) and (11)]. Open symbols refer to measurement in CD_3OD

RR and RS of the 3-butene-2-ol complex, for example, have similar log*K* values (0.89 and 0.74), but they differ by 41 ppm in chemical shift. A better understanding of the structural origin of such small differences might permit the assignment of the stereochemistry of such isomers on the basis of relative chemical shifts alone.



PtCl$_3$(2-methyl-3-butene-2-ol)$^-$

SCHEME 4

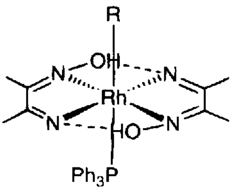
RHODOXIMES WITH σ-CARBON LIGANDS OR HALOGENIDES

Lately, some Rh-NMR studies of Rh(III)(diglyoxamato)(L)(R) complexes have been reported.[37–39] A large number of organic R ligands and halogenides or pseudohalogenides as well as different ligands L = PMe_3, PPh_3, $P(OPh)_3$, pyridine and H_2O have been studied.

For these compounds there are no equilibrium data available, but for the PPh_3 and pyridine complexes, a number of crystal structures exist.[40] It is tempting to use the metal–ligand bond distances as indications of bond energy in search for a correlation of the type we have already seen. However, since the chemical shift reflects the total changes in the coordination sphere, this is a risky business. The *trans*-influence of the organo ligand will be substantial, thus the Rh–P bond length may also change significantly. Furthermore, the rhodium-glyoxamato unit is known to be somewhat flexible.

Indeed, for the series R = ethyl, vinyl and phenylacetylid, we observe a trend of higher chemical shifts with decreasing bond lengths. This is attributed to the different hybridizations of R, influencing their relative σ-donor capacities.[37]

This last example was cited in order to stress that the chemical shift will be sensitive to *all* changes in the coordination sphere, just as the stability constant. Only in special cases do we expect properties of individual M–L bonds to correlate with the transition metal–NMR chemical shifts.



Rh(diglyoxamato)(PPh_3)R

SCHEME 5

A THEORETICAL MODEL FOR THE TRANSITION METAL CHEMICAL SHIFT-LOGK RELATION

In the introduction I discussed the transition metal NMR chemical shift and its possible relation to the stability of complexes in a qualitative way. Here a more stringent derivation of the experimentally found correlation is attempted.

We assume that the chemical shift and that the relative stability of the complex are dependent only on $\Delta E_{d\text{-}d}$. This can be regarded as the ligand field theory extended to the chemical shift.

In all our correlations we have a complex with a stability constant defined as one. Typically for an octahedral complex:

$$\mathrm{ML_6} + 6\mathrm{L} \rightleftarrows \mathrm{ML_6} + 6\mathrm{L}, \quad K = 1, \quad \log K = 0. \tag{12}$$

The stability of this complex versus a hypothetical complex with coordinated ligands but a metal ion without d-orbital splitting is taken as a reference state:

$$\Delta G_{ref} \approx \Delta H_{ref} = -\frac{\Delta E_{d-d}^{ref}}{5}(2n_{t2g} - 3n_{eg}) = -\Delta E_{d-d}^{ref} \cdot k_1 . \tag{13}$$

Where n_{t2g} and n_{eg} are the number of $t2g$ and eg electrons. We then define the reference state stability constant:

$$\ln K_{ref} = -\frac{\Delta G_{ref}}{RT} \approx \frac{\Delta E_{d-d}^{ref} \cdot k_1}{RT} . \tag{14}$$

For another complex in the same series we then have the relative free energy and enthalpy (supposing ligand–solvent interactions are the same for all ligands.):

$$\Delta G_{rel} \approx \Delta H_{rel} = \Delta H - \Delta H_{ref} . \tag{15}$$

The corresponding stability constant can be expressed using the ligand field splitting:

$$\ln K = \frac{\Delta E_{d-d} \cdot k_1}{RT} - \ln K_{ref} \Rightarrow \Delta E_{d-d} = \frac{RT}{k_1}(\ln K + \ln K_{ref}) \tag{16}$$

According to our initial assumption we have for the chemical shift:

$$\delta = \delta_{dia} + \frac{k_2}{\Delta E}. \tag{17}$$

Substituting the expression for $\Delta E_{d\text{-}d}$ we get:

$$\delta = \delta_{dia} + \frac{k_1 k_2}{RT(\ln K + \ln K_{ref})} = \delta_{dia} + \frac{k_1 k_2}{RT} \cdot \frac{1}{(\ln K + \ln K_{ref})}. \tag{18}$$

Now, $\Delta E_{d\text{-}d}$ for $Rh(H_2O)_6^{3-}$ is about 26,000 cm^{-1} and using Eq. (13) for a low-spin d^6-metal ion we get a stabilization energy of 750 kJ/mol which equals $\ln K_{ref} = 300$. Thus, normally the $\ln K_{ref}$ term will be much larger than the $\ln K$ term and we can use the two first terms in the development of $1/(1+x)$ in a power series to rewrite the last factor in the equation as

$$\frac{1}{1+x} = 1 - x + 2x^2 - \cdots \Rightarrow \frac{1}{(\ln K + \ln K_{ref})} \approx \frac{1}{\ln K_{ref}}\left(1 - \frac{\ln K}{\ln K_{ref}}\right). \tag{19}$$

For the chemical shift we finally get:

$$\begin{aligned} \delta &= \delta_{dia} + \frac{k_1 k_2}{RT}\frac{1}{\ln K_{ref}}\left(1 - \frac{\ln K}{\ln K_{ref}}\right) \\ &= \delta_{dia} + \frac{k_1 k_2}{RT}\frac{1}{\ln K_{ref}} - \frac{k_1 k_2}{RT}\frac{1}{\ln K_{ref}}\frac{\ln K}{\ln K_{ref}} = A - \frac{B \log K}{\log e}. \end{aligned} \tag{20}$$

We note that the slope and the intercept in this equation has a certain relationship. Since the diamagnetic shift is known for rhodium(III), $\delta_{dia} = -5000 \pm 1000$ ppm,[8] we can subtract this value from the constant term in the least-squares fitted equation for Fig. 1: $\delta = 10{,}000 - 200 \log K$. We then obtain 15,000 ppm, and by dividing this number with the slope and $\log e$ we get $\ln K_{ref} = 170$ which is in reasonable agreement with the $\ln K_{ref} = 300$ calculated above since we know that the $\langle r^{-3}\rangle_d$ factor also varies in this case.

CONCLUSIONS

Numerous examples have shown that the two terms $1/\Delta E$ and $\langle r^{-3}\rangle_d$ in the simplified version of Ramsey's equation are normally responsible for the change in transition metal NMR chemical shifts. Only in cases of deviation from ideal symmetry do we have to consider the imbalance of charge, ΣQ_N. An analysis of these two factors in terms of metal–ligand bond energies lends credibility to the empirically found correlation of metal shifts with stability constants. Furthermore, if we consider only the $1/\Delta E$ parameter for shifts and stabilities, a linear relationship can be derived.

The examples shown also clearly demonstrate the scope and limitations of the correlation. The metal–ligand bond has to remain of the same type. This is a rather ill-defined condition, but, for example, large deviations in the mixture of covalent–ionic bond, possibilities of a change of formal oxidation state of the metal, and change in the ligand donating orbital (e.g., sp-sp^2-sp^3) seem to be important factors.

A change of symmetry may also have an influence, and, of course, when entropy changes are important for the stability, for example when two unidentate ligands are changed for a bidentate, the method is not applicable.

As for the uses of this type of correlation, it may be of importance for stability estimates in cases where the experimental values are very difficult, or impossible, to obtain. Typically this would be for the transition metals with extremely slow ligand exchange rates. Of these, for example, Co(III) (low spin), Rh(III) and Pt(II) have reasonable NMR characteristics.

Moreover, this analysis clearly shows the usefulness of the simplified version of Ramsey's equation and may help in future interpretations of transition metal NMR chemical shifts.

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References

1. Philipsborn, W. v. *Pure & Appl. Chem.* **1986**, *58*, 513.
2. *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; Vol. 13.
3. General references to invers detection: Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285, Bax, A.; Marion, D. *J. Magn. Reson.* **1988**, *78*, 186.
4. Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.
5. Mason, J. *Chem. Rev.* **1987**, *87*, 1299.
6. Juranic, N. *Coord. Chem. Rev.* **1989**, *96*, 253.
7. Read, M. C.; Glaser, J.; Sandström, M. *J. Chem. Soc. Dalton* **1992**, 233.
8. Read, M. C.; Glaser, J.; Persson, I.; Sandström, M. *J. Chem. Soc. Dalton* **1994**, 3243.
9. Calderazzo, F.; Lucken, A. C.; Williams, D. F. *J. Chem. Soc. A* **1967**, 154.
10. Dean, R. R.; Green, J. C. *J. Chem. Soc. A* **1968**, 3047.
11. Mason, J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 197.
12. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 4th ed.; Wiley: New York, 1989.
13. Mann, B. E. in *NMR of Newly Accessible Nuclei*; Laszlo, P. Ed.; Academic Press: New York, 1983; Vol. 2, p 302.
14. Mann, B. E. in *Transition Metal Nuclear Magnetic Resonance*, Pregosin, P. S. Ed.; Elsevier: Amsterdam, 1991; Vol. 13, p 177.
15. Freeman, W.; Pregosin, P. S.; Sze, S. N.; Venanzi, L. M. *J. Magn. Resonance* **1976**, *22*, 473
16. Pesek, J. J.; Mason, W. R. *J. Magn. Resonance* **1977**, *25*, 519.
17. Appleton, T. G.; Hall, J. R.; Ralph, S. F.; Thompson, C. S. M. *Inorg. Chem.* **1984**, *23*, 3521.
18. Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, 1964, Special Publication 17.
19. Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976, Vol. 4, Inorganic Complexes.
20. Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1982, Vol. 5, First Supplement.
21. Högfeldt, E. *Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands*; Pergamon: Oxford, 1982.
22. Coley, R. F.; Martin, D. S. *Inorg. Chim. Acta* **1972**, *7*, 573.
23. Miller, S. E.; Gerard, J.; House, D. A. *Inorg. Chim. Acta* **1991**, *190*, 135.
24. Jestin, J.-L.; Chottard, J. C.; Frey, U.; Laurenczy, G.; Merbach, A. E. *Inorg. Chem.* **1994**, *33*, 4277.
25. Rochon, F. D.; Morneau, A. *Magn. Res. Chem.* **1991**, *29*, 120.
26. Keppler, B. K. *New J. Chem.* **1990**, *14*, 389.
27. Haiduc, I.; Silvestru, C. *Coord. Chem. Rev.* **1990**, *99*, 253.
28. Bancroft, D. P.; Lepre, C. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 6860.
29. Macdonald, F. M.; Sadler, P. J. *Magn. Reson. in Chem.* **1991**, *29*, S52.
30. Åkermark, B.; Blomberg, M.; Glaser, J.; Öhrström, L.; Wahlberg, S.; Wärnmark, K.; Zetterberg, K. *J. Am. Chem. Soc.* **1994**, *116*, 3405.
31. Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621–4626.
32. Bender, B. R.; Koller, M.; Nanz, D.; Philipsborn, W. v. *J. Am. Chem. Soc.* **1993**, *115*, 5889.
33. Curnow, O. J.; Hughes, R. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 3153
34. Ohkuma, T.; Noyori, R. *Chemtr.-Org. Chem.* **1993**, *6*, 325.
35. Tedesco, V.; Philipsborn, W. v. *Organometallics* **1995**, *14*, 3600.
36. Erickson, L. E.; Hooper, J. *unpublished data* **1995**.

37. Ludwig, M.; Öhrström, L.; Steinborn, D. *J. Magn. Res.* **1995**, *33*, 984.
38. Ludwig, M. *Untersuchungen zum trans-Einfluss von Organogruppen in Bis(dimethylglyoximato)rhodium(III)-Komplexen*; Ludwig, M., thesis; Martin-Luther-Universität Halle-Wittenberg, 1995.
39. Asaro, F.; Costa, G.; Dreos, R.; Pellizer, G.; Philipsborn, W. v. *J. Organomet. Chem.*, submitted for publication.
40. (a) Pahor, N. B.; Dreos-Garlatti, R.; Geremia, S.; Randaccio, L.; Tauzher, G.; Zangrando, E. *Inorg. Chem.* **1990**, *29*, 3437, (b) Randaccio, L.; Geremia, S.; Dreos-Garlatti, R.; Tauzher, G.; Asaro, F.; Pellizer, G. *Inorg. Chim. Acta* **1992**, *194*, 1, (c) Dunaj-Jurco, M.; Kettmann, V.; Steinborn, D.; Ludwig, M. *Acta Cryst.* **1994**, *C50*, 1427, (d) Dunaj-Jurco, M.; Kettmann, V.; Steinborn, D.; Ludwig, M. *Acat Cryst.* **1994**, *C51*, 210. (e) Kettmann, V.; Dunaj-Jurco, M.; Steinborn, D.; Ludwig, M. *Acta Cryst.* **1994**, *C50*, 1239, (f) Dunaj-Jurco, M.; Kettmann, V.; Steinborn, D.; Ludwig, M. *Acta Cryst. C* **1995**, *in press*, (g) Dunaj-Jurco, M.; Dusan, M.; Potocnak, I.; Steinborn, D.; Ludwig, M. *Acta Cryst. C* **1995**, *in press*, (h) Potocnak, I.; Dunaj-Jurco, M.; Steinborn, D.; Ludwig, M. *Acta Cryst. C* **1995**, *in press*.