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RAPID COMMUNICATION

One-Bond $^{103}Rh,^{15}N$ Coupling Constants of Axial and Equatorial Ligands in Rhodoximes†

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The $^{103}Rh,^{15}N$ coupling constants and ^{15}N chemical shifts of $XRh^{III}(Hdmg)_2L$ rhodoximes (Hdmg = dimethylglyoximate, L = PPh_3 or pyridine, X = halide, alkyl, haloalkyl) were extracted from gradient-selected ($^1H,^{15}N$)-HSQC experiments. Coupling between rhodium and the equatorial oxime nitrogens is large (18–21 Hz) and shows little sensitivity to the nature of the *cis*-oriented ligands X and L. In contrast, coupling between rhodium and the axial pyridine nitrogen is small (6–9 Hz) for X = alkyl but increases to 16–18 Hz in the halide complexes ('*trans* influence'). The structural implications are discussed in conjunction with x-ray data.

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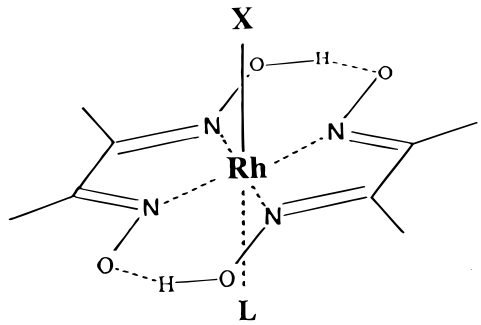
INTRODUCTION

Scalar one-bond coupling constants $^1J(^{15}N,M)$ of transition metal coordination compounds can provide important information on ligand binding, geometry and electronic structure.[2] The application of ^{15}N NMR spectroscopy to rhodium complexes containing nitrogen ligands is limited by the low natural abundance and sensitivity of the ^{15}N nucleus and until recently has required high sample concentrations. For the first time, Bose and Abbott[3] reported $^{103}Rh,^{15}N$ coupling constants of Rh^{III} complexes with alkyldiamine and aza-aromatic ligands from ^{15}N NMR measurements with natural isotope abundance (2 M samples). However, the accumulation time was still up to 15 h when the sensitivity of the experiment was enhanced by proton noise decoupling. A few other $^{103}Rh,^{15}N$ coupling constants have been reported and determined by using ^{15}N-enriched compounds[2,4–9] or with the polarization transfer INEPT pulse sequence.[10–12] Today, inverse detection techniques allow one to obtain readily ^{15}N NMR spectra from samples with natural isotope abundance and offer the possibility of novel applications. The rhodoximes $XRh^{III}(Hdmg)_2L$ are rhodium coordination compounds where the four nitrogen atoms of the equatorial bisdimethylglyoximate ligand, $(Hdmg)_2$ are roughly coplanar with the metal, which bears two further ligands X and L in axial positions (Scheme 1).

Recently, the ^{103}Rh and ^{31}P chemical shifts and coupling constants[13,14] and several x-ray structures[15–19] of rhodoximes (L = PPh_3 or pyridine, X = halide, alkyl, haloalkyl) were reported. The $^{103}Rh,^{31}P$ coupling constants proved very sensitive to the electronic properties of the ligand X in phosphine rhodoximes and the '*trans* influence' of X was monitored by means of this parameter.[13,14,20] ^{15}N NMR offers an interesting opportunity to obtain information on the less well characterized '*cis* influence' of X and L on the equatorial oxime ligands and to investigate further the '*trans* influence' of X and L via the nitrogen parameters.



trans-[XRh(Hdmg)$_2$py]: X = Me (**1**); ^{n}Pr (**2**); ^{n}Bu (**3**); ^{i}Bu (**4**); ^{s}Bu (**5**); ^{neo}Pent (**6**); CH_2Cl (**7**); CH_2CF_3 (**8**); I (**9**); Cl (**10**)
trans-[XRh(Hdmg)$_2PPh_3$]: X = Me (**11**); Et (**12**), ^{i}Pr (**13**); ^{t}Bu (**14**); CH_2Cl (**15**); CH_2CF_3 (**16**); Cl (**17**)
trans-[MeRh(Hdmg)$_2D_2O$] (**18**)

Scheme 1. Rhodoxime complexes investigated.

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EXPERIMENTAL

Compounds

The rhodoxime complexes [XRh(Hdmg)$_2$py] [X = Me (**1**), ^{n}Pr (**2**), ^{n}Bu (**3**), ^{i}Bu (**4**), ^{s}Bu (**5**), ^{neo}Pent (**6**), CH_2Cl (**7**), CH_2CF_3 (**8**), I (**9**), Cl (**10**)], [XRh(Hdmg)$_2$PPh$_3$] [X = Me (**11**), Et (**12**), ^{i}Pr (**13**), ^{t}Bu (**14**), CH_2Cl (**15**), CH_2CF_3 (**16**), Cl (**17**)] and [MeRh(Hdmg)$_2$H$_2$O] (**18**) were synthesized according to previously described procedures.[14,21,22] In the following we give the ^{1}H, ^{13}C and ^{31}P NMR data for **9**, **10**, **15** and **16** not yet reported in the literature.

IRh(Hdmg)$_2$py (9). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 [m, 2H, C(2)-H py], 7.84 [m, 1H, C(4)-H py], 7.40 [m, 2H, C(3)-H py], 2.24 (s, 12H, CH_3 Hdmg). ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 152.5 (C=N), 149.6 [C(2) py], 139.3 [C(4) py], 126.3 [C(3) py], 12.6 (CH_3 Hdmg).

ClRh(Hdmg)$_2$py (10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 [m, 2H, C(2)-H py], 7.84 [m, 1H, C(4)-H py], 7.38 [m, 2H, C(3)-H py], 2.27 (s, 12H, CH_3 Hdmg). ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 151.9 (C=N), 150.8 [C(2) py], 139.3 [C(4) py], 126.5 [C(3) py], 12.5 (CH_3 Hdmg).

$ClCH_2$Rh(Hdmg)$_2$PPh$_3$ (15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.25 [m, 15H, P(C_6H_5)$_3$], 1.88 [d, 12H, CH_3 Hdmg, ^5J(P,H) = 2.5 Hz], 3.44 [dd, 2H, CH_2Cl, ^2J(Rh,H) = 2.5, ^3J(P,H) = 2.5 Hz]. ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 149.5 (C=N), 133.5 [d, C(2) PPh_3, ^2J(P,C) = 9 Hz], 130.2 [C(4) PPh_3], 129.6 [d, C(1) PPh_3, ^1J(P,C) = 33 Hz], 128.4 [d, C(3) PPh_3, ^3J(P,C) = 9 Hz], 47.5 (dd, CH_2Cl), 11.8 (CH_3, Hdmg). ^{31}P NMR (161.7 MHz, $CDCl_3$): δ 10.0 [d, ^1J(Rh,P) = 68 Hz].

CF_3CH_2Rh(Hdmg)$_2$PPh$_3$ (16). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.25 [m, 15H, P(C_6H_5)$_3$], 1.84 [d, 12H, CH_3 Hdmg, ^5J(P,H) = 2Hz], 1.41 [m, 2H, ^2J(Rh,H) = 3, ^3J(P,H) = 8, ^3J(F,H) = 15.5 Hz]. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 149.8 (C=N), 133.6 [d, C(2) PPh_3, ^2J(P,C) = 11 Hz], 131.5 [q, CF_3, ^1J(F,C) = 277 Hz], 130.3 [C(4) PPh_3, ^4J(P,C) = 1 Hz], 129.0 [d, C(1) PPh_3, ^1J(P,C) = 36 Hz], 128.2 [d, C(3) PPh_3, ^3J(P,C) = 10 Hz], 24.7 (m, CH_2), 11.7 (CH_3, Hdmg). ^{31}P NMR (242.9 MHz, $CDCl_3$): δ 11.3 [dq, ^1J(Rh,P) = 72 Hz, ^4J(P,F) = 16 Hz].

NMR measurements

Chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ are reported relative to internal tetramethylsilane, $\delta(^{31}P)$ relative to 85% H_3PO_4 and $\delta(^{15}N)$ relative to neat CH_3NO_2 as external standards. All spectra were acquired at 300 K. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on JEOL EX-400 and Bruker AMX-600 spectrometers. The ^{31}P NMR data for **11**–**14**[14] and **17**[20] have been reported previously. The ^{15}N spectra were measured on a Bruker AMX-600 spectrometer using a 5 mm ^{1}H, ^{13}C, ^{15}N triple-resonance gradient probe. Using the 2D gs-(^{1}H,^{15}N)-HSQC experiment[23] we obtained spectra with good signal-to-noise ratios in *ca* 1 h from 20–30 mg samples dissolved in 0.4 ml of $CDCl_3$ or D_2O (0.02 M). For polarization transfer either three-bond ^{15}N,^{1}H coupling (4–5 Hz) with the equatorial methyl groups or the larger two-bond coupling in the pyridine ligand (15 Hz) were employed. Spectral widths of 200–1000 Hz in the F_2 and 200 Hz in the F_1 dimension were used. The two data sets for every t_1 increment were acquired with echo and anti-echo gradient selection and stored separately. Data matrices of 160–240 times 256 complex points in t_1 and t_2, respectively, were recorded. In both dimensions data were weighted with a shifted sine-bell function and zero-filled to 512 complex points prior to the Fourier transformation. The ^{103}Rh,^{15}N coupling constants are expected to be accurate to $\pm$1 Hz.

RESULTS AND DISCUSSION

One-bond ^{103}Rh,^{15}N coupling

The ^{103}Rh,^{15}N coupling constants were extracted from gradient-selected (^{1}H,^{15}N)-HSQC experiments.[23] Passive Rh,N coupling appears in the F_1 domain of the 2D spectra because of 100% natural abundance of ^{103}Rh. The results are given in Table 1.

Spin coupling between rhodium and the equatorial oxime nitrogen atoms is relatively large (17.9–21.4 Hz) but shows little sensitivity to the axial ligands X and L. In contrast, coupling with the axial pyridine nitrogen is smaller for X = alkyl (5.5–8.7 Hz) and increases considerably for the iodo and chloro complexes (15.6 and 17.8 Hz, respectively). It appears that the alkyl and substituted alkyl groups X exert similar donor effects whereas the reduced donor properties of the halogen

Table 1. ^1J(Rh,N) coupling constants ($\pm$1 Hz) of XRh^{III}(Hdmg)$_2$L complexes[a]) (L = pyridine, PPh$_3$) in $CDCl_3$

	L = pyridine		L = PPh_3
Complex	$^1J(Rh,N_{eq})$ (Hz)	$^1J(Rh,N_{ax})$ (Hz)	$^1J(Rh,N_{eq})$ (Hz)
CH_3Rh(Hdmg)$_2$L	20.4	7.2	19.9
CH_3CH_2Rh(Hdmg)$_2$L			20.4
^{n}PrRh(Hdmg)$_2$py	21.1	6.8	
^{i}PrRh(Hdmg)$_2$L			20.3
^{n}BuRh(Hdmg)$_2$py	21.1	6.4	
^{s}BuRh(Hdmg)$_2$py	21.3 and 21.4	5.5	
^{i}BuRh(Hdmg)$_2$L	20.8	6.2	
^{t}BuRh(Hdmg)$_2$L			20.7
^{neo}PenRh(Hdmg)$_2$L	20.8	5.8	
$ClCH_2$Rh(Hdmg)$_2$L	20.2	8.1	19.7
CF_3CH_2Rh(Hdmg)$_2$L	19.3	8.7[b]	19.0
IRh(Hdmg)py	18.3	15.6	
ClRh(Hdmg)$_2$L	17.9	17.8	18.1

[a] CH_3Rh(Hdmg)$_2D_2O$, $^1J(Rh,N_{eq})$ = 21.2 Hz.
[b] Broadening of the ^{15}N signal due to ^4J(F,N).

Table 2. Rh—N(pyridine) distances[15–17] and ^1J(Rh,N) coupling constants in XRh(Hdmg)$_2$py complexes

Complex	r(Rh—N$_{py}$) (Å)	^1J(Rh,N$_{ax}$) (Hz)
MeRh(Hdmg)$_2$py (**1**)	2.220(3)	7.2
ClCH$_2$Rh(Hdmg)$_2$py (**7**)	2.178(3)	8.1
CF$_3$CH$_2$Rh(Hdmg)$_2$py (**8**)	2.145(3)	8.7
IRh(Hdmg)$_2$py (**9**)	2.079(3)	15.6
ClRh(Hdmg)$_2$py (**10**)	2.046(1)	17.8

ligands are reflected in a typical '*trans* influence' on the axial Rh,N coupling. The resulting increase in ^1J(Rh,N) correlates with the decrease in the Rh—N distance[15–17] (Table 2) and can thus be attributed to stronger coordination of the pyridine ligand. A similar trend was observed for the coupling constants ^1J(Rh,P).[13–16]

^{15}N chemical shifts

The ^{15}N chemical shifts of the pyridine ligand range from −112.1 to −131.6 ppm (Table 3). Shielding of the pyridine ligand is higher in the XRh(Hdmg)$_2$py complexes than in the free ligand [$\delta(^{15}N) = -60.6$ ppm[24]] and increases in the order X = alkyl < alkyl with electron-withdrawing substituents < halides. Hence the shielding of the complexed axial nitrogen follows the trend of the Rh,N coupling constants in becoming larger with weaker donor ligands X. Furthermore, it may be inferred from the chemical shifts of the pyridine γ-carbon atoms[14] that in the halide complexes the electron withdrawal from the pyridine ligand is more efficient.

For the investigated XRh(Hdmg)$_2$py complexes the shielding of the equatorial oxime nitrogen atoms increases in the same order from −54.9 to −69.6 ppm. A parallel dependence of the bismethylglyoximate nitrogen shielding on the electronic properties of X is found in the triphenylphosphine derivatives. Also, the ligand L noticeably affects the equatorial nitrogen shielding, which increases on going from L = py (−56.6 ppm) to L = PPh$_3$ (−58.6 ppm) and L = D$_2$O (−67.5 ppm) in the MeRh(Hdmg)$_2$L complexes.

The sp^2 nitrogen of the pyridine and oxime undergoes low-frequency shifts upon protonation or complexation with metals.[25–27] In so far as these shift changes are attributable to variations of the relevant n–π^* excitation energy, they can reflect the strength of the rhodium–nitrogen interactions in the compounds studied.

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Table 3. ^{15}N chemical shifts of XRh^{III}(Hdmg)$_2$L complexes[a] (L = pyridine, PPh$_3$) in CDCl$_3$

	L = pyridine		L = PPh$_3$
Complex	$\delta(^{15}N_{eq})$ (ppm)	$\delta(^{15}N_{ax})$ (ppm)	$\delta(^{15}N_{eq})$ (ppm)
CH$_3$Rh(Hdmg)$_2$L	−56.6	−117.6	−58.6
CH$_3$CH$_2$Rh(Hdmg)$_2$L			−58.0
^{n}PrRh(Hdmg)$_2$py	−55.9	−114.8	
^{i}PrRh(Hdmg)$_2$L			−58.3
^{n}BuRh(Hdmg)$_2$py	−55.8	−114.8	
^{s}BuRh(Hdmg)$_2$py	−54.9 and −55.3	−112.1	
^{i}BuRh(Hdmg)$_2$L	−55.7	−114.8	
^{t}BuRh(Hdmg)$_2$L			−57.5
^{neo}PenRh(Hdmg)$_2$L	−56.4	−113.0	
ClCH$_2$Rh(Hdmg)$_2$L	−59.7	−125.4	−61.8
CF$_3$CH$_2$Rh(Hdmg)$_2$L	−61.9	−128[b]	−64.6
IRh(Hdmg)$_2$py	−69.6	−131.6	
ClRh(Hdmg)$_2$L	−67.3	−131.6	−67.6

[a] CH$_3$Rh(Hdmg)$_2$D$_2$O, $\delta(^{15}N_{eq}) = -67.5$ ppm.
[b] The signal is very broad.

REFERENCES

1. A. Gisler, M. Schaade, E. J. M. Meier, T. Linden and W. von Philipsborn, *J. Organomet. Chem.* in press.
2. G. Appleton, J. R. Hall and S. F. Ralph, *Inorg. Chem.* **27**, 4435 (1988).
3. K. S. Bose and E. H. Abbott, *Inorg. Chem.* **16**, 3190 (1977).
4. R. Meij, D. J. Stufkens, K. Vrieze, W. van Gerresheim and C. H. Stam, *J. Organomet. Chem.* **164**, 353 (1979).
5. W. Preetz, G. Peters and J.-U. Vogt, *Z. Naturforsch, Teil B* **48**, 348 (1993).
6. L. K. Bell, D. M. P. Mingos, D. G. Tew, L. F. Larkworthy, B. Sandell, D. C. Povey and J. Mason, *J. Chem. Soc., Chem. Commun.* 125 (1983).
7. A. R. Siedle, R. A. Newmark and R. D. Howells, *Inorg. Chem.* **27**, 2473 (1988).

8. J. R. Dilworth, S. Donovan-Mtunzi, C. T. Kan, R. L. Richard and J. Mason, *Inorg. Chim. Acta* **53**, L161 (1981).
9. L. Carlton and R. Weber, *Inorg. Chem.* **35**, 5843 (1996).
10. L. Carlton and M. P. Belciug, *J. Organomet. Chem.* **378**, 469 (1989).
11. B. T. Heaton, C. Jacob, W. Heggie, P. R. Page and I. Villax, *Magn. Reson. Chem.* **29**, *S*21 (1991).
12. B. T. Heaton, J. A. Iggo, C. Jacob, J. Nadarajah, M. A. Fontaine, R. Messere and A. F. Noels, *J. Chem. Soc., Dalton Trans*. 2875 (1994).
13. M. Ludwig, L. Öhrström and D. Steinborn, *Magn. Reson. Chem.* **33**, 984 (1995).
14. F. Asaro, G. Costa, R. Dreos, G. Pellizer and W. von Philipsborn, *J. Organomet. Chem.* **513**, 193 (1996).
15. I. Potocnak, M. Dunaj-Jurco, M. Ludwig and D. Steinborn, *Acta Cryatllogr., Sect. C* **51**, 1999 (1995).
16. V. Kettmann, M. Dunaj-Jurco, D. Steinborn and M. Ludwig, *Acta Crystallogr., Sect. C* **52**, 1399 (1996).
17. S. Geremia, R. Dreos, L. Randaccio, G. Tauzher and L. Antolini, *Inorg. Chim. Acta* **216**, 125 (1994).
18. N. Bresciani Pahor, R. Dreos-Garlatti, S. Geremia, L. Randaccio, G. Tauzher and E. Zangrando, *Inorg. Chem.* **29**, 3437 (1990).
19. L. Randaccio, S. Geremia, R. Dreos-Garlatti, G. Tauzher, F. Asaro and G. Pellizer, *Inorg. Chim. Acta* **194**, 1 (1992).
20. F. Asaro, R. Dreos Garlatti, G. Pellizer and G. Tauzher, *Inorg. Chim. Acta* **211**, 27 (1993).
21. R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.* 1951 (1965).
22. P. Powell, *J. Chem. Soc. A* 2418 (1969).
23. L. E. Kay, P. Keifer and T. Saarinen, *J. Am. Chem. Soc.* **114**, 10663 (1992).
24. A. J. DiGioia, G. T. Furst, L. Psota and R. L. Lichter, *J. Chem. Phys.* **82**, 1644 (1978).
25. W. von Philipsborn and R. Müller, *Angew. Chem., Int. Ed. Engl.* **25**, 383 (1986).
26. R. Hollenstein and E. Stupperich, *Helv. Chim. Acta* **76**, 1258 (1993).
27. C. Bremard, B. Mouchel and S. Sueur, *Inorg. Chem.* **22**, 3562 (1983).

