Steric and Electronic Effects on the ^{103}Rh NMR Shifts of (COD)Rh(phosphine) Complexes

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^{103}Rh NMR data of several series of (COD)Rh(phosphine) complexes, (COD)Rh(PR$_3$)Me, (COD)Rh(PR$_3$)Cl, {(COD)Rh(PR$_3$)$_2$)}Y, {(COD)Rh(PPh$_3$)(py)}PF$_6$, (COD)Rh(PR$_3$)$_2$Me, and of one NBD complex, {(NBD)Rh(PPh$_3$)$_2$}PF$_6$, have been measured by inverse two-dimensional ^{1}H,^{103}Rh- or ^{31}P,^{103}Rh{^{1}H} NMR. Within the series, $\delta(^{103}\mathrm{Rh})$ extends from −332 for (COD)Rh(PMe$_3$)$_2$Me to +557 ppm for (COD)Rh(P(NMe$_2$)$_3$)Cl. Upon variations in the first coordination sphere, deshielding increases in the order PR$_3$ < CH$_3$ < py ~ Cl. Going from P(OMe)$_3$ to trialkylphosphines to P(NMe$_2$)$_3$ the same trend for $\delta(^{103}\mathrm{Rh})$ is observed within different series of compounds, which allows an interpretation of the Rh shift which is based on the properties of the phosphorus ligand. A systematic variation of PR$_3$ reveals that paramagnetic shielding of the metal nucleus is caused by an increase in the basicity as well as the cone angle of the ligand. Within a subseries, $\delta(^{103}\mathrm{Rh})$ may quantitatively be described by invoking parameters that are a measure of the basicity and the cone angle of the phosphine ligand. There is no general correlation between $\delta(^{103}\mathrm{Rh})$ and ^{31}P NMR data. Explanations of the observed trends in $\delta(^{103}\mathrm{Rh})$ in terms of the paramagnetic shift are given.

Introduction

^{103}Rh NMR has long been considered to be difficult due to the low gyromagnetic ratio of the ^{103}Rh nucleus (Ξ = 3.16 MHz).[1] Although direct observation on high-field spectrometers has been shown to be possible,[2,3] polarization transfer techniques like INEPT[4,5] and inverse 2D NMR[6−11] have proved more convenient. Inverse 2D ^{103}Rh, X NMR leads to a theoretical sensitivity enhancement of 360 for X = ^{31}P and 5630 for X = ^{1}H, respectively, and therefore provides a powerful tool to obtain ^{103}Rh NMR data for compounds with an observable ^{1}H,^{103}Rh or ^{31}P,^{103}Rh coupling constant.

The number of ^{103}Rh NMR data in the literature still remains restricted although some reviews have been published.[12−15] To take account of changes in the first coordination sphere, a series of the most common ligand atoms has been given by Mann;[15] the Rh nucleus is deshielded in the order O > Cl ~ N > Br > I > S ~ Se > Te > P ~ As ~ Sb ~ H ~ C* ~ C (C* = sp^2-carbon) and hence follows more or less the spectrochemical series.

However, there is still a lack of systematic shift structure correlations which allow a more detailed interpretation of the data in terms of the paramagnetic shift. Von Philipsborn et al.[16] investigated mononuclear Rh(0) diene complexes and found some general trends how the ^{103}Rh chemical shifts depend on the nature of the diene ligands. Moreover, Graham et al.[17] demonstrated that the ^{103}Rh shift correlates with a variety of substituent parameters in ring-substituted (η^5-cyclopentadienyl)dicarbonylrhodium complexes.

Bonnaire et al.[2] studied the complexes (COD)Rh(PPh$_{3-x}$Cy$_x$)Cl with $0 < x < 3$ and found a correlation between the ^{103}Rh chemical shifts and the $^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ coupling constants as well as between $\delta(^{103}\mathrm{Rh})$ and the basicity of the phosphine. As such a correlation would a priori not be expected and since the authors take only four closely related compounds into account and do not consider steric effects, we found it timely to study some series of complexes apt to observe how the ^{103}Rh shift changes upon a systematic variation of the phosphorus ligands. This procedure should also give insight in factors leading to small differences in ^{103}Rh shifts of only some tens of parts per million.

Results and Discussion

The ^{31}P and ^{103}Rh NMR spectra of the following compounds were measured: (i) (COD)Rh(PR$_3$)Me, **1−6**; (ii) (COD)Rh(PR$_3$)Cl, **7−18**; (iii) {(COD)Rh(PR$_3$)$_2$}Y, **19−22**; (iv) {(COD)Rh(PPh$_3$)(py-X)}PF$_6$, **23−25**; (v) (COD)Rh(PR$_3$)$_2$Me, **26−27**; (vi) {(NBD)Rh(PPh$_3$)$_2$}PF$_6$, **28**. Their ^{103}Rh and ^{31}P NMR shifts and $^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ coupling constants have been compiled in Table 1.

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(1) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10A*, 1.
(2) Bonnaire, R.; Davoust, D.; Platzer, N. *Org. Magn. Reson.* **1984**, *22*, 80.
(3) Grüninger, K.-D.; Schwenck, A.; Mann, B. E. *J. Magn. Reson.* **1980**, *41*, 354.
(4) Brevard, C.; Schimpf, R. *J. Magn. Reson.* **1982**, *47*, 528.
(5) Brevard, C.; van Stein, G. C.; van Koten, G. *J. Am. Chem. Soc.* **1981**, *103*, 6746.
(6) Benn, R.; Brevard, C. *J. Am. Chem. Soc.* **1986**, *108*, 5622.
(7) Benn, R.; Brenneke, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *320*, 115.
(8) Benn, R.; Rufinska, A. *Magn. Reson. Chem.* **1988**, *26*, 895.
(9) Elsevier, C. J.; Ernsting, J. M.; de Lange, W. G. J. *J. Chem. Soc., Chem. Commun.* **1989**, 585.
(10) Ernsting, J. M.; Elsevier, C. J.; de Lange, W. G. J.; Timmer, K. *Magn. Reson. Chem.* **1991**, *29*, 118.
(11) Bender, B. R.; Koller, M; Nanz, D.; von Philipsborn, W. *J. Am. Chem. Soc.* **1993**, *115*, 5889.
(12) Kidd, R. G.; Goodfellow, R. J. in: Harris, R. K., Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978.
(13) Benn, R.; Rufinska, A. *Angew. Chem.* **1986**, *98*, 861.
(14) von Philipsborn, W. *Pure Appl. Chem.* **1986**, *58*, 513.
(15) Mann, B. E. in: Pregosin, P. S. *Transition Metal Nuclear Magnetic Resonance*; Elsevier: Amsterdam, 1991; p 177.
(16) Maurer, E.; Rieker, S.; Schollbach, M.; Schwenk, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 26.
(17) Graham, P. B.; Rausch, M. D.; Täschler, K.; von Philipsborn, W. *Organometallics* **1991**, *10*, 3049.

Table 1. ^{103}Rh and ^{31}P NMR Data for Complexes **1–28**^{a,b}

no.	compound	$\delta(^{103}\mathrm{Rh})^c$ (ppm)	$\delta(^{31}\mathrm{P})$ (ppm)	$^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ (Hz)
1	$\mathrm{(COD)Rh(P(OMe)_3)Me}$	−129	139.8	307
2	$\mathrm{(COD)Rh(PMe_3)Me}$	23	−13.8	175
3	$\mathrm{(COD)Rh(PEt_3)Me}$	57	18.4	174
4	$\mathrm{(COD)Rh(P^nPr_3)Me}$	73	8.9	174
5	$\mathrm{(COD)Rh(P^nBu_3)Me}$	73	10.9	175
6	$\mathrm{(COD)Rh(P(NMe_2)_3)Me}$	165	126.7	245
7	$\mathrm{(COD)Rh(P(OMe)_3)Cl}$	253	123.0	249
8	$\mathrm{(COD)Rh(PEt_3)Cl}$	385	22.4	148
9	$\mathrm{(COD)Rh(P^nPr_3)Cl}$	401	13.0	147
10	$\mathrm{(COD)Rh(P^nBu_3)Cl}$	402	13.9	146
11	$\mathrm{(COD)Rh(P^iPr_3)Cl}$	519	38.6	144
12	$\mathrm{(COD)Rh(PCy_3)Cl}$	527	27.0	142
13	$\mathrm{(COD)Rh(PBz_3)Cl}$	417	24.1	151
14	$\mathrm{(COD)Rh(PMe_2Ph)Cl}$	358	2.4	148
15	$\mathrm{(COD)Rh(PMePh_2)Cl}$	348	18.6	151
16	$\mathrm{(COD)Rh(PPh_3)Cl}$	393	31.4	152
17	$\mathrm{(COD)Rh(PpTol_3)Cl}$	402	29.5	151
18	$\mathrm{(COD)Rh(P(NMe_2)_3)Cl}$	557	110.4	199
19	$\mathrm{\{(COD)Rh(PPh_3)_2\}BPh_4}$	−145	27.1	147
20	$\mathrm{\{(COD)Rh(PPh_2Me)_2\}ClO_4}$	−267	11.8	145
21	$\mathrm{\{(COD)Rh(P^nBu_3)_2\}BPh_4}$	−94	4.8	140
22	$\mathrm{\{(COD)Rh(PEt_3)_2\}BPh_4}$	−132	12.5	140
23	$\mathrm{\{(COD)Rh(PPh_3)(py)\}PF_6}$	415	26.0	151
24	$\mathrm{\{(COD)Rh(PPh_3)(p\text{-}Me\text{-}py)\}PF_6}$	419	26.0	152
25	$\mathrm{\{(COD)Rh(PPh_3)(p\text{-}Me_2N\text{-}py)PF_6}$	436	26.1	152
26^d	$\mathrm{(COD)Rh(PMe_3)_2Me}$	−332	−18.1	123
27^e	$\mathrm{(COD)Rh(PMe_2Ph)_2Me}$	−278	−4.0	125
28	$\mathrm{\{(NBD)Rh(PPh_3)_2\}PF_6}$	−4	29.8	155

^{a} T = 298 K unless otherwise specified. ^{b} Cationic complexes in $\mathrm{CDCl_3}$, all other complexes in $\mathrm{C_6D_6}$ unless otherwise specified. ^{c} Relative to Ξ = 3.16 MHz; ± 1.5 ppm. ^{d} In $\mathrm{C_7D_8}$ at 253 K. ^{e} In $\mathrm{CD_2Cl_2}$ at 255 K.

Nuclear magnetic shielding of transition metal nuclei is composed of a diamagnetic and a paramagnetic term. It is widely accepted that the former has almost no influence on the nuclear magnetic shielding of transition metals,[18–19] so only the paramagnetic term σ_p given by the Ramsey equation[20] later developed by Griffith and Orgel[21] has to be taken into account:

$$|\sigma_\mathrm{p}| = \mathrm{const.}(\Delta E)^{-1}\langle r_\mathrm{d}^{-3}\rangle\sum Q_\mathrm{N} \qquad (1)$$

In this equation, ΔE is the average excitation energy, r_d is the expectation value of the d-orbital radius and ΣQ_N is the angular imbalance of charge.

Changes in ΣQ_N generally bear a large influence on σ_p, but as the d-electron configuration, the symmetry and the nature of the ligands are kept constant within the investigated series (with the exception of compounds **26–28**), a discussion of the observed ^{103}Rh NMR shifts can be focussed on ΔE and r_d alone.[22]

The total chemical shift range of the ^{103}Rh nucleus is about 12.000 ppm.[15] For the square-planar d^8-complexes of this study, the obtained values extend from −267 ppm for $\mathrm{\{(COD)Rh(PPh_2Me)_2\}ClO_4}$ to +557 ppm for $\mathrm{(COD)Rh(P(NMe_2)_3)Cl}$ and thus lie at the low frequency end of the whole range. This can be explained by the fact that ΔE assumes large absolute values for square-planar complexes which leads to low values of the paramagnetic shifts.

Replacing COD for NBD in the cation $\mathrm{\{(COD)Rh(PPh_3)_2\}}$ results in a high-frequency shift from −145 ppm in compound **19** to −4 ppm in compound **28**. This is in qualitative and quantitative agreement with earlier obtained results[2,10] and thus justifies the idea of sticking to one series of diene complexes, *i.e.* the COD complexes in this investigation.

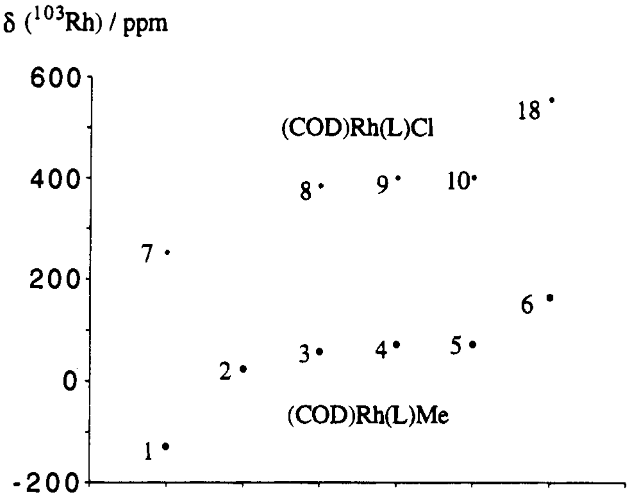

Figure 1. Rh shifts of Me complexes **1–6** and Cl complexes **7–10** and **18**.

Influence of the Ligands in the First Coordination Sphere. The dependence of $\delta(^{103}\mathrm{Rh})$ on the substituents in the first coordination sphere parallels the above mentioned series given by Mann.[15] As for the neutral complexes **1–18**, the methyl compounds appear approximately 350–400 ppm shifted to low frequencies when compared to the chlorides. This can be explained by taking into account that the lone pair of the methyl anion has a higher energy level than that of the chloride anion. In a simple MO consideration, it therefore matches better with the d-orbitals of the metal center which leads to a larger energy splitting ΔE and a smaller paramagnetic shift and thus to a low-frequency shift.

A comparison of the ^{103}Rh chemical shift of the cationic complexes $\mathrm{\{(COD)Rh(PPh_3)_2\}BPh_4}$, **19**, and $\mathrm{\{(COD)Rh(PPh_3)(py)\}PF_6}$, **23**, reveals that substitution of $\mathrm{PPh_3}$ for pyridine causes a high-frequency shift of 560 ppm. As above, this effect may again be explained by the relative energies of the corresponding lone pairs which are generally higher for phosphines than for amines. Moreover, phosphines have a larger π-acceptor ability than pyridine and the effective π-interaction causes an additional increase in ΔE, which accounts for the relatively large low-frequency shift of the bis(phosphine) complexes.

Influence of the Substituents on the Coordinating Atom. For various first row transition metal $\mathrm{PR_3}$ complexes, i.e. of V, Mn, Co, and Ni,[23] shielding differences caused by variation of steric and electronic properties of R have been investigated. It has been shown that the metal shift parallels the bulk and the basicity of the ligand. However, for the ^{103}Rh nucleus, analogous investigations have so far not been carried out in a systematic way. From Table 1 it can be seen that, in going from $\mathrm{P(OMe)_3}$ to the homologous trialkylphosphines and finally to $\mathrm{P(NMe_2)_3}$, the same trend of increasing $\delta(^{103}\mathrm{Rh})$ is observed for the methyl compounds $\mathrm{(COD)Rh(PR_3)Me}$ and for the chlorides $\mathrm{(COD)Rh(PR_3)Cl}$ (cf. Figure 1). In the cationic complexes $\mathrm{\{(COD)Rh(PR_3)_2\}Y}$, a substitution of $\mathrm{PEt_3}$ for $\mathrm{P^nBu_3}$ leads to a high frequency shift of 38 ppm (cf. **21** and **22**), which is slightly more than double the value of 17 ppm found for the corresponding pair of $\mathrm{(COD)Rh(PR_3)Cl}$ complexes (cf. **8** and **10**), matching the replacement of two ligands instead

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(18) Schmidt, H.; Rehder, D. *Transition Met. Chem.* **1980**, *5*, 214.

(19) Nakano, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 661.

(20) Ramsey, N. F. *Phys. Rev.* **1950**, *77*, 567; **1950**, *78*, 699; **1951**, *83*, 540; **1952**, *86*, 243.

(21) Griffith, J. S.; Orgel, L. E. *Trans. Faraday Soc.* **1957**, *53*, 601.

(22) Mason, J. *Chem. Rev.* **1987**, *87*, 1299.

(23) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.

Table 2. $\delta(^{103}\text{Rh})$ NMR Data for (COD)Rh(PR_3)Cl Complexes **7**−**18** and Parameters of the Corresponding Phosphorus Ligands

no.	PR_3	$\delta(^{103}\text{Rh})$	θ (deg)[a]	ν (cm^{-1})[b]
7	$P(OMe)_3$	253	107	2079.5
8	PEt_3	385	132	2061.7
9	P^nPr_3	401	132	2061.0[c]
10	P^nBu_3	402	132	2060.3
11	P^iPr_3	519	160	2059.2
12	PCy_3	527	170	2056.4
13	PBz_3	417	165	2066.4
14	PMe_2Ph	358	122	2065.3
15	$PMePh_2$	348	136	2067.0
16	PPh_3	393	145	2068.9
17	Pp-Tol_3	402	145	2066.7
18	$P(NMe_2)_3$	557	157	2061.9

[a] Tolman's cone angle.[24] [b] Tolman's electronic parameter.[24] [c] Mean value of entry **8** and **10**.

of one phosphine ligand in **21**/**22** as compared to **8**/**10**. Replacing PPh_2Me by PPh_3 causes a high-frequency shift of 122 ppm in case of the cations (cf. **19** and **20**) and of 45 ppm in case of the chlorides (cf. **15** and **16**). It can be concluded that the trend observed for the neutral complexes (COD)Rh(PR_3)Cl and (COD)Rh(PR_3)Me is even amplified in case of the cationic compounds $\{(COD)Rh(PR_3)_2\}Y$ where substitution of two phosphine ligands is considered. These observations show that an interpretation of the Rh shift is possible by focussing on the properties of the phosphorus ligands. A priori, factors like the cone angle and the basicity of the phosphine would seem to be crucial parameters.

The steric properties of the phosphines are best characterized by Tolman's cone angle θ, and the basicity is taken into account by using Tolman's electronic parameter ν.[24] The latter is the IR frequency of the A_1 carbonyl mode of $Ni(CO)_3L$ which can also be considered to be a measure of the combined σ-donor and π-acceptor ability of the ligands L. For the chloride compounds **7**−**18**, the Rh shifts and the corresponding cone angles and electronic parameters have been collected in Table 2.

In order to seperate the steric and electronic parameters, pairs of compounds with similar cone angles, but fairly large differences in basicity and vice versa are considered. On the one hand, $\delta(^{103}\text{Rh})$ of the compounds **8** and **10**, **8** and **15**, **11** and **13**, and **16** and **17**, shows that an increase in basicity (i.e. increase in energy of the lone pair) leads to an increase of the paramagnetic shielding of the Rh nucleus and hence shift towards higher frequency. On the other hand, $\delta(^{103}\text{Rh})$ of pairs of compounds **9** and **11**, **8** and **18**, and **15** and **17** indicates that larger cone angles also cause an increase of paramagnetic shielding. Within the series of the $PMe_{3-x}Ph_x$ complexes (x = 1−3) the steric and electronic effects are opposed. For this reason no linear dependence of $\delta(^{103}\text{Rh})$ on the number of methyl groups is observed within that series.

In order to get an idea about the relationship between the Rh shift and the variables cone angle and basicity, linear regression has been applied to the data set of the chloride compounds **7** to **17**. Model selection based on R^2 as well as stepwise regression support the selection of the equation:[25]

$$\delta(^{103}\text{Rh}) = 395.3 + 2.24(\theta - \theta_{av}) - 7.1(\nu - \nu_{av}) - 0.08(\theta - \theta_{av})(\nu - \nu_{av})$$

By doing so, 95% of the variability of the Rh shift can be explained by this equation. Compared to the remaining variability of 5% the terms ν^2 and θ^2 do not significantly contribute and can be neglected. When substituting numerical values into this equation, it appears that the terms involving θ and ν contribute almost equally to the shift and the product term only to a small extent.

For an interpretation of the steric and electronic influences, these parameters must be brought into connection with the parameters ΔE and r_d in eq 1. The bulkier the phosphorus ligands in (COD)Rh(PR_3)Cl are, the larger is the deviation from 90° geometry and the weaker is the Rh−P bond. Weak interaction between metal and ligands gives rise to smaller ΔE and thus a high-frequency shift. Furthermore, the bond is less covalent and the d-electrons are closer to the metal nucleus; following eq 1, smaller values of r_d reinforce the effect of deshielding the rhodium nucleus. A comparable effect has been observed for bis(diphenylphosphine)methane complexes of the types $\{(COD)Rh(L_2)\}^+$ and $\{Rh(L_2)_2\}^+$, respectively:[10] a strong deviation from the ideal geometry of square-planar d^8-complexes leads to a considerable high-frequency shift.

Electronic effects related to the relative donor character of the phosphines are less important. More basic ligands will increase the electron density on Rh and hence reinforce local paramagnetic effects, leading to high-frequency shifts. Apparently, this effect is stronger than the expected (slight) increase of ΔE, which should lead to an opposite shift. Increase of π-acceptor character (as in the aryl phosphines) will lead to larger values of ΔE and cannot explain the observed high-frequency shift of the Rh nucleus in those cases.

In the pyridine complexes $\{(COD)Rh(PPh_3)(py)\}PF_6$, **23**−**25**, introduction of electron-donating groups (Me, NMe_2) at the para-position leads to a slight increase of electron density on rhodium which, by the line of argumentation used above, produces a larger paramagnetic shift.

Comparison of the Rh Shifts of Chelate Compounds with Those of Open-Chain Analogues. Ring size effects in chelate complexes are reflected by the chemical shift of various transition metals like vanadium,[26] platinum,[27] and rhodium.[10] In all cases strong deviations from ideal geometry which are found in the four-membered chelate rings of dppm-complexes lead to an appreciable high-frequency shift as compared to systems with bond angles of 90° such as five-membered chelates.

In the series $\{(diene)Rh(R_2P(CH_2)_nPR_2)\}Y$[10] as well as in chelate complexes of other metals[26,27] an appreciable low-frequency shift is observed for the four-, six-, and eight-membered metallacycles. In the rhodium complexes, the lowest $\delta(^{103}\text{Rh})$ values are found for the five-membered rings; upon increase or decrease of the ring size, the Rh shift increases steadily. In order to seperate the chelate effect from other parameters, we substituted the bidentate ligand $R_2P(CH_2)_nPR_2$ by two monodentate ligands R_2PMe or R_2PEt (cf. compounds **20** and **22**), which should hardly influence the basicity of the phosphorus ligands. Thus $\Delta\delta$ of corresponding pairs of complexes expresses the influence of the chelate effect on the Rh NMR shift:

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(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(25) Where θ_{av} and ν_{av} represent the average Tolman cone angle (140.5°) and Tolman electronic parameter (2064.8 cm^{-1}), respectively, within the series. The standard deviation in the constant is 6.5; s.d.'s in the coefficients are 0.40, 1.3, and 0.04.

(26) Rehder, D. *J. Magn. Reson.* **1980**, *38*, 419.

(27) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *169*, 107.

$$\Delta\delta = \delta(^{103}\text{Rh})\{(\text{COD})\text{Rh}(\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2)\}\text{Y} - \delta(^{103}\text{Rh})\{(\text{COD})\text{Rh}(\text{R}_2\text{PR}')_2\}\text{Y}$$

In the case of R = Ph, R′ = Me, $\Delta\delta$ is 238 ppm for $n = 2$ and 4 ppm for $n = 4$; in the case R = R′ = Et, $\Delta\delta$ is 401 ppm for $n = 2$ and 6 ppm for $n = 5$. These data clearly imply that the chelate effect does not influence the Rh shift of seven- and eight-membered diphospharhodacycles, whereas a large chelate effect operates in small rings.

In five- to seven-membered diphosphametallacycles a similar trend for the metal shift is not always found: as in $\{(\text{COD})\text{Rh}(\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2)\}\text{Y}$, the metal shift increases steadily in the vanadium complexes *cis*-$[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]$ and $\text{HV}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ upon increase of the ring size from five to seven atoms and approaches the values observed for the open-chain compounds.[26] However, irregularities are observed in the series $(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{PtMe}_2$[27] and cis-$[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{Ph}_2\text{P-}(\text{CH}_2)_n\text{PPh}_2)]$;[26] in the latter, the vanadium nucleus in the $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ complex is much more shielded than in the $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ complex and the shift value of the former deviates strongly from that in the corresponding Ph_2PMe complex.

In the trigonal-bipyramidal, 18-electron complexes $(\text{COD})\text{Rh}(\text{PR}_3)_2\text{Me}$, **26** and **27**, the charge imbalance factor is probably very different from that in the square-planar d^8-complexes $(\text{COD})\text{Rh}(\text{PR}_3)\text{Me}$, **1−6**; hence direct comparison with known compounds or **1−25** is not warranted. It is striking, however, that the shift of **27** does not differ much from that of **20**, so one could argue that the effect of the fifth (alkyl) ligand is not very large. The data for **26** and **27** represent, together with those of compounds **1−6**, a significant contribution to the very few known shifts of *alkyl*rhodium(I) complexes.

Lack of Correlation between the Rh Shift and the P, Rh Coupling Constant. $^1J(^{31}\text{P},^{103}\text{Rh})$ is a measure of the σ-bond order of the P−Rh bond and therefore reflects the strength of the metal−phosphorus bond. The degree of metal−ligand interaction bears a strong influence on ΔE and r_d and involves mainly d-orbital energies and radii. Therefor, an attempt to correlate $\delta(^{103}\text{Rh})$ and $^1J(\text{P,Rh})$ seems to be a priori unwarranted.

Nevertheless, Bonnaire et al.,[2] who studied the chlorides (COD)Rh(L)Cl with $\text{L} = \text{PPh}_{3-x}\text{Cy}_x$ ($x = 0$ −3) have correlated the observed linear increase of the Rh shift with increase of the number of cyclohexyl groups to $^1J(\text{P,Rh})$ for these compounds. The observed correlation is not surprising because the basicity and cone angle within this limited series of phosphines change into the same direction upon substitution of phenyl for cyclohexyl. Our results given in Table 1 clearly show that, as expected, such a correlation does not exist when the extended series **7−18** is taken into account.

The trend in the series of the $\text{PPh}_{3-x}\text{Cy}_x$ complexes can be explained as follows: $^1J(^{31}\text{P},^{103}\text{Rh})$ is an indicator for the strength of the P,Rh bond. As bulky ligands weaken the metal−phosphorus bond, slightly lower J values for the P^iPr_3 and PCy_3 complexes of 144 and 142 Hz, respectively, result (entries **11** and **12**). Thus, the correlation between $\delta(^{103}\text{Rh})$ and $^1J(^{31}\text{P},^{103}\text{Rh})$ in the series of the phenylcyclohexylphosphine complexes is accidental and is due to changes in the same direction of s-orbital and d-orbital overlap due to steric effects; i.e., upon successive introduction of cyclohexyl groups there is a steady decrease in overlap between the metal and lone pair on phosphorus, resulting in smaller ΔE and higher Rh frequency, which at the same time (but due to less s-overlap) also results in a steady decrease in $^1J(^{31}\text{P},^{103}\text{Rh})$.

Experimental Section

The complexes were prepared following literature procedures: **1−6**,[28] **7−18**,[29] **19−20**,[30] **21−22**,[31] **23−25**,[32] **26**,[28] **27**,[33] **28**.[30]

Routine ^{1}H NMR spectra to check purity and to obtain $^2J(^1\text{H},^{103}\text{Rh})$ and routine ^{31}P NMR spectra to obtain $^1J(^{31}\text{P},^{103}\text{Rh})$ were recorded on a Bruker AMX 300 spectrometer (300.13 and 121.15 MHz, respectively). All ^{103}Rh NMR measurements were carried out under temperature control at 298 K in 10-mm tubes under nitrogen unless otherwise stated, solutions were about 0.1 M in concentration.

Compounds **1−6** and **26−27** were measured by inverse 2D ^{1}H,^{103}Rh NMR taking advantage of the relatively large value of $^2J(^1\text{H},^{103}\text{Rh})$ of the methyl protons (ca. 1.5 Hz). For all the other compounds, inverse 2D ^{31}P,^{103}Rh{^{1}H} NMR spectra[9] were acquired.

Inverse two-dimensional ^{1}H,^{103}Rh NMR and ^{31}P,^{103}Rh{^{1}H} NMR spectra were recorded on a Bruker AC 100 NMR spectrometer with inverse modification, a 10-mm ^{103}Rh/^{31}P/^{1}H probe, a second PTS 160 frequency synthesizer with 90° phase shift capability and a BSV-3 heteronucleus decoupler provided with an 80 W selective ^{103}Rh amplifier. The pulse sequence given by Bax et al.[34] was used with either ^{1}H or ^{31}P as the sensitive nucleus; ^{1}H, ^{31}P, and ^{103}Rh pulses {90° (^{1}H) 27 μs, 90° (^{31}P) 38 μs, 90° (^{103}Rh) 18 μs} were applied. In case of ^{31}P,^{103}Rh{^{1}H} NMR continuous BB decoupling (2 W) of ^{1}H was carried out throughout the experiment.

The spectral width was 1500 Hz for ^{1}H and 400−500 Hz for ^{31}P. In the first measurement, the spectral width for ^{103}Rh was 6000 Hz (ca. 2000 ppm) which was covered by 128 t_1 increments, the preparation time was 2 s for ^{1}H,^{103}Rh correlation and 8 s for ^{31}P,^{103}Rh{^{1}H} correlation, two dummy scans were used. To exclude folding and improve resolution, a second and sometimes third measurement with modified ν_0(Rh) values and smaller spectral widths (at most 300 Hz in F_1 using 128 increments) were carried out. The digital resolution of $\delta(^{103}\text{Rh})$ was at least 1.5 ppm. After zero filling in F_1, the 256 × 256 matrix was transformed applying a sine−bell weighting function. The ^{103}Rh spectrum is obtained in F_1, and the ^{1}H or ^{31}P spectrum, respectively, in F_2. The absolute ^{103}Rh frequency was determined by relating it to the reference frequency $\Xi = 3.16$ MHz, scaled for the operating field (^{1}H 100, 131, 316 Hz) to $\nu_\text{ref} = 3.16415$ MHz. Signals at higher frequencies are taken as positive.

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(28) Kulzick, M. A., Price, R. T.; Anderson, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1987**, 333, 105.
(29) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.
(30) Schrock, R. R; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.
(31) Haines, L. M. *Inorg. Chem.* **1970**, 9, 1517.
(32) Crabtree, R. H.; Gautier, A.; Giordano, G.; Khan, T. *J. Organomet. Chem.* **1977**, *141*, 113.
(33) Rice, D. P.; Osborn, J. A. *J. Organomet. Chem.* **1971**, *30*, C84.
(34) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.