Steric effects in organometallic compounds. A [103]Rh NMR study of alkylrhodoximes [1]

Fioretta Asaro [b,2], Giacomo Costa [a], Renata Dreos [a], Giorgio Pellizer [a,*],
Wolfgang von Philipsborn [b]

[a] *Dipartimento di Scienze Chimiche dell'Università di Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy*
[b] *Organisch-chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland*

Abstract

Three series of alkylrhodoximes $[Rh(Hdmg)_2RL]$ (Hdmg = monoanion of dimethlyglyoxime) (L = H_2O, R = Me, Et, ^nPr, ^iPr, ^nBu, ^iBu, $^{neo}Pent$; L = py, R = Me, Et, ^nPr, ^iPr, ^nBu, ^iBu, ^sBu, ^tBu, $^{neo}Pent$, adam, CH_2Cl, CH_2CF_3; L = PPh_3, R = Me, Et, ^nPr, ^iPr, ^nBu, ^iBu, ^tBu, $^{neo}Pent$, adam) were prepared and characterized by ^1H, ^{13}C and ^{31}P NMR spectra; several of the reported compounds are new. The rhodium-103 chemical shifts were measured by (^1H, ^{103}Rh)-2D inverse correlation for the complexes with L = H_2O and py and by (^{31}P, ^{103}Rh)-$\{^1H\}$-2D inverse correlation for those with L = PPh_3. Rh shielding decreases in the order Et > Me > ^nBu > ^iPr > ^sBu > $^{neo}Pent$ > ^tBu. Discussion of the shift dependence on the various alkyl parameters allows us to conclude that, in these compounds the R ligand affects rhodium shielding mainly through distortions of the coordination site due to its bulk. The $^1J[Rh,P]$ values reflect the rhodium–phosphine binding interaction.

Keywords: Rh; Alkylrhodoximes; ^{103}Rh NMR; Steric effects; Chemical shifts

1. Introduction

The chemical shift variation of a transition-metal nucleus in its coordination compounds is usually determined by the paramagnetic shielding term. This depends primarily on the nature of the directly bonded atoms, but can also be strongly influenced by other factors [2]. Owing to the wide shielding range observed for several transition elements, the isotropic metal shift can be a powerful magnifier of small changes of electronic structure and geometry at the coordination site, while the atoms in the first coordination sphere are kept constant. It can be expected that this parameter correlates with other physical and chemical properties of the complexes, also dependent on electronic structure and geometry. Indeed such correlations have been found, e.g. for Co and Rh with catalytic activity [3] and

reactivity [4], hence the metal shielding is becoming an investigation tool of increasing importance. Noticeably, at the same time that small distortions of the coordination site, induced by interaction with the apoenzyme, were invoked to explain the dramatic increase (10^{13}) of the rate of Co–C bond cleavage on going from B_{12} cofactor to the holoenzyme [5], a significant dependence of the ^{59}Co chemical shifts on the bulk of R was pointed out [6] in $alkylCo(Hdmg)_2$ and $alkylCo(DO)(DOH)pn$ complexes, both considered as models for the vitamin B_{12} compounds. Also, in iron(II) and Co(III) porphyrins the metal chemical shifts have been found to reflect both the electronic and geometrical changes induced by different macrocycle rufflings [7]. Furthermore, ^{57}Fe and ^{103}Rh chemical shifts were shown to depend on diene geometry and steric effects of the alkyl substituents in the $[(diene)Fe(CO)_3]$ and $[(indenyl)Rh(diene)]$ complexes [3a]. Excellent correlations between ^{59}Co chemical shifts, catalytic activity and regioselectivity have been evidenced for $[CpCo(diene)]$ and $[(indenyl)Co(diene)]$ complexes [3].

The subject of ^{103}Rh NMR spectroscopy has been reviewed by several authors [3a,8].

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* Corresponding author.
[1] Transition-Metal NMR Spectroscopy Part XXVIII; Part XXVII Ref. [1].
[2] Present address: Dipartimento di Scienze Chimiche dell'Università di Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy.

In addition, it is worth mentioning that a correlation between the magnetic anisotropy of the $[Co(Hdmg)_2$-$PR_3CH_3OH]^+$ species, due mainly to the temperature independent paramagnetic term of the cobalt valence electrons, and the bulk of the axial phosphine, was proposed to explain the trend of CH_3OH methyl proton shifts [9]. To justify this it was suggested that bulkier phosphines cause larger displacements of the equatorial atoms from planarity.

In order to understand further how the various structural factors influence the metal chemical shift, we studied the ^{103}Rh spectra of rhodoximes and compared them with the ^{59}Co spectra of the analogous cobaloximes [6].

Previous investigations on these species allowed us to propose that the overall steric interactions between ligands are smaller in rhodium than in cobalt derivatives, in agreement with the larger metal ionic radius of rhodium [10].

2. Results and discussion

2.1. Rhodium chemical shifts

The rhodium chemical shifts of three series of organorhodoximes $[Rh(Hdmg)_2RL]$ are reported in Table 1. In these compounds a chemical shift range of 2033–2818 ppm is observed, while for the species $[Rh(NH_3)_6]^{3+}$ the resonance occurs at 4776 ppm [11] (Fig. 1). For each alkyl group δRh increases in the order $PPh_3 <$ py $< H_2O$ (Table 1), in agreement with the magnetochemical series [2] and with the behaviour of the ^{59}Co shift in cobaloximes [6]. For any of the L considered, δRh increases in the order Et $<$ Me $<$ ^nBu $<$ ^iPr $<$ ^sBu $<$ $^{neo}Pent$ $<$ ^tBu (Table 1). According to their magnitude, the observed chemical shift variations must be attributed mainly to changes in the ΔE^{-1} and
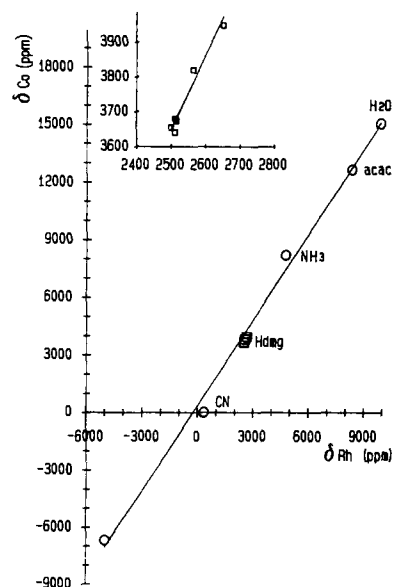

Fig. 1. ^{59}Co chemical shifts vs. ^{103}Rh chemical shifts. O, in ML_6 complexes (L = H_2O δRh = 9924 [a] δCo = 15050 [b]; L_2 = acac δRh = 8350 [b] δCo = 12630 [b]; L = NH_3 δRh = 4776 [a] δCo = 8175 [b]; L = CN δRh = 340 [a] δCo = 0 [b]; diamagnetically shielded nucleus δRh = −5000 [b] δCo = −6700 [b]) □, in $[M(Hdmg)_2Rpy]$ (R = Me, Et, ^nPr, ^iPr, ^nBu, $^{neo}Pent$; δRh [c], δCo [d]). δRh (ppm) from absolute frequency Ξ_{ref} = 3.16 MHz, δCo (ppm) from $[Co(CN)_6]^{3-}$. acac = acetylacetonate; [a] Ref. [11]; [b] Ref. [2]; [c] present work; [d] Ref. [6].

$\langle r^{-3} \rangle$ factors of the paramagnetic term of the Ramsey equation.

The carbon shifts of pyridine, as of other aromatic heterocycles, correlate well with the carbon total electron densities [12]. Thus, the C(4) chemical shift can indicate the electronic charge donated by the pyridine in a coordination compound; of course this charge withdrawal is affected by the other ligands. For the $[Co(Hdmg)_2Xpy]$ complexes the chemical shifts of the pyridine C(4) carbon allowed us to define a parameter, EP (Table 2), which monitors the electronic effect of X transmitted through the metal to the trans ligand [13]. Principal component analysis showed that the EP, de-

Table 1
^{103}Rh and ^{31}P NMR data for $[Rh(Hdmg)_2RL]$ complexes

R	L = H_2O [b]	L = py [c]	L = PPh_3 [c]	
	δRh [a]	δRh [a]	δRh [a]	δP [d]
Me	2672	2509	2038	8.4 (66)
Et	2656	2500	2033	8.3 (62)
^nPr	2665	2516	2057	8.1 (61)
^iPr	2714	2564	2110	8.2 (56)
^nBu	2681	2512	2048	8.0 (61)
^iBu	2712	2552	2086	7.9 (61)
^sBu		2605		
^tBu		2669	2196	9.6 (49)
$^{neo}Pent$	2818	2653	2199	7.4 (57)
adam		2680	2212	9.6 (48)
CH_2Cl		2621		
CH_2CF_3		2741		

[a] δ values in ppm from Ξ_{ref} = 3.16 MHz. [b] D_2O solutions. [c] $CDCl_3$ solutions. [d] $^1J[Rh,P]$ (± 1 Hz) in parentheses.

Table 2
Electronic and steric parameters of the R groups

R	EP [a]	Es [b]	Es' [b]	Ω_s [b]
Me	0	0.0	0.0	0.206
Et	+0.12	−0.07	−0.08	0.256
^nPr	+0.18	−0.36	−0.31	0.269
^iPr	+0.24	−0.47	−0.47	0.304
^nBu		−0.39	−0.31	0.269
^iBu	+0.20	−0.93	−0.93	0.298
^sBu	+0.30	−1.13	−1.00	0.326
^tBu		−1.54	−1.43	0.352
$^{neo}Pent$	+0.19	−1.74	−1.63	0.331
adamantyl	+0.48			
CH_2Cl	−0.35			
CH_2CF_3	−0.55			

[a] Ref. [13]. [b] Ref. [15].
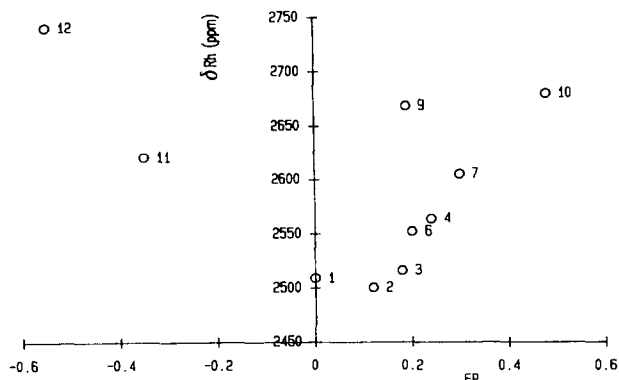
Fig. 2. ^{103}Rh chemical shifts in [Rh(Hdmg)$_2$Rpy] vs. EP (R = Me (1), Et (2), ^{n}Pr (3), ^{i}Pr (4), ^{t}Bu (6), ^{s}Bu (7), ^{neo}Pent (9), adam (10), CH$_2$Cl (11), CH$_2$CF$_3$ (12)).

Fig. 3. ^{103}Rh chemical shifts in [Rh(Hdmg)$_2$Rpy] vs. $- Es$ (R = Me (1), Et (2), ^{n}Pr (3), ^{i}Pr (4), ^{n}Bu (5), ^{i}Bu (6), ^{s}Bu (7), ^{t}Bu (8), ^{neo}Pent (9)).

termined mainly by electronic parameters σ_I and σ_R^-, also takes into account the variations of the donor capacity of X due to steric interactions with the other ligands [14].

For the compounds [Rh(Hdmg)$_2$Xpy], X = CH$_2$CF$_3$, CH$_2$Cl, CH$_3$, the rhodium shift diminishes with increasing EP values [13] (Fig. 2), i.e. as X becomes a better donor. Both $\langle r^{-3} \rangle$ and, in a simplified ligand field description, ΔE^{-1} are expected to decrease as the tendency of X to release electronic charge grows, and this can easily explain the trend of shifts observed within the above triad. For the non-functionalized alkyl derivatives [Rh(Hdmg)$_2$Rpy], the slope of the plot of δRh vs. EP is reversed (Fig. 2): δRh increases as R becomes a better donor and large shift differences are also found between compounds that differ only weakly in electron releasing ability. Some factors different from those dominating the EP parameter must be responsible for the trend of rhodium shifts within this series of compounds.

The rhodium chemical shifts of the compounds [Rh(Hdmg)$_2$Rpy] correlate both with the Taft steric parameter Es [15] ($R = 0.951$) (Fig. 3), and with the modified Taft parameter Es' [15] ($R = 0.948$) (Fig. 4). Es and Es' (Table 2) were determined from kinetic measurements. The former is an average value obtained from the rate constants of two hydrolysis and two esterification reactions [15]. The latter relies on a single accurately chosen standard reaction (the acid catalysed esterification of carboxylic acids in methanol at 40°C) and correlates with the Van der Waals radius of the substituent with $R^2 = 0.99986$ [15].

The rhodium chemical shifts of the compounds [Rh(Hdmg)$_2$Rpy] correlate with the solid angle Ω_s [15,16] ($R = 0.886$) as well. This correlation improves to $R = 0.977$ when the methyl derivative is excluded (Fig. 5). The parameter Ω_s (Table 2) was proposed by Hirota and coworkers [16] as an indicator of the steric hindrance of a substituent at the access of a reagent, and
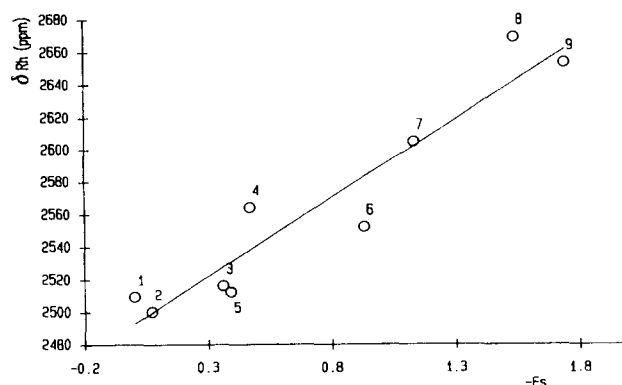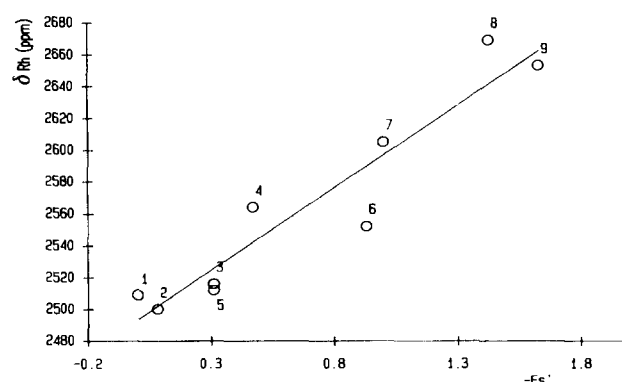

Fig. 4. ^{103}Rh chemical shifts in [Rh(Hdmg)$_2$Rpy] vs. $- Es'$ (R = Me (1), Et (2), ^{n}Pr (3), ^{i}Pr (4), ^{n}Bu (5), ^{i}Bu (6), ^{s}Bu (7), ^{t}Bu (8), ^{neo}Pent (9)).
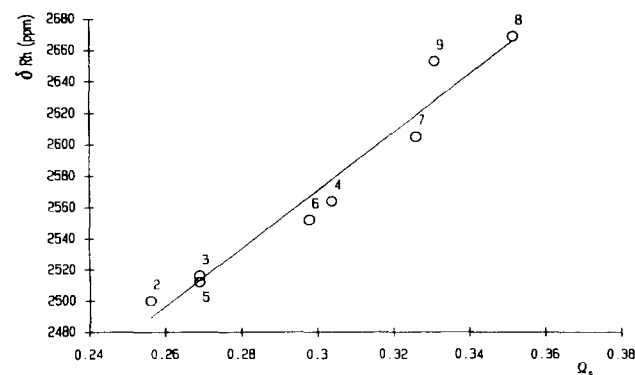
Fig. 5. ^{103}Rh chemical shifts in [Rh(Hdmg)$_2$Rpy] vs. Ω_s (R = Et (2), ^{n}Pr (3), ^{i}Pr (4), ^{n}Bu (5), ^{i}Bu (6), ^{s}Bu (7), ^{t}Bu (8), ^{neo}Pent (9)).

was calculated as the solid angle associated to the area of the shadow projected by a substituent on the surface of a sphere when the centres of projection and of reaction coincide with the centre of the sphere. The contours of the substituent were defined through the Van der Waals radii of the constituent atoms. Ω_s values were calculated for several substituents R from R–COOH and R–CH$_3$ molecules, with reaction centres respectively at the carboxylic and methyl carbon, using the molecular force field.

Solid state X-ray structures of rhodoximes and cobaloximes [10,17,18] showed that the steric interactions between axial and equatorial ligands cause distortions at the coordination site [5]. These structural changes must imply variations at least in the ΔE term of the Ramsey equation. It is likely that more distorted coordinations, like those observed when R is more branched [19], have weaker metal ligand binding interactions and, therefore, smaller relevant ΔEs and larger paramagnetic shieldings. This is in agreement with the correlations we find between the rhodium shifts and the steric parameters of the alkyls. Thus the steric properties of R can be considered the main factor determining the trend of the rhodium chemical shifts in the series [Rh(Hdmg)$_2$Rpy].

The distortions due to the inter-ligand repulsions affect various geometrical features of the coordination site. The dependence of the ΔEs on the distortions is not necessarily simple. The available steric parameters are probably not very adequate to quantitatively define the relevant geometrical changes near the metal. Therefore, the correlations found between rhodium chemical shifts and alkyl steric parameters are even better than one could expect.

We cannot give a satisfactory explanation for the above reported remarkable improvement in the correlation between δRh and Ω_s when the methyl derivative is neglected, but we recall that within the compounds [Rh(Hdmg)$_2$Rpy] the Rh–C bond is also unexpectedly long when R = Me [10].

The prominent role of the steric interactions between ligands in determining the trend of rhodium chemical shifts in the unsubstituted alkylrhodoximes is supported by the comparison between metal shifts of homologous cobalt and rhodium compounds. Notwithstanding their large chemical shift ranges, the two elements have almost the same magnetochemical series and there is a very good correlation ($R = 0.992$) between the metal shifts in hexacoordinate high-symmetry Co(III) and Rh(III) species [M(H$_2$O)$_6$]$^{3+}$, [M(CN)$_6$]$^{3-}$, [M(NH3)$_6$]$^{3+}$, M(acac)$_3$ [2,11] (Fig. 1). The values of δCo(III) and δRh(III), extrapolated to zero paramagnetic term [2], properly enter the correlation as well. Cobalt shows a stronger dependence on the chemical environment, the slope in the δCo(III) vs. δRh(III) plot being 1.5. Also, for the compounds [M(Hdmg)$_2$Rpy]

with non-functionalized alkyl groups R, there is a good direct correlation between the cobalt [6] and the rhodium shifts (Fig. 1). This indicates that the trend of metal shifts should have the same explanation in these alkylrhodoximes and alkylcobaloximes, thus confirming that the steric factors also play a dominant role in the latter compounds, as previously suggested [6]. However, for these complexes the slope is 2.1, noticeably higher than for the ML$_6$ compounds. The distortions of the coordination site caused by the steric interactions between ligands have been found to be larger in the alkylcobaloximes than in the corresponding alkylrhodoximes [10]; this accounts satisfactorily for the increased sensitivity of the cobalt relative to the rhodium shift upon ligand changes. Interestingly, if one considers only the CF$_3$CH$_2$ and CH$_3$ derivatives the slope returns to the usual 1.5 value.

The rhodium shifts for the compounds [Rh(Hdmg)$_2$-RH$_2$O] and [Rh(Hdmg)$_2$RPPh$_3$] have trends parallel to those of the pyridine series (Table 1), in line with the above explanation.

2.2. Rhodium–phosphorus coupling constants and phosphorus chemical shifts

For the triphenylphosphine rhodoximes [Rh(Hdmg)$_2$-XPPh$_3$], the rhodium–phosphorus coupling constant diminishes strongly on going from X = H$_2$O (139 Hz), to X = Cl (123 Hz) [20], to X = CH$_3$ (66 Hz), to X = other non-functionalized alkyls (61–48 Hz) (Table 1). Quite often the variations of the direct metal–phosphorus coupling constant reflect changes in the metal–phosphorus binding interaction; thus the above trend of ^1J[Rh,P] indicates a weakening of the rhodium–phosphorus bond as the donor ability of X increases, as expected. Such observations were also recently made in [(COD)Rh(phosphine)] complexes [21].

Kinetic measurements on the reaction

$$[Rh(Hdmg)_2Xpy] + PPh_3$$

$$\rightarrow [Rh(Hdmg)_2XPPh_3] + py$$
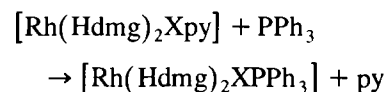
have shown that the rate constant, which depends on the rhodium pyridine binding energy, increases as X becomes a better donor [10]. Thus, in the [Rh(Hdmg)$_2$XL] rhodoximes, the electronic properties of X, reflected by the pyridine C(4) chemical shift, show consistent overall monotonic correlations both with the "trans influence" exerted by the ligand X trans to the metal–phosphorus bond monitored through ^1J[Rh,P] when L = PPh$_3$ [22], and with the "trans effect" of X defined through kinetic measurements. This holds for a wide range of X. Therefore the electronic properties of X can be considered the main factor for the above "trans influence" and "trans effect".

As in PMe$_3$Fe(II)tetraphenylporphyrins [23], in the

compounds [Rh(Hdmg)$_2$XPPh$_3$] the phosphorus chemical shift [20] correlates with the metal shift when X = H$_2$O, Cl, PPh$_3$, CH$_3$ [24], but for the non-functionalized alkyl derivatives the variations in phosphorus shielding are small and no correlation with the rhodium shifts can be envisaged.

3. Conclusions

The steric interactions between the axial alkyl and the equatorial macrocycle explain the trends of the metal shifts in the unsubstituted alkyl derivatives of rhodoximes and cobaloximes. These findings provide further evidence for the important role that the steric properties can have in determining the trend of metal chemical shifts within organometallics series.

The discussion of our data confirms that the chemical shift of the metal can efficiently monitor the distortions of its coordination site. Such distortions are supposed to be very important in modulating the chemical properties of complexes, especially the catalytic and enzymatic ones. Thus, transition metal shielding proves increasingly promising as a detector of relevant subtle structural changes.

Because of their very high sensitivity and good correlations, the metal chemical shifts in organorhodoximes and organocobaloximes could become the basis for the definition of a steric parameter for non-functionalized alkyl groups. One should not expect this parameter to be suitable for all organometallics, differences in metal electronic configuration and coordination geometry being fundamental in determining the kinds of distortion and their effects on the metal chemical shift. For example, our rhodium shifts do not correlate properly with the ^{195}Pt shifts in CpPt(IV)RMe$_2$ complexes (R = Me, Et, ^{n}Pr, ^{n}Bu, ^{i}Pr) [25], that are far from octahedral, but such parameters could be useful for pseudo-octahedral systems where the alkyl bonded to the metal interacts sterically with the cis ligands.

After this work was completed the authors became aware of a related study on rhodoximes and organorhodoximes in which electronic ligand effects were investigated by ^{103}Rh NMR [26].

4. Experimental section

4.1. ^{1}H, ^{13}C, ^{31}P NMR spectra

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AM-400 and JEOL EX-400 spectrometers (^{1}H at 400 MHz, ^{13}C at 100.4 MHz, ^{31}P at 161.7 MHz).

Solvents were CDCl$_3$ for [Rh(Hdmg)$_2$Rpy] and [Rh(Hdmg)$_2$RPPh$_3$] and D$_2$O for [Rh(Hdmg)$_2$RH$_2$O]. For the ^{1}H and ^{13}C spectra, TMS and DSS were used as

internal standards respectively in the CDCl$_3$ and D$_2$O solutions. For the ^{31}P spectra, H$_3$PO$_4$ (10%) was used as external standard.

4.2. ^{103}Rh NMR measurements

The ^{103}Rh spectra were measured at 298 ± 1 K from about 2 × 10^{-2} molar solutions in 5 mm sample tubes on Bruker AM-400 and AMX-600 spectrometers, both equipped with a triple resonance inverse probehead. The ^{103}Rh chemical shifts are reported in ppm from the absolute frequency standard of Ξ_{ref} = 3.16 MHz. For the [Rh(Hdmg)$_2$RPPh$_3$] series, polarization transfer from ^{31}P was exploited, since the latter is directly bonded to ^{103}Rh. In the [Rh(Hdmg)$_2$Rpy] and [Rh(Hdmg)$_2$RH$_2$O] complexes, polarization transfer was accomplished from ^{1}H through ^2J[Rh,H] (about 2–3 Hz) for the alkyls bearing one hydrogen atom in α-position. For R = adam and ^{t}Bu, vicinal Rh,H coupling (~ 1 Hz) to the pyridine C$_2$-H could be utilized.

On the AM-400 the pulse sequences used for (^{31}P, ^{103}Rh)-{^{1}H} inverse correlation were [27]: (a) zero-quantum-filtered 2D-inverse shift correlation $\pi/2$ (^{31}P)-Δ-$\pi/2$(^{103}Rh)/π(^{31}P)-t1-$\pi/2$(^{103}Rh)-Acq, Δ = $1/(2 \times J$[Rh,P]) and (b) "Overbodenhausen-transfer" 2D-correlation $\pi/2$(^{31}P)-Δ-π(^{103}Rh)/π(^{31}P)-Δ-$\pi/2$(^{103}Rh)/$\pi/2$(^{31}P)-t1-$\pi/2$(^{103}Rh)/$\pi/2$(^{31}P)-Acq, Δ = $1/(4 \times J$[Rh,P]), both with continuous broad-band ^{1}H decoupling by means of WALTZ 16 sequence. For the phase sensitive 2D (^{1}H, ^{103}Rh) correlation via heteronuclear zero and double quantum coherence, the pulse sequence was $\pi/2$(^{1}H)-Δ-$\pi/2$(^{103}Rh)-t1/2-π(^{1}H)-t1/2-$\pi/2$(^{103}Rh)-Δ-Acq, Δ = $1/(2 \times J$[Rh,H]).

On the AMX-600 the following pulse sequences were used. For (^{31}P, ^{103}Rh)-{^{1}H} inverse correlation: $\pi/2$(^{31}P)-Δ-$\pi/2$(^{103}Rh)-t1/2-π(^{31}P)-t1/2-$\pi/2$-(^{103}Rh)-Δ-Acq, Δ = $1/(2 \times J$[Rh,P]); for the (^{1}H, ^{103}Rh) correlation: $\pi/2$(^{1}H)-Δ-$\pi/2$(^{103}Rh)-t1/2-π(^{1}H)-t1/2-$\pi/2$(^{103}Rh)-Acq, Δ = $1/(2 \times J$[Rh,H]).

4.3. Preparation

4.3.1. [Rh(Hdmg)$_2$Rpy] (R = Me (1), Et (2), ^{n}Pr (3), ^{i}Pr (4), ^{n}Bu (5), ^{i}Bu (6), ^{s}Bu (7), ^{t}Bu (8), ^{neo}Pent (9), adam (10), CH$_2$Cl (11), CH$_2$CF$_3$ (12))

The [Rh(Hdmg)$_2$Rpy] were prepared as previously reported [10].

1. ^{1}H NMR (CDCl$_3$): δ 8.50 (m, 2H, C$_2$-H py), 7.73 (m, 1H, C$_4$-H py), 7.31 (m, 2H, C$_3$-H py), 2.14 (s, 12H, CH$_3$ Hdmg), 0.28 (d, 3H, CH$_3$, ^2J[Rh,H] = 2.5 Hz). ^{13}C NMR (CDCl$_3$): δ 149.5 (C=N), 149.6 (C$_2$ py), 137.8 (C$_4$ py), 125.7 (C$_3$ py), 11.8 (CH$_3$ Hdmg), −0.6 (d, CH$_3$, ^1J[Rh,C] = 23 Hz).

2. ^{1}H NMR (CDCl$_3$): δ 8.47 (m, 2H, C$_2$-H, py), 7.70 (m, 1H, C$_4$-H py), 7.30 (m, 2H, C$_3$-H py), 2.13 (s, 12H, CH$_3$ Hdmg), 1.24 (dq, 2H, CH$_2$CH$_3$,

^2J[Rh,H] = 2.5, ^3J[H,H] = 8 Hz), 0.59 (dt, 3H, CH_2CH_3, ^3J[Rh,H] = 1, ^3J[H,H] = 8 Hz). ^{13}C NMR (CDCl$_3$): δ 149.6 (C_2 py), 149.2 (C=N), 137.5 (C_4 py), 125.4 (C_3 py), 15.2 (d, CH_2CH_3, ^1J[Rh,C] = 24 Hz), 14.9 (CH_2CH_3), 11.8 (CH_3 Hdmg).

3. ^{1}H NMR (CDCl$_3$): δ 8.46 (m, 2H, C_2–H py), 7.69 (m, 1H, C_4–H py), 7.29 (m, 2H, C_3–H py), 2.13 (s, 12H, CH_3 Hdmg), 1.14 (m, 2H, $CH_2CH_2CH_3$), 1.04 (m, 2H, $CH_2CH_2CH_3$), 0.77 (t, 3H, $CH_2CH_2CH_3$, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 149.5 (C_2 py), 149.2 (C=N), 137.5 (C_4 py), 125.4 (C_3 py), 24.5 (d, $CH_2CH_2CH_3$, ^1J[Rh,C] = 23 Hz), 23.1 ($CH_2CH_2CH_3$), 16.2 ($CH_2CH_2CH_3$), 11.8 (CH_3 Hdmg).

4. ^{1}H (CDCl$_3$): δ 8.47 (m, 2H, C_2–H py), 7.70 (m, 1H, C_4–H py), 7.28 (m, 2H, C_3–H py), 2.12 (s, 12H, CH_3 Hdmg), 1.46 (m, 1H, $CH(CH_3)_2$, ^3J[H,H] = 7, ^2J[Rh,H] = 3 Hz), 0.76 (dd, 6H, $CH(CH_3)_2$, ^3J[H,H] = 7, ^3J[Rh,H] = 1 Hz). ^{13}C NMR (CDCl$_3$): δ 149.5 (C_2 py), 149.2 (C=N), 137.3 (C_4 py), 125.3 (C_3 py), 28.6 (d, $CH(CH_3)_2$, ^1J[Rh,C] = 23 Hz), 25.5 ($CH(CH_3)_2$), 11.8 (CH_3 Hdmg).

5. ^{1}H NMR (CDCl$_3$): δ 8.46 (m, 2H, C_2–H py), 7.70 (m, 1H, C_4–H py), 7.30 (m, 2H, C_3–H py), 2.13 (s, 12H, CH_3 Hdmg), 1.2–1.1 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.00 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.77 (t, 3H, $CH_2CH_2CH_2CH_3$, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 149.5 (C_2 py), 149.2 (C=N), 137.5 (C_4 py), 125.4 (C_3 py), 32.1 ($CH_2CH_2CH_2CH_3$), 24.9 ($CH_2CH_2CH_2CH_3$), 21.7 (d, $CH_2CH_2CH_2CH_3$, ^1J[Rh,C] = 24 Hz), 14.0 ($CH_2CH_2CH_2CH_3$), 11.8 (CH_3 Hdmg).

6. ^{1}H NMR (CDCl$_3$): δ 8.48 (m, 2H, C_2–H py), 7.71 (m, 1H, C_4–H py), 7.31 (m, 2H, C_3–H py), 2.14 (s, 12H, CH_3 Hdmg), 1.17 (m, 2H, $CH_2CH(CH_3)_2$, ^2J[Rh,H] = 2 Hz), 1.15 (m obs., 1H, $CH_2CH(CH_3)_2$, ^3J[Rh,H] = 1 Hz), 0.76 (d, 6H, $CH_2CH(CH_3)_2$, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 149.4 (C_2 py), 149.3 (C=N), 137.5 (C_4 py), 125.4 (C_3 py), 31.9 (d, $CH_2CH(CH_3)_2$, ^1J[Rh,C] = 24 Hz), 28.7 (CH_2CH-($CH_3)_2$), 25.5 ($CH_2CH(CH_3)_2$), 11.9 (CH_3 Hdmg).

7. ^{1}H (CDCl$_3$): δ 8.46 (m, 2H, C_2–H py), 7.68 (m, 1H, C_4–H py), 7.28 (m, 2H, C_3–H py), 2.12 (s, 12H, CH_3 Hdmg), 1.23 (m, 1H, $CH(CH_3)CH_2CH_3$), 0.92 (m, 2H, $CH(CH_3)CH_2CH_3$), 0.78 (t, 3H, $CH(CH_3)CH_2CH_3$, ^3J[H,H] = 7 Hz), 0.77 (d, 3H, $CH(CH_3)CH_2CH_3$, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 149.5 (C_2 py), 149.3 (C=N), 137.4 (C_4 py), 125.3 (C_3 py), 36.7 (d, $CH(CH_3)CH_2CH_3$, ^1J[Rh,C] = 23 Hz), 31.1 ($CH(CH_3)CH_2CH_3$), 20.7 ($CH(CH_3)CH_2CH_3$), 13.3 ($CH(CH_3)CH_2CH_3$), 11.8 (CH_3 Hdmg).

8. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.43 (m, 2H, C_2–H py), 7.67 (m, 1H, C_4–H py), 7.27 (m, 2H, C_3–H py), 2.08 (s, 12H, CH_3 Hdmg), 0.64 (d, 9H, $C(CH_3)_3$, ^3J[Rh,H] = 1 Hz). ^{13}C NMR (CDCl$_3$): δ 149.7 (C=N),

149.2 (C_2 py), 137.5 (C_4 py), 125.3 (C_3 py), 33.7 ($C(CH_3)_3$), 32.8 (d, $C(CH_3)_3$, ^1J[Rh,C] = 26 Hz), 11.8 (CH_3 Hdmg).

9. ^{1}H NMR (CDCl$_3$): δ 8.47 (m, 2H, C_2–H py), 7.69 (m, 1H, C_4–H py), 7.29 (m, 2H, C_3–H py), 2.10 (s, 12H, CH_3 Hdmg), 1.34 (d, 2H, $CH_2C(CH_3)_3$, ^2J[Rh,H] = 3 Hz), 0.77 (s, 9H, $CH_2C(CH_3)_3$). ^{13}C NMR (CDCl$_3$): δ 149.8 (C=N), 149.1 (C_2 py), 137.5 (C_4 py), 125.4 (C_3 py), 37.4 (d, $CH_2C(CH_3)_3$, ^1J[Rh,C] = 26 Hz), 35.3 ($CH_2C(CH_3)_3$), 31.5 (CH_2C-($CH_3)_3$), 11.9 (CH_3 Hdmg).

10. ^{1}H NMR (CDCl$_3$): δ 8.40 (m, 2H, C_2–H py), 7.66 (m, 1H, C_4–H py), 7.26 (m, 2H, C_3–H py), 2.09 (s, 12H, CH_3 Hdmg), 1.75 (m, 3H, H_γ adam), 1.73 (m, 6H, H_β adam), 1.65 (m, 3H, H_δ adam, ^3J[H_δ,$H_{\delta'}$] = 12 Hz), 1.54 (m, 3H, $H_{\delta'}$ adam, ^3J[H_δ,$H_{\delta'}$] = 12 Hz). ^{13}C NMR (CDCl$_3$): δ 149.7 (C=N), 149.3 (C_2 py), 137.4 (C_4 py), 125.2 (C_3 py), 46.7 (C_α adam), 42.9 (d, C_1 adam, ^1J[Rh,C] = 26 Hz), 37.9 (C_γ adam), 32.7 (C_β adam), 11.9 (CH_3 Hdmg).

11. ^{1}H NMR (CDCl$_3$): δ 8.49 (m, 2H, C_2–H py), 7.75 (m, 1H, C_4–H py), 7.34 (m, 2H, C_3–H py), 3.60 (d, 2H, CH_2Cl, ^2J[Rh,H] = 3 Hz), 2.16 (s, 12H, CH_3 Hdmg). ^{13}C NMR (CDCl$_3$): δ 150.3 (C=N), 149.7 (C_2 py), 138.1 (C_4 py), 125.7 (C_3 py), 38.8 (d, CH_2Cl, ^1J[Rh,C] = 30 Hz), 11.9 (CH_3 Hdmg).

12. ^{1}H NMR (CDCl$_3$): δ 8.48 (m, 2H, C_2–H py), 7.76 (m, 1H, C_4–H py), 7.34 (m, 2H, C_3–H py), 2.13 (s, 12H, CH_3 Hdmg), 1.34 (dq, 2H, CH_2CF_3, ^2J[Rh,H] = 3, ^3J[F,H] = 15.5 Hz). ^{13}C NMR (CDCl$_3$): δ 150.6 (C=N), 149.5 (C_2 py), 138.3 (C_4 py), 132.0 (q, CH_2CF_3, ^2J[C,F] = 276 Hz), 125.8 (C_3 py), 12.2 (dq, CH_2CF_3, ^1J[Rh,C] = 28, ^2J[C,F] = 56 Hz), 11.8 (CH_3 Hdmg).

4.3.2. [Rh(Hdmg)₂RH₂O] (R = Me(13), Et (14), ^{n}Pr (15), ^{i}Pr (16), ^{n}Bu (17), ^{i}Bu (18), ^{neo}Pent (19))

The [Rh(Hdmg)$_2$RH$_2$O] complexes were obtained from the corresponding [Rh(Hdmg)$_2$RI] derivatives [28], dissolved in methanol, by treatment with a stoichiometric amount of AgNO$_3$ dissolved in water. After partial evaporation of the methanol the product separated as a dark yellow powder. Care was taken to avoid acidic conditions, since the [Rh(Hdmg)$_2$RH$_2$O] derivatives undergo protonation at the equatorial ligand more easily than the corresponding aquocobaloximes [18,24].

13. ^{1}H NMR (D$_2$O): δ 2.24 (s, 12H, CH_3 Hdmg), 0.41 (d, 3H, CH_3, ^2J[Rh,H] = 2.7 Hz). ^{13}C NMR (D$_2$O): δ 157.1 (C=N), 14.4 (CH_3 Hdmg), -1.1 (d, CH_3, ^1J[Rh,C] = 26 Hz).

14. ^{1}H NMR (D$_2$O): δ 2.24 (s, 12H, CH_3 Hdmg), 1.50 (dq, 2H, CH_2CH_3, ^2J[Rh,H] = 3, ^3J[H,H] = 7.3 Hz), 0.47 (dt, 3H, CH_2CH_3, ^3J[Rh,H] = 1.5, ^3J[H,H] = 7.5 Hz). ^{13}C (D$_2$O): δ 157.1 (C=N), 18.0 (d, CH_2CH_3, ^1J[Rh,C] = 26 Hz), 17.9 (CH_2CH_3), 14.4 (CH_3 Hdmg).

15. ^{1}H NMR (D$_2$O): δ 2.23 (s, 12H, CH_3 Hdmg), 1.37 (m, 2H, CH_2CH$_2$CH$_3$, ^2J[Rh,H] = 3, ^3J[H,H] = 8 Hz), 0.97 (m, 2H, CH$_2$CH_2CH$_3$, ^3J[H,H] = 8, ^3J[H,H] = 7 Hz), 0.72 (t, 3H, CH$_2$CH$_2$CH_3, ^3J[H,H] = 7 Hz). ^{13}C (D$_2$O): δ 157.1 (C=N), 26.6 (d, CH_2CH$_2$CH$_3$, ^1J[Rh,C] = 24 Hz), 26.3 (CH$_2$CH_2CH$_3$), 17.1 (CH$_2$CH$_2$CH_3), 14.4 (CH_3 Hdmg).

16. ^{1}H NMR (D$_2$O): δ 2.23 (s, 12H, CH_3 Hdmg), 1.93 (m, 1H, CH(CH$_3$)$_2$, ^2J[Rh,H] = 3, ^3J[H,H] = 7 Hz), 0.65 (d, 6H, CH(CH_3)$_2$, ^3J[H,H] = 7 Hz). ^{13}C NMR (D$_2$O): δ 157.1 (C=N), 33.7 (d, CH(CH$_3$)$_2$, ^1J[Rh,C] = 26 Hz), 28.2 (CH(CH_3)$_2$), 14.5 (CH_3 Hdmg).

17. ^{1}H NMR (D$_2$O): δ 2.23 (s, 12H, CH_3 Hdmg), 1.41 (m, 2H, CH_2CH$_2$CH$_2$CH$_3$, ^3J[H,H] = 8, ^2J[Rh,H] = 3 Hz), 1.12 (m, 2H, CH$_2$CH$_2$CH_2CH$_3$, ^3J[H,H] = 7, ^3J[H,H] = 7 Hz), 0.94 (m, 2H, CH$_2$CH_2CH$_2$CH$_3$, ^3J[H,H] = 8, ^3J[H,H] = 7 Hz), 0.74 (t, 3H, CH$_2$CH$_2$CH$_2$CH_3, ^3J[H,H] = 7 Hz). ^{13}C NMR (D$_2$O): δ 157.0 (C=N), 35.2 (CH$_2$CH$_2$CH_2CH$_3$), 26.1 (CH$_2$CH$_2$CH$_2$CH$_3$), 24.0 (d, CH_2CH$_2$CH$_2$CH$_3$, ^1J[Rh,C] = 24 Hz), 15.8 (CH$_2$CH$_2$CH_2CH$_3$), 14.45 (CH_3 Hdmg).

18. ^{1}H NMR (D$_2$O): δ 2.24 (12H, CH_3 Hdmg), 1.39 (dd, 2H, CH_2CH(CH$_3$)$_2$, ^2J[Rh,H] = 3, ^3J[H,H] = 5.5 Hz), 1.07 (m, 1H, CH$_2$CH(CH$_3$)$_2$), 0.70 (d, 6H, CH$_2$CH(CH_3)$_2$, ^3J[H,H] = 6.5 Hz). ^{13}C NMR (D$_2$O): δ 157.2 (C=N), 34.0 (d, CH_2CH(CH$_3$)$_2$, ^1J[Rh,C] = 26 Hz), 31.6 (CH$_2$CH(CH$_3$)$_2$), 26.6 (CH$_2$CH(CH_3)$_2$), 14.5 (CH_3 Hdmg).

19. ^{1}H NMR (D$_2$O): δ 2.23 (s, 12H, CH_3 Hdmg), 1.54 (d, 2H, CH_2C(CH$_3$)$_3$, ^2J[Rh,H] = 3 Hz), 0.71 (s, 9H, CH$_2$C(CH_3)$_3$). ^{13}C NMR (D$_2$O): δ 157.6 (C=N), 39.7 (d, CH_2C(CH$_3$)$_3$, ^1J[Rh,C] = 28 Hz), 37.0 (CH$_2$C(CH$_3$)$_3$), 32.8 (CH$_2$C(CH_3)$_3$), 14.5 (CH_3 Hdmg).

4.3.3. [Rh(Hdmg)$_2$RPPh$_3$](R = Me(20), Et(21), ^{n}Pr (22), ^{i}Pr (23), ^{n}Bu (24), ^{i}Bu (25), ^{t}Bu (26), ^{neo}Pent (27), adam (28))

The [Rh(Hdmg)$_2$RPPh$_3$] were prepared in acetone by adding a stoichiometric amount of PPh$_3$ to the corresponding [Rh(Hdmg)$_2$RH$_2$O]. This synthetic route is different from those reported in the literature for the compounds **20–25** [29].

20. ^{1}H NMR (CDCl$_3$): δ 7.50–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.87 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2 Hz), 0.50 (dd, 3H, CH_3, ^3J[P,H] = 6, ^2J[Rh,H] = 2 Hz). ^{13}C NMR (CDCl$_3$): δ 148.4 (C=N), 133.4 (d, C$_2$ PPh$_3$, ^2J[P,C] = 10 Hz), 130.4 (d, C$_1$ PPh$_3$, ^1J[P,C] = 30 Hz), 129.8 (C$_4$ PPh$_3$), 128.1 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 15.1 (dd, CH_3, ^2J[P,C] = 78.5, ^1J[Rh,C] = 20 Hz), 11.6 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 8.4 (d, ^1J[Rh,P] = 66 Hz).

21. ^{1}H NMR (CDCl$_3$): δ 7.50–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.86 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2.5

Hz), 1.31 (m, 2H, CH_2CH$_3$, ^2J[Rh,H] = 2.5, ^3J[P,H] = 7, ^3J[H,H] = 8 Hz), 0.58 (dt, 3H, CH$_2$CH_3, ^3J[H,H] = 8, ^4J[P,H] = 8 Hz). ^{13}C NMR (CDCl$_3$): δ 148.4 (C=N), 133.5 (d, C$_2$ PPh$_3$, ^2J[P,C] = 11 Hz), 130.6 (d, C$_1$ PPh$_3$, ^1J[P,C] = 30 Hz), 129.8 (C$_4$ PPh$_3$), 128.1 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 29.0 (dd, CH_2CH$_3$, ^2J[P,C] = 77, ^1J[Rh,C] = 20 Hz), 13.6 (CH$_2$CH_3), 11.6 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 8.3 (d, ^1J[Rh,P] = 62 Hz).

22. ^{1}H NMR (CDCl$_3$): δ 7.50–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.85 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2 Hz), 1.21 (m, 2H, CH_2CH$_2$CH$_3$, ^3J[H,H] = 6, ^2J[Rh,H] = 2 Hz), 0.98 (m, 2H, CH$_2$CH_2CH$_3$), 0.73 (t, 3H, CH$_2$CH$_2$CH_3, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 148.4 (C=N), 133.5 (d, C$_2$ PPh$_3$, ^2J[P,C] = 11 Hz), 130.3 (d, C$_1$ PPh$_3$, ^1J[P,C] = 26 Hz), 129.7 (C$_4$ PPh$_3$), 128.1 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 37.9 (dd, CH_2CH$_2$CH$_3$, ^2J[P,C] = 76, ^1J[Rh,C] = 20.5 Hz), 21.6 (s, CH$_2$CH_2CH$_3$), 16.2 (d, CH$_2$CH$_2$CH_3, ^4J[P,C] = 13 Hz), 11.5 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 8.1 (d, ^1J[Rh,P] = 61 Hz).

23. ^{1}H NMR (CDCl$_3$): δ 7.50–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.83 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2.5 Hz), 1.29 (m, 1H, CH(CH$_3$)$_2$, ^3J[P,H] = 7.0, ^3J[H,H] = 7.0, ^2J[Rh,H] = 2.5 Hz), 0.75 (d, 6H, CH(CH_3)$_2$, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 148.2 (C=N), 133.5 (d, C$_2$ PPh$_3$, ^2J[P,C] = 12 Hz), 130.8 (d, C$_1$ PPh$_3$, ^1J[P,C] = 26 Hz), 129.6 (C$_4$ PPh$_3$), 128.0 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 40.0 (dd, CH(CH$_3$)$_2$, ^2J[P,C] = 78.5, ^1J[Rh,C] = 20 Hz), 24.1 (d, CH(CH_3)$_2$, ^3J[P,C] = 3 Hz), 11.5 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 8.25 (d, ^1J[Rh,P] = 56 Hz).

24. ^{1}H NMR (CDCl$_3$): δ 7.40–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.86 (d, CH_3 Hdmg, ^5J[P,H] = 2.5 Hz), 1.23 (m, 2H, CH_2CH$_2$CH$_2$CH$_3$, ^2J[Rh,H] = 2.5 Hz), 1.11 (tq, 2H, CH$_2$CH$_2$CH_2CH$_3$, ^3J[H,H] = 7 Hz), 0.94 (m, 2H, CH$_2$CH_2CH$_2$CH$_3$), 0.73 (t, 3H, CH$_2$CH$_2$CH$_2$CH_3, ^3J[H,H] = 7 Hz). ^{13}C NMR (CDCl$_3$): δ 148.3 (C=N), 133.5 (d, C$_2$ PPh$_3$, ^2J[P,C] = 11 Hz), 130.6 (d, C$_1$ PPh$_3$, ^1J[P,C] = 29 Hz), 129.7 (C$_4$ PPh$_3$), 128.1 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 35.3 (dd, CH_2CH$_2$CH$_2$CH$_3$, ^1J[Rh,C] = 20, ^2J[C,P] = 75 Hz), 30.7 (d, CH$_2$CH_2CH$_2$CH$_3$, ^3J[P,C] = 4 Hz), 24.9 (d, CH$_2$CH$_2$CH_2CH$_3$, ^4J[P,C] = 10 Hz), 14.0 (CH$_2$CH$_2$CH$_2$CH$_3$), 11.4 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 8.0 (d, ^1J[Rh,P] = 61 Hz).

25. ^{1}H NMR (CDCl$_3$): δ 7.40–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.85 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2 Hz), 1.23 (m, 2H, CH_2CH(CH$_3$)$_2$, ^2J[Rh,H] = 2.5 Hz), 1.13 (m, 1H, CH$_2$CH(CH$_3$)$_2$, ^3J[H,H] = 6 Hz), 0.69 (d, 6H, CH$_2$CH(CH_3)$_2$, ^3J[H,H] = 6 Hz). ^{13}C NMR (CDCl$_3$): δ 148.3 (C=N), 133.5 (d, C$_2$ PPh$_3$, ^2J[P,C] = 11 Hz), 130.5 (d, C$_1$ PPh$_3$, ^1J[P,C] = 28 Hz), 129.75 (C$_4$ PPh$_3$), 128.1 (d, C$_3$ PPh$_3$, ^3J[P,C] = 9 Hz), 45.5 (dd, CH_2CH(CH$_3$)$_2$, ^2J[P,C] = 75, ^1J[Rh,C] = 20 Hz), 27.8 (CH$_2$CH(CH$_3$)$_2$), 25.7 (d, CH$_2$CH(CH_3)$_2$, ^4J[P,C] =

5.5 Hz), 11.6 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 7.9 (d, ^1J[Rh,P] = 61 Hz).

26. ^{1}H NMR (CDCl$_3$): δ 7.40–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.75 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2 Hz), 0.58 (d, 9H, C(CH_3)$_3$, ^4J[P,H] = 8 Hz). ^{13}C NMR (CDCl$_3$): δ 148.8 (C=N), 133.7 (d, C_2 PPh$_3$, ^2J[P,C] = 11 Hz), 130.9 (d, C_1 PPh$_3$, ^1J[P,C] = 26 Hz), 129.6 (C_4 PPh$_3$), 128.0 (d, C_3 PPh$_3$, ^3J[P,C] = 9 Hz), 40.4 (dd, C(CH$_3$)$_3$, ^2J[P,C] = 83, ^1J[Rh,C] = 22 Hz), 32.1 (C(CH_3)$_3$), 11.5 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 9.6 (d, ^1J[Rh,P] = 49 Hz).

27. ^{1}H NMR (CDCl$_3$): δ 7.40–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.80 (d, 12H, CH_3 Hdmg, ^5J[P,H] = 2 Hz), 1.41 (dd, 2H, CH_2C(CH$_3$)$_3$, ^3J[P,H] = 6, ^2J[Rh,H] = 2.5 Hz), 0.72 (s, 9H, CH$_2$C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$): δ 148.9 (C=N), 133.6 (d, C_2 PPh$_3$, ^2J[P,C] = 11 Hz), 130.4 (d, C_1 PPh$_3$, ^1J[P,C] = 28 Hz), 129.75 (C_4 PPh$_3$), 128.1 (d, C_3 PPh$_3$, ^3J[P,C] = 9 Hz), 50.6 (dd, CH_2C(CH$_3$)$_3$, ^2J[P,C] = 81, ^1J[Rh,C] = 22 Hz), 36.7 (CH$_2$C(CH$_3$)$_3$), 31.6 (d, CH$_2$C(CH_3)$_3$, ^4J[P,C] = 5.5 Hz), 11.5 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 7.4 (d, ^1J[Rh,P] = 57 Hz).

28. ^{1}H NMR (CDCl$_3$): δ 7.40–7.25 (m, 15H, P(C$_6H_5$)$_3$), 1.76 (s, 12H, CH_3 Hdmg), 1.72 (m, 3H, H_γ adam), 1.60 (m, 6H, H_β adam), 1.58 (m, 3H, H_δ adam, ^2J[H$_\delta$,H$_{\delta'}$] = 12 Hz), 1.51 (m, 3H, $H_{\delta'}$ adam, ^2J[H$_\delta$,H$_{\delta'}$] = 12 Hz). ^{13}C NMR (CDCl$_3$): δ 148.6 (C=N), 133.7 (d, C_2 PPh$_3$, ^2J[P,C] = 9 Hz), 131.15 (d, C_1 PPh$_3$, ^1J[P,C] = 24 Hz), 129.6 (C_4 PPh$_3$), 128.0 (d, C_3 PPh$_3$, ^3J[P,C] = 9 Hz), 44.6 (C_α adam), 37.7 (C_γ adam), 33.45 (C_β adam), 11.6 (CH_3 Hdmg). ^{31}P NMR (CDCl$_3$): δ 9.6 (d, ^1J[Rh,P] = 48 Hz).

Acknowledgements

References

[1] E.J.M. Meier, W. Kozminski and W. von Philipsborn, *Magn. Reson. Chem.*, (1995), in press.

[2] N. Juranic, *Coord. Chem. Rev.*, 96 (1989) 253.

[3] (a) W. von Philipsborn, *Pure Appl. Chem.*, 58 (1986) 513; C.M. Adams, G. Cerioni, A. Hafner, H. Kalchhauser, W. von Philipsborn, R. Prewo and A. Schwenk, *Helv. Chim. Acta, 71* (1988) 1116. (b) R. Bönnemann, *Angew. Chem., Int. Ed. Engl., 27* (1985) 248.

[4] (a) V. Tedesco and W. von Philipsborn, *Organometallics, 14* (1995) 3600. (b) B.R. Bender, M. Koller, D. Nanz and W. von Philipsborn, *J. Am. Chem. Soc., 115* (1993) 5889. (c) M. Koller and W. von Philipsborn, *Organometallics, 11* (1992) 467.

[5] L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L.G. Marzilli, *Chem. Soc. Rev., 18* (1989) 225.

[6] C. Tavagnacco, G. Balducci, G. Costa, K. Täschler and W. von Philipsborn, *Helv. Chim. Acta, 73* (1990) 1469.

[7] (a) L. Baltzer and M. Landergren, *J. Am. Chem. Soc., 112* (1990) 2804. (b) H. Bang, J.O. Edwards, J. Kim, R.G. Lawler, K. Reynolds, W.J. Ryan and D.A. Sweigart, *J. Am. Chem. Soc., 114* (1992) 2843.

[8] (a) B.E. Mann, in P.S. Pregosin, (ed.) *Transition Metal NMR Spectroscopy*, Elsevier, Amsterdam, 1991. (b) B.E. Mann, in G.A. Webb, (ed.) *Annual Reports on NMR Spectroscopy*, Vol. 23, Academic Press, London, 1991. (c) R.J. Goodfellow, in J. Mason, (ed.) *Multinuclear NMR*, Plenum Press, New York, 1987.

[9] L.G. Marzilli, P.J. Toscano, J.H. Ramsden, L. Randaccio and N. Bresciani-Pahor, *Adv. Chem. Ser., 196* (1982) 85.

[10] L. Randaccio, S. Geremia, R. Dreos-Garlatti, G. Tauzher, F. Asaro and G. Pellizer, *Inorg. Chim. Acta, 194* (1992) 1.

[11] M.C. Read, J. Glaser, I. Persson and M. Sandström, *J. Chem. Soc., Dalton Trans.*, (1994) 3243.

[12] A. Marker, A.J. Canty, R.T.C. Brownlee, *Aust. J. Chem., 31* (1978) 1255.

[13] E. Zangrando, N. Bresciani-Pahor, L. Randaccio, J.-P. Charland and L.G. Marzilli, *Organometallics, 5* (1986) 1938.

[14] L. Randaccio, S. Geremia, E. Zangrando and C. Ebert, *Inorg. Chem., 33* (1994) 4641.

[15] D. White and N.J. Coville, *Adv. Organomet. Chem., 36* (1994) 95.

[16] T. Komatsuzaki, I. Akai, K. Sakakibara and M. Hirota, *Tetrahedron, 48* (1992) 1539.

[17] N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, *Coord. Chem. Rev., 63* (1985) 1.

[18] N. Bresciani-Pahor, R. Dreos-Garlatti, S. Geremia, L. Randaccio, G. Tauzher and E. Zangrando, *Inorg. Chem., 29* (1990) 3437.

[19] S. Geremia, L. Randaccio, E. Zangrando and L. Antolini, *J. Organomet. Chem., 425* (1992) 131.

[20] F. Asaro, R. Dreos Garlatti, G. Pellizer and G. Tauzher, *Inorg. Chim. Acta, 211* (1993) 27.

[21] C.J. Elsevier, B. Kowall and H. Kragten, *Inorg. Chem., 34* (1995) 4836.

[22] D.W. Meek and T.J. Mazanec, *Acc. Chem. Res., 14* (1981) 266.

[23] L.M. Mink, K.A. Christensen and F.A. Walker, *J. Am. Chem. Soc., 114* (1992) 6930.

[24] W. von Philipsborn, F. Asaro and G. Pellizer, unpublished results, 1993.

[25] L.D. Boardman and R.A. Newmark, *Magn. Reson. Chem., 30* (1992) 481.

[26] M. Ludwig, L. Öhrström and D. Steinborn, *Magn. Reson. Chem.*, (1995), in press.

[27] D. Nanz, *Ph.D. Thesis*, University of Zürich, 1993.

[28] G.N. Schrauzer and R.J. Windgassen, *J. Am. Chem. Soc., 88* (1966) 3738.

[29] D. Steinborn and M. Ludwig, *J. Organomet. Chem., 463* (1993) 65.