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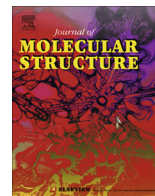


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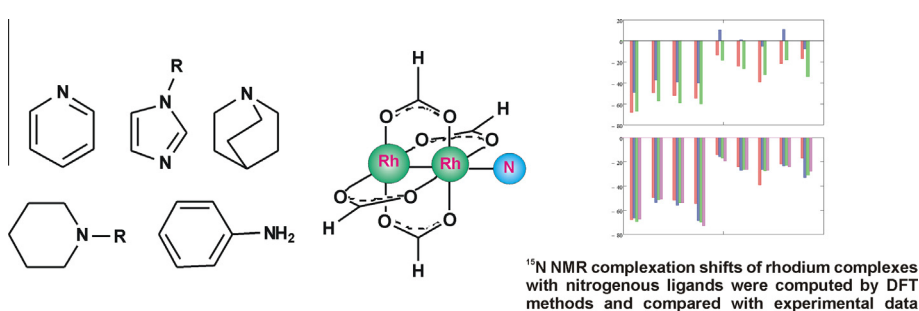
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HIGHLIGHTS

- DFT calculations of ^{15}N NMR parameters for rhodium(II) complexes were performed.
- Two conversion methods of the shielding scale to chemical shift scales were compared.
- The equations used for chemical shifts scaling were parameterised.
- ^{15}N NMR complexation shifts were evaluated and compared with the experiment.

GRAPHICAL ABSTRACT



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ABSTRACT

Benchmark calculations of ^{15}N NMR shielding constants for a set of model complexes of rhodium(II) tetraformate with nine organic ligands using the Density Functional Theory (DFT) methods have been carried out. The calculations were performed by means of several methods: the non-relativistic, relativistic scalar ZORA, and spin-orbit ZORA approaches at the CGA-PBE/QZ4P theory level, and the GIAO NMR method using the B3PW91 functional with the 6-311++G(2d,p) basis set for C, H, N, O atoms and the Stuttgart basis set for the Rh atom. The geometry of compounds was optimised either by the same basis set as for the NMR calculations or applying the B3LYP functional with the 6-31G(2d) basis set for C, H, N, O atoms and LANL2DZ for the Rh atom. Computed ^{15}N NMR shielding constants σ were compatible with experimental ^{15}N chemical shifts δ of complexes exhibiting similar structure and fulfil the linear equation $\delta = a\sigma + b$. The a and b parameters for all data sets have been estimated by means of linear regression analysis.

In contrast to the correlation method giving “scaled” chemical shifts, the conversion of shielding constants to chemical shifts with respect to the reference shielding of CH_3NO_2 provided very inaccurate “raw” δ values. The application of the former to the calculation of complexation shifts $\Delta\delta$ ($\Delta\delta = \delta_{\text{compl}} - \delta_{\text{lig}}$) reproduced experimental values qualitatively or semi-quantitatively. The non-relativistic B3PW91/[6-311++G(2d,p), Stuttgart] theory level reproduced the NMR parameters as good as the more expensive relativistic CGA-PBE//QZ4P ZORA approaches.

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Introduction

A complexation shift $\Delta\delta$, defined as the difference between the NMR chemical shift of a nucleus in a complex and the corresponding chemical shift in a free ligand is a useful parameter for compound characterisation. This parameter allows determining the

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complexation site in multifunctional ligands, or the stability constant of the complex. Complexation shifts of heteroatoms appear to be especially useful, whereas the theoretical prediction of $\Delta\delta$ is an important task in the spectroscopy of coordination compounds. The calculation of chemical shifts δ in the complex and free ligand, and subsequent subtraction of corresponding values appears to be a reasonable approach to estimating the theoretical value of $\Delta\delta$ parameter. However, such a procedure provides often unrealistic, erroneous $\Delta\delta$ values. It is known that the calculated and experimental chemical shifts follow the linear equation $\delta_{\text{exp}} = a\delta_{\text{calc}} + b$, where coefficients a and b depend on the method of calculation, namely the basis set, the functional and the class of compounds. In order to obtain reliable chemical shifts, one has to apply the scaling procedure using the equation $\delta_{\text{scal}} = a\delta_{\text{calc}} + b$, where the parameterisation of the equation (i.e. the determination of the coefficients a and b) may be accomplished using computed and experimental chemical shifts of reference compounds [1]. Because ligands are purely organic species, and complexes contain a transition metal atom, they belong to the different classes of compounds, so their corresponding a and b parameters may differ. Consequently, prior to $\Delta\delta$ estimation, both data sets have to be scaled individually. This procedure was applied in our previous works, for the complexes of some organic ligands (Fig. 1) with dimeric rhodium(II) tetraacetate Rh_2ac_4 ($R = \text{CH}_3$) and tetrakis(trifluoroacetate) Rh_2tfa_4 ($R = \text{CF}_3$) [2–4].

Dirhodium tetraacylates can bind organic ligands reversibly in solution [5]. The complexation occurs in situ, immediately after mixing of reagents; ligands can be easily exchanged or removed. Due to their complexation properties, these compounds were applied in numerous areas, as auxiliary reagents in NMR [6] and CD [7–9] spectroscopy, anticancer agents in biology and medicine [10], organic catalysts in the synthesis including the synthesis of the chiral compounds [11,12]. Complexes of dirhodium salts, especially with nitrogenous ligands, were subjected to numerous studies by NMR spectroscopy. The $\Delta\delta$ parameter served as a means to complex characterisation and to the determination of complexation sites [13–16]. We attempted to estimate the $\Delta\delta$ parameters in rhodium complexes with oxygen ligands [2], nitrogenous ligands [15] and aromatic N-oxides [4]. In the case of ^1H and ^{13}C NMR we obtained rather unsatisfactory $\Delta\delta$ values, either only qualitative or too inaccurate to be useful. Better results were obtained in case of ^{15}N NMR spectroscopy for the ligand bearing pyridine-type nitrogen atoms. However, investigations on $\Delta\delta(^{15}\text{N})$ computing in dirhodium complexes were rather fragmentary and unmethodical. In the present work a few calculation methods were benchmarked using a set of reference ligands 1–9

(Fig. 1). There were two purposes of the work: the testing of some low-cost DFT (Density Functional Theory) methods applicable in the laboratory of an organic chemist, and the parameterisation of the scaling equations $\delta_{\text{exp}} = a\delta_{\text{calc}} + b$, i.e. finding the a and b coefficients. The results were intended to be applied in the further works.

Experimental

The calculations were performed for ligands 1–9 (Fig. 1) and their complexes with model rhodium(II) salt, tetraformate Rh_2form_4 ($R = \text{H}$), assuming isolated molecules in vacuum. Two program packages: Gaussian 09 [17] and ADF Amsterdam Density Functional (ADF) [18] were applied. In the case of the former, geometry optimisations of compounds were performed applying the B3LYP functional (Becke, three-parameter, Lee–Yang–Parr), the 6-31G(2d) basis set for C, H, N, and O atoms and the LANL2DZ basis set for Rh atoms. The GIAO NMR calculations were performed using the B3PW91 functional (Becke, three-parameter, Perdew–Wang 91), the 6-311G++(2d,p) basis set for C, H, N, and O atoms and the Stuttgart RSC 1997 ECP basis set for Rh atoms [19]. For comparison purposes, some NMR calculations were performed using the same theory level for geometry optimisation and NMR calculations, namely the B3PW91/[6-311G++(2d,p), Stuttgart] (such an approach increased calculation cost). For selected ligands and complexes the calculations were performed applying the IEFPCM(CHCl_3) solvation model (Integral Equation Formalism variant of Polarizable Continuum Model) for both geometry optimisation and GIAO calculations. The reference shielding constants for nitromethane CH_3NO_2 were computed using the two above mentioned methods and assuming the IEFPCM (Integral Equation Formalism variant of Polarizable Continuum Model) of solvation with CH_3NO_2 as the solvent. The reference $\sigma_{\text{CH}_3\text{NO}_2}$ shielding constants of -156.70 ppm and -151.45 ppm were obtained respectively. All calculations with the ADF program suite were performed at the CGA-PBE/QZ4P theory level applying in turn the non-relativistic method, scalar ZORA (Zeroth Order Regular Approximation) and spin-orbit ZORA methods. The same theory level was applied for both geometry optimisation and NMR shielding calculations; isolated molecules were assumed in all steps of computing. A similar approach was applied in case of CH_3NO_2 , i.e. the same calculation method and basis set for both steps of calculations and the assumption of the isolated molecule in vacuum. The following reference shielding constants $\sigma_{\text{CH}_3\text{NO}_2}$ were obtained: -141.56 (non-relativistic level), -142.47 (scalar ZORA),

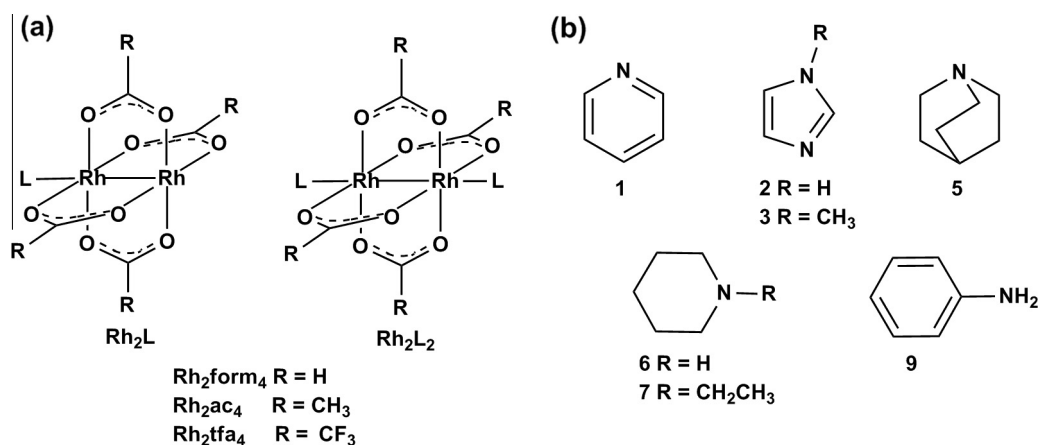


Fig. 1. (a) Complexes of rhodium(II) tetraacylates, the 1:1 (Rh_2L_4) and 1:2 (Rh_2L_2); and (b) ligands discussed in the present work. Numbers 4 and 8 correspond to ligands CH_3CN and $\text{N}(\text{CH}_3)_3$ (not shown in the figure).

and -139.38 ppm (spin-orbit ZORA). Because ligands **6** and **7** and their complexes can occur in various conformers; their molar fractions x were estimated on the basis of calculated molecular energies using Boltzmann relationship, and computed shielding constants were averaged according to the formula $\sigma = \sum \sigma_i x_i$.

Chemical shifts of ligands available in literature or measured in the present work, and the chemical shifts of dirhodium adducts of Rh_2ac_4 and Rh_2tfa_4 , previously published [13,14,20–22], were used as a reference data set. The shielding scale was converted to the nitromethane chemical shift scale ($\delta_{\text{CH}_3\text{NO}_2} = 0.0$ ppm) by two ways. Non-scaled (raw) chemical shifts δ_{raw} were obtained according to the equation $\delta = \sigma_{\text{CH}_3\text{NO}_2} - \sigma_{\text{calc}}$, where σ_{calc} was the computed shielding constant of a compound and $\sigma_{\text{CH}_3\text{NO}_2}$ was the corresponding reference shielding of nitromethane, calculated at the same theory level as the compounds in question. The second approach provided scaled chemical shifts δ_{scal} and was based on the equation $\delta_{\text{scal}} = a\sigma_{\text{calc}} + b$, where a and b parameters were estimated from linear regression using the equation $\delta_{\text{exp}} = a\sigma_{\text{calc}} + b$. The quality of the correlation was evaluated by the Pearson's correlation coefficient r^2 and standard error rms ($[\sum(\delta_{\text{exp}} - a\sigma_{\text{calc}} - b)^2]/(n - 2))^{0.5}$ (*corr* and *stderr* Mathcad's [23] functions). The results of linear regression analysis have been collected in Table 1. Computed ^{15}N NMR shielding constants and corresponding chemical shifts, as well as experimental data have been collected in Tables 1S–4S (Supplementary Materials). Additionally, inaccuracies in calculated chemical shifts have been presented in Tables 2 and 3.

Complexation shifts $\Delta\delta(^{15}\text{N})$ were estimated as the difference between computed ^{15}N chemical shifts of an atom in a complex, and corresponding chemical shift in a ligand ($\Delta\delta = \delta_{\text{compl}} - \delta_{\text{lig}}$), using either non-scaled or scaled chemical shifts. Computed $\Delta\delta(^{15}\text{N})$ together with the experimental values were collected in Table 4.

Results and discussion

Five methods of calculations have been tested, including two methods comprising relativistic effects (scalar and spin-orbit ZORA). The calculations have been performed for model ligands **1–9** (Fig. 1) having various nitrogen functionalities, and for their complexes with Rh_2form_4 as the salt of choice. This relatively small dirhodium core ($R = H$) was selected in order to reduce the calculations cost. It was assumed that the calculated ^{15}N shielding constants of Rh_2form_4 complexes would be a good approximation of shielding constants in similar complexes, with Rh_2ac_4 or Rh_2tfa_4 .

Calculated ^{15}N shielding constants σ_{calc} correlate satisfactorily with the experimental chemical shifts (correlation coefficient varied from -0.991 to -0.995 , rms from 10.4 to 14.1), although some dispersion of points occurred in the case of amines (Fig. 2). All calculation methods performed similarly; there were no significant differences between them.

Conversion of the shielding scale to the chemical shift scale

Computed ^{15}N shielding constants have been converted to chemical shifts by two ways, using the shielding of a reference compound and by the correlation method. The first conversion has been accomplished according to the formula $\delta = \sigma_{\text{CH}_3\text{NO}_2} - \sigma_{\text{calc}}$, where σ_{calc} denotes computed shielding constants of the compound in question, $\sigma_{\text{CH}_3\text{NO}_2}$ denotes the shielding constant of a reference compound (CH_3NO_2) calculated at the same theory level. Because these references were also computed and bore certain error, so the resulting chemical shifts suffered from inaccuracy of calibration. The comparison of ^{15}N chemical shifts of two reference compounds, CH_3NO_2 and NH_3 , could serve as an example. Chemical shifts of the latter with respect to CH_3NO_2 (0.0 ppm) varied from -417.1 to -398.7 ppm, depending on the calculation method (Table 2S). Especially large errors occurred in the case of complexes. For instance, inaccuracy of chemical shifts estimated by the scalar ZORA method varied from ca. -24 to $+44$ ppm (rms of 26.3 ppm) for ligands and from ca. $+5$ to $+61$ ppm (rms of 47.6 ppm) for complexes (Tables 2 and 3). Such inaccuracies can be explained in terms of the different nature of the compounds in question. Ligands and CH_3NO_2 are entirely organic species, whereas complexes contain additionally transition metal atoms. Thus, the comparison of shielding constants of nitromethane and ligands appear to be reasonable, whereas the comparison with ^{15}N shieldings of N-Rh moiety certainly not. Because of these inaccuracies, chemical shifts obtained by above procedure were considered as the raw data, δ_{raw} .

The second method was based on the equation $\delta_{\text{scal}} = a\sigma_{\text{calc}} + b$, where the a and b parameters were estimated from linear regression analysis using the equation $\delta_{\text{exp}} = a\sigma_{\text{calc}} + b$ (in fact, this approach utilises experimental data set as a reference, instead of single shielding constant of a reference compound). Alternatively, one can apply the equivalent equation $\delta_{\text{scal}} = a'\delta_{\text{raw}} + b'$, where $a' = -a$. The application of correlation methods reduced errors of scale conversions, up to rms from ca. 13 to 17 ppm. It was noticeable that the calculation at the

Table 1
Parameters of the linear regression analysis of calculated ^{15}N shielding constants and experimental ^{15}N NMR chemical shifts.^a

Theory level	a	b	b'	r^2	rms	n
B3PW91/[6-311G++(2d,p), Stuttgart] ^b	-0.88 ± 0.04	-155 ± 6	-18	-0.993	13.3	11
	$[-0.92 \pm 0.04]$	$[-147 \pm 5]$	$[-4]$	$[-0.994]$	$[12.2]$	$[9]$
	-0.90 ± 0.04	-178 ± 6	-38	-0.995	10.4	9
	$[-0.91 \pm 0.05]$	$[-171 \pm 6]$	$[-30]$	$[-0.994]$	$[10.6]$	$[7]$
B3PW91/[6-311G++(2d,p), Stuttgart] ^c	-0.86 ± 0.05	-153 ± 6	-19	-0.992	14.0	7
	-0.86 ± 0.04	-180 ± 6	-49	-0.995	11.1	7
CGA-PBE/QZ4P (non-relativistic) ^d	-0.87 ± 0.04	-166 ± 6	-43	-0.993	13.4	11
	-0.96 ± 0.05	-193 ± 8	-58	-0.991	14.0	9
CGA-PBE/QZ4P (scalar ZORA) ^d	-0.87 ± 0.04	-167 ± 6	-42	-0.993	13.4	11
	-0.96 ± 0.05	-190 ± 7	-53	-0.991	14.0	9
CGA-PBE/QZ4P (spin-orbit ZORA) ^d	-0.87 ± 0.04	-166 ± 6	-44	-0.993	13.3	11
	-0.99 ± 0.05	-168 ± 8	-30	-0.991	14.1	8

^a A linear equation $\delta_{\text{exp}} = a\sigma_{\text{calc}} + b$ was assumed, where σ_{calc} and δ_{exp} denote calculated ^{15}N shielding constants and experimental ^{15}N NMR chemical shifts, r^2 denote Pearson's r correlation coefficient, rms means $[\sum(\delta_{\text{exp}} - (a\sigma_{\text{calc}} + b))^2]/(n - 2))^{0.5}$, n denotes the number of points. The first row in each entry concerns free ligands, the second row adducts; the numbers in square brackets correspond to the calculations with the use of the IEPPCM(CHCl_3) solvation model. The b' coefficient concerns the equation $\delta_{\text{scal}} = a'(\sigma_{\text{CH}_3\text{NO}_2} - \sigma_{\text{calc}}) + b' = a'\delta_{\text{raw}} + b'$ where $a' = -a$; this relationship can be applied also for the chemical shift scaling.

^b The geometry of molecules was optimised applying the B3LYP functional, 6-31G(2d) basis set for C, H, O and N atoms, and LANL2DZ basis set for Rh.

^c The geometry of molecules was optimised applying the B3PW91 functional, 6-311++G(2d,p) basis set for C, H, O and N atoms, and Stuttgart basis set for Rh.

^d The same method was applied for the geometry optimisation and NMR calculations.

Table 2Inaccuracies of calculated ^{15}N NMR chemical shifts (ppm) for ligands **1–9**.^a

Ligand	Theory levels					Exp.
	B3PW91/[6-311++G(2d,p)]		CGA-PBE/QZ4P			
	Non-relativistic ^b	Non-relativistic ^c	Non-relativistic ^d	Scalar ZORA ^d	Spin-orbit ZORA ^d	
1	3.9(−6.6) [−8.6(−6.0)]	6.7(−7.2)	33.4(−5.0)	32.8(−5.0)	34.7(−5.3)	−67.7
2 (=N−)	17.1(13.8) [3.7(11.2)]	20.1(14.1)	44.5(13.6)	44.1(13.8)	46.2(13.8)	−138 ^e
2 (NH)	−34.9(−22.7) [−26.0(−9.8)]	−31.5(−20.4)	−8.0(−22.9)	−8.6(−23.1)	−6.3(−22.7)	−210 ^e
3 (=N−)	3.5(0.3) [−9.8(−2.2)]	6.8(0.9)	32.4(−1.4)	31.9(1.5)	34.0(1.5)	−125.2
3 (NCH ₃)	−14.8(−3.9) [−8.1(7.4)]	−12.1(−2.3)	13.8(−2.7)	13.3(−2.7)	15.3(−2.6)	−220.0
4 ^f	7.9(5.6) [−10.3(−1.8)]	9.1(4.3)	31.9(2.5)	31.3(2.4)	33.3(2.4)	−135.8 ^g , −137.4 ^h
5 ⁱ	−14.9(14.2) [−13.8(14.7)]	−13.2 (16.6)	14.4(16.4)	14.2(16.5)	15.6(16.3)	−364.5, −365.6 ^e
6	−18.2(8.2)	Not calc.	11.5(10.8)	11.1(10.7)	12.7(10.7)	−340.5
7	−19.4(5.4)	Not calc.	4.0(2.4)	3.7(2.4)	5.2(2.3)	−326.1
8	−50.6(−21.2) [−49.8(−21.2)]	−47.0 (−16.5)	−23.6(−21.0)	−23.7(−20.8)	−22.2(−20.9)	−331.6
9	−17.7(6.9) [−18.0(7.5)]	−14.1(10.8)	6.4(4.6)	5.9(4.4)	7.6(4.5)	−326.8
CH ₃ NO ₂ ^j	0.0	0.0	0.0	0.0 ^p	0.0	0.0
NH ₃	−37.1(−3.4)	−32.5(2.2)	−19.4(−11.1)	−19.9(−10.4)	−18.7(−11.6)	−380
<i>a</i> , <i>b</i> ^k	<i>a</i> −0.875, <i>b</i> −155.5 [<i>a</i> −0.915, <i>b</i> −147.5]	<i>a</i> −0.862, <i>b</i> −152.8	<i>a</i> −0.872, <i>b</i> −166.3	<i>a</i> −0.873, <i>b</i> −166.7	<i>a</i> −0.871, <i>b</i> −165.7	
rms ^l	25.0(13.3)[24.0(12.2)]	29.3(16.6)	26.6(13.4)	26.3(14.4)	27.6(13.3)	

^a All values were estimated as a difference between computed and experimental ^{15}N chemical shifts ($\delta_{\text{calc}} - \delta_{\text{exp}}$), where δ_{calc} denotes either non-scaled δ_{raw} or scaled δ_{scal} (in parentheses) chemical shifts (Table 2S, supplementary material). If not marked otherwise, the experimental chemical shifts were acquired in CDCl₃ solution.

^b Geometry of molecules was optimised at the B3LYP/6-31G(2d) theory level; the numbers in square brackets correspond to the calculations with the use of the IEPPCM(CHCl₃) solvation model.

^c Geometry of molecules were optimised at the B3PW91/6-311++G(2d,p) theory level.

^d The same theory levels were applied for the geometry optimisation and shielding calculations.

^e From ^{15}N CPMAS NMR.

^f The averaged chemical shift of –136.6 ppm was assumed as the experimental value for the error estimation.

^g Neat CH₃(CH₂)₃CN.

^h CH₃(CH₂)₃CN in CDCl₃.

ⁱ The averaged chemical shift of –365.0 ppm was assumed as the experimental value for the error estimation.

^j Chemical shifts of CH₃NO₂ were assumed to be 0.0 ppm in all cases.

^k The *a* and *b* coefficients (not rounded) applied for scaling.

^l rms denotes $[\sum(\delta_x - \delta_{\text{exp}})^2 / (n-2)]^{0.5}$, where δ_x denotes δ_{raw} or δ_{scal} (estimated for ligands **1–9**).

Table 3Inaccuracies of calculated ^{15}N NMR chemical shifts (ppm) for complexes of ligands **1–9**.^a

Adduct	Theory level					Exp.
	B3PW91/[6-311G++(2d,p), Stuttgart]		CGA-PBE/QZ4P			
	Non-relativistic ^b	Non-relativistic ^c	Non-relativistic ^d	Scalar ZORA ^d	Spin-orbit ZORA ^d	
Rh₂1	15.5(−9.9) [10.2(−7.3)] 22.2(−3.6) ^e	22.0(−11.6)	50.2(−4.0)	42.8(−6.8)	24.1(−4.9)	−135.5
Rh₂1₂	35.2(7.8)	Not calc.	Not calc.	Not calc.	Not calc.	Not av.
Rh₂2 (=N−)	30(8.4) [22.7(8.7)]	40.0(11.0)	62.5 (9.9)	60.5(12.1)	41.4(12.4)	−187.7
Rh₂3 (=N−) ^f	21.2(0.0) [14.5(0.8)]	30.9(2.4)	54.5(2.0)	52.5(4.2)	33.2(4.2)	−177.0, −187.7 ^g
Rh₂4	23.2(2.8) [12.1(−0.6)]	27.1(0.5)	40.4(−11.0)	35.2(−12.1)	13.1(−15.7)	−192.0 ^h
Rh₂5	8.8(8.7) [11.7(15.7)]	13.8(14.3)	58.1(14.2)	53.2(12.5)	38.4(10.6)	−378.2 ^{g,i} −379.2 ^j
Rh₂5₂	−3.2(−2.7)		37.8 (−5.4)	35.0(−5.2)	Not av.	−373.1 ^{g,i}
Rh₂6	6.8(5.5)		52.0(7.8)	49.3(8.2)	36.2(8.3)	−364.5 ^k
Rh₂7	14.4(12.4)		59.5(15.0)	55.1(13.8)	42.2(14.3)	−365.1 ^l
Rh₂8	−17.8(−17.8) [−16.2(−12.0)]	−11.9(−11.2)	20.6(−22.7)	17.9(−22.4)	4.8(−23.0)	−353.2 ^m
	−19.9(−19.7) ^e					
Rh₂8₂	−26.5(−26.2) [−7.9(−5.3)] −27.0(−26.7) ^e		6.5(−36.4)	4.8(−35.2)	−0.3(−28.0)	−347.6 ^m
Rh₂9	−8.0(−9.9)	−3.6(5.3)	33.0(−11.3)	31.5(−9.7)	21.6(−6.3)	−343.8
<i>a</i> , <i>b</i> ⁿ	<i>a</i> −0.899, <i>b</i> −178.4 [<i>a</i> −0.911, <i>b</i> −171.4]	<i>a</i> −0.864, <i>b</i> −179.8	<i>a</i> −0.955, <i>b</i> −193.4	<i>a</i> −0.961, <i>b</i> −190.3	<i>a</i> −0.994, <i>b</i> −168.4	
rms ^o	20.8(14.9)[17.0(10.6)]	28.6(11.1)	51.3(17.4)	47.6(17.1)	32.9(16.5)	

^a All values were estimated as a difference between computed and experimental ^{15}N NMR chemical shifts ($\delta_{\text{calc}} - \delta_{\text{exp}}$), where δ_{calc} denotes either non-scaled δ_{raw} or scaled δ_{scal} (in parentheses) values (Table 4S, supplementary materials). If not marked otherwise, the experimental chemical shifts were acquired in CDCl₃ solution, for complexes of Rh₂ac₄; the calculations were performed for hypothetical Rh₂form₄ complexes.

^b The geometry of molecules was optimised using the B3LYP method, the 6-31G(2d) basis set for C, H, N, and O atoms, and the LANL2DZ basis set for Rh; the numbers in square brackets correspond to the calculations with the use of the IEPPCM(CHCl₃) solvation model.

^c Geometry of molecules was optimised using the B3PW91 method, the 6-311++G(2d,p) basis set for C, H, N, and O atoms, and the Stuttgart basis set for Rh.

^d The same theory levels were applied for geometry optimisation and shielding calculations.

^e The calculations performed for the complex of rhodium tetraacetate Rh₂ac₄ (R = CH₃).

^f The averaged chemical shift of –182.0 ppm was assumed as the experimental value for error estimation.

^g Chemical shifts of complex with rhodium tetrakis(trifluoroacetate) (R = CF₃).

^h The experimental values for the complex of CH₃(CH₂)₃CN.

ⁱ Slow exchange regime.

^j From ^{15}N CPMAS NMR.

^k At 233 K, slow exchange regime.

^l At 233 K, slow exchange regime.

^m At 263 K, slow exchange regime. Complex of N(C₂H₅)₃ with Rh₂tfa₄.

ⁿ The *a* and *b* coefficients (not rounded) applied for scaling.

^o rms denotes $[\sum(\delta_x - \delta_{\text{exp}})^2 / (n-2)]^{0.5}$, where δ_x denotes δ_{raw} or δ_{scal} .

Table 4
Calculated and experimental ^{15}N NMR complexation shift $\Delta\delta$ (ppm).^a

Adducts	Theory levels				Exp.	
	B3PW91/[6-311G++(2d,p), Stuttgart]		CGA-PBE/QZ4P ^d			
	(^b)	(^c)	Non-relativistic	Scalar-ZORA		Spin-orbit-ZORA
Rh₂1	−66.9(−49.2) [−69.1]	−72.0	−66.7	−69.5(−57.6)	−67.3	−67.8
Rh₂2	−56.8(−36.9) [−52.2]	−52.8	−53.4	−51.3(−33.3)	−51.0	−49.7
Rh₂3	−58.8(−39.1) [−54.3]	−55.2	−56.2	−54.1(−36.2)	−54.0	−56.8 ^e
Rh₂4	−59.8(−40.1) [−55.0]	−60.0	−68.8	−69.8(−51.5)	−73.0	−55.4 ^f
Rh₂5	−18.5(10.5) [−11.7]	−16.0	−15.5	−17.1(25.8)	−19.0	−13.2 ^{g,h}
Rh₂5₂	−24.6(3.6)		−30.0	−29.7(−11.3)	----	−8.1 ^{g,h}
Rh₂6	−26.6(1.0)		−27.1	−26.4(14.2)	−26.4	−24.0 ^h
Rh₂7	−32.0(−5.2)		−26.5	−27.5(12.4)	−27.1	−39.0 ^h
Rh₂8	−17.9(11.2) [−12.4]	−15.8	−23.4	−23.1(20.0)	−23.7	−21.6 ^h
Rh₂8₂	−20.7(8.1)		−31.6	−30.3(−4.6)	−23.2	−16.0 ^h
Rh₂9	−33.8(−7.3) [−29.8]	−33.0	−32.9	−31.0(8.6)	−27.8	−17.0
rms ⁱ	9.4(23.8) [7.3]	8.3	12.4	11.8(31.3)	9.3	

^a ^{15}N NMR complexation shifts $\Delta\delta$ (ppm) were calculated as a difference between ^{15}N chemical shift in a complex and corresponding ^{15}N chemical shift in an uncomplexed ligand, $\Delta\delta = \delta_{\text{add}} - \delta_{\text{lig}}$. The estimations were performed using scaled chemical shifts δ_{scal} . For the comparison purposes, some values obtained from non-scaled chemical shifts δ_{raw} were given in parentheses. The numbers in square brackets correspond to the calculations with the use of the IEFPCM(CHCl_3) solvation model.

^b Geometry of molecules was optimised using the B3LYP method, the 6-31G(2d) basis set for C, H, N, and O atoms, and the LANL2DZ basis set for Rh; GIAO NMR shielding calculations were performed applying the B3PW91 method, the 6-311++G(2d,p) basis set for C, H, N, and O atoms, and the Stuttgart basis set for Rh.

^c Optimisation of the geometry of molecules and NMR calculations were performed using the B3PW91 functional, the 6-311++G(2d,p) basis set for C, H, N, and O atoms, and the Stuttgart basis set for Rh.

^d The same calculation method was applied to molecular geometry optimisation and NMR calculations.

^e The averaged chemical shift of –182.0 ppm was assumed as the experimental value for the complex.

^f The averaged chemical shift of –136.6 ppm was assumed as the experimental value for the ligand.

^g The averaged chemical shift of –365.0 ppm was assumed as the experimental value for the ligand.

^h $\Delta\delta$ calculated on the basis of complex chemical shifts measured in the solid state or in the slow exchange regime.

ⁱ rms was defined as $[\sum(\Delta\delta_{\text{calc}} - \Delta\delta_{\text{exp}})^2 / (n - 2)]^{0.5}$, where $\Delta\delta_{\text{calc}}$ denotes computed complexation shift.

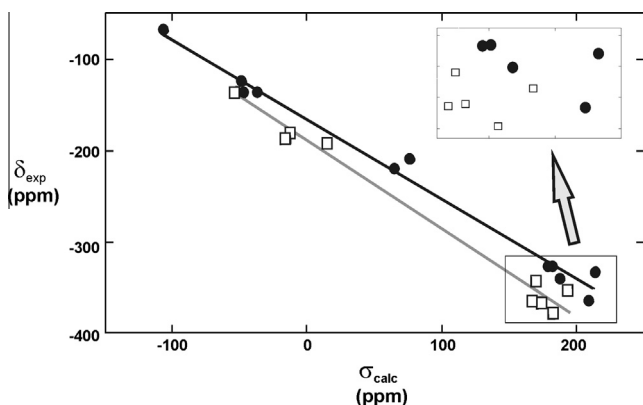


Fig. 2. An example of the correlations between calculated ^{15}N shielding constants σ_{calc} and experimental ^{15}N chemical shifts δ_{exp} for ligands **1–9** (black line and circles) and their complexes with rhodium(II) tetracarboxylates (grey line and squares). An inset shows a part of graph concerning amines **5–9** and their complexes. The calculations were performed at the CGA-PBE/QZ4P (scalar ZORA) theory level. Different trend-lines for complexes and free ligands are noticeable.

non-relativistic level, B3PW91/[6-311++G(2d,p), Stuttgart], performed better (rms of ca. 14 ppm) than advanced, time-consuming methods such as scalar and spin-orbit ZORA (rms of ca. 17 ppm). The application of the same theory level to geometry optimisations and to shielding constants computing, i.e. the optimisation at the B3PW91/[6-311++G(2d,p), Stuttgart] level instead of the cheaper method B3LYP/[6-31G(2d), LANL2DZ] only slightly improve the results for complexes (rms of 11.1 and 13.9 ppm respectively). In the case of free ligands, the results were even worse (rms of 16.6 and 13.3 ppm). Finally, it is worth noting that the correlation method performs well as far as a set of data is considered, but sometimes worsen individual chemical shifts, c.f. chemical shifts of NH in **2**, Table 2.

Computed and experimental chemical shifts have been collected in Tables 2 and 3, and visualised in the histogram (Fig. 3).

Estimation of complexation shifts $\Delta\delta(^{15}\text{N})$

The subtraction of the two theoretically calculated chemical shifts, of a complex and free ligand, appear to be the simplest way of $\Delta\delta$ estimation, as long as errors stemmed from the scale conversion cancel. Direct subtraction of computed shielding constants instead of chemical shifts cancels calibration errors but does not eliminate inaccuracies arising from different relationships between computed and experimental data for both classes of compounds, i.e. various a and b parameter of corresponding trend-lines. The use of scaling chemical shifts appears to be the best solution. In the present work, a few approaches were tested. The experimental and estimated complexation shifts were collected in Table 4 and visualised in Fig. 4.

The calculations of the complexation shifts $\Delta\delta(^{15}\text{N})$ based on non-scaled chemical shifts provided quite inaccurate values. Computed $\Delta\delta(^{15}\text{N})$ varied from ca. –58 to +11 ppm depending on the complex and theory level applied, whereas experimental values were always negative and ranged from ca. –68 to –13 ppm for the complexes in question. The differences between computed and experimental varied from ca. 12 to 34 ppm (rms of 23.8 ppm) for non-relativistic calculations and from ca. 3 to 52 ppm (rms of 31.3 ppm) for the data arising from the scalar ZORA approach. In contrast, the $\Delta\delta(^{15}\text{N})$ obtained from scaled chemical shifts were always negative, and their rms parameter varied from 7.8 to 11.7 ppm, depending on the data set. It is interesting that the non-relativistic approach, i.e. the use of the B3PW91/[6-311++G(2d,p), Stuttgart] theory level performed better than relativistic methods (rms of 7.8 and 8.3 vs. 9.3 and 11.7 ppm). At the relativistic levels, the spin-orbit ZORA performed better than scalar ZORA (rms of 11.7 and 9.3 ppm, respectively). Unfortunately, the calculation procedures did not reproduce some subtle effects. Namely, the magnitudes of experimental $\Delta\delta(^{15}\text{N})$ of 1:2 adducts were always less than those of 1:1 complexes; the calculations suggested the opposite. Summarising, the method based on scaled chemical shifts reproduced experimental values at least qualitatively or semi-quantitatively.

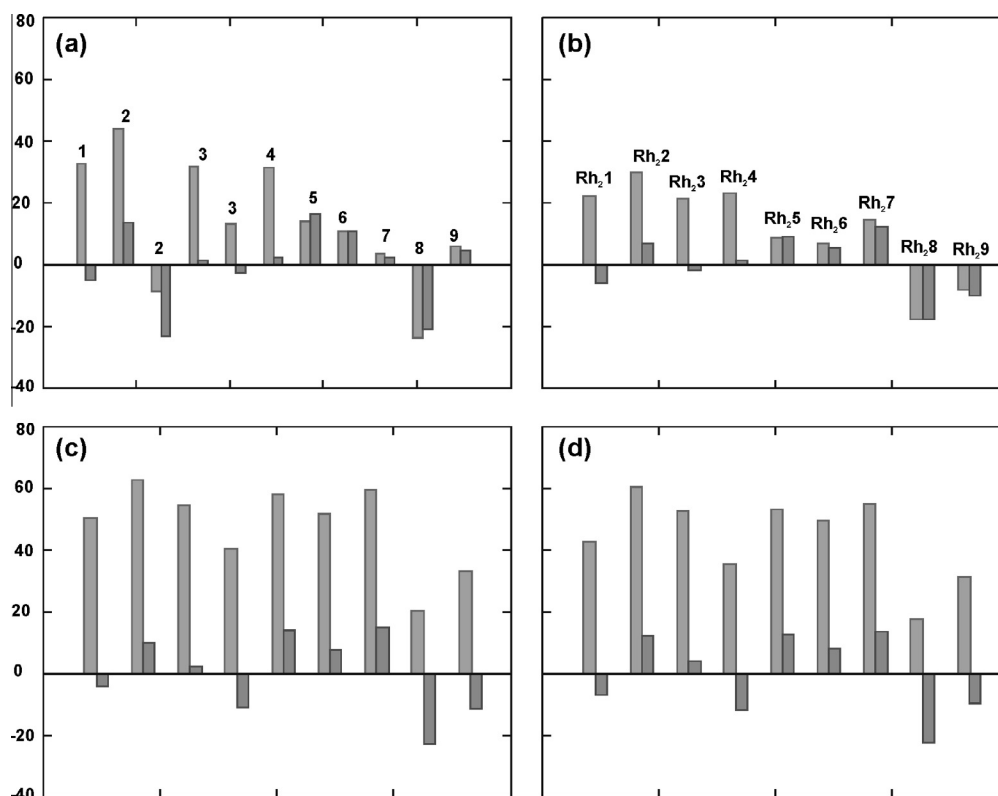


Fig. 3. Inaccuracies of calculated ^{15}N NMR chemical shifts, $\delta_{\text{calc}} - \delta_{\text{exp}}$ (the first bar in each entry) and $\delta_{\text{scal}} - \delta_{\text{exp}}$ (the second bar) for ligands **1–9** (a) and their 1:1 complexes (b–d). All calculations were performed for Rh_2form_4 complexes; experimental values arose from Rh_2ac_4 or Rh_2tfa_4 complexes. The calculations were performed at the following theory levels: (a) B3PW91/[6-311++G(2d,p)]//B3LYP/[6-31G(2d)], (b) B3PW91/[6-311++G(2d,p), Stuttgart]//B3LYP/[6-31G(2d), LANL2DZ], (c) PBE-CGA/QZ4P (non-relativistic), and (d) PBE-CGA/QZ4P (scalar ZORA). A similarity between the two last histograms is noticeable.

The calculations with the use of the IEFPCM(CHCl_3) solvation model

For selected ligands and complexes the calculations were repeated applying the IEFPCM(CHCl_3) solvation model (Tables 1–4 and 1S–4S). The calculations did not improve significantly the accuracy of computed chemical shifts of ligands (rms of 12.2 vs. 13.3), but slightly improved computed chemical shifts of complexes and $\Delta\delta$ values (rms of 10.6 vs. 14.9 and 7.3 vs. 9.4, respectively).

Expected sources of error

A question arises which is a reason for inaccuracies. The comparison of correlation parameters allows excluding insufficient basis set and lack of relativistic correction as the main source of errors. The calculations at the B3PW91/[6-311++G(2d,p), LANL2DZ] or CGA-PBE/QZ4P theory levels using non-relativistic and relativistic ZORA methods provided similar rms values. The application of the simple IEFPCM(CHCl_3) solvation model did not improve the results significantly, at least at non-relativistic levels. Presumably, one can recognise two reasons for inaccuracies: non-uniform experimental data and limitations of the molecular model used as an input for the calculations. Experimental data arose from very similar but not the same compounds (rhodium(II) tetraacetates and trifluoroacetates instead of tetraformates, $\text{N}(\text{C}_2\text{H}_5)_3$ and $\text{CH}_3(\text{CH}_2)_3\text{CN}$ instead of $\text{N}(\text{CH}_3)_3$ and CH_3CN). The measurements were performed either in slow or fast exchange regimes. Finally, chemical shifts were acquired in CDCl_3 solution or taken from CPMAS spectra. The calculations have been performed assuming a rigid, isolated molecule of 1:1 complex of rhodium(II) tetraformate. However, the 1:1 complexes do not exist practically in solution; these complexes are expected to form various associates

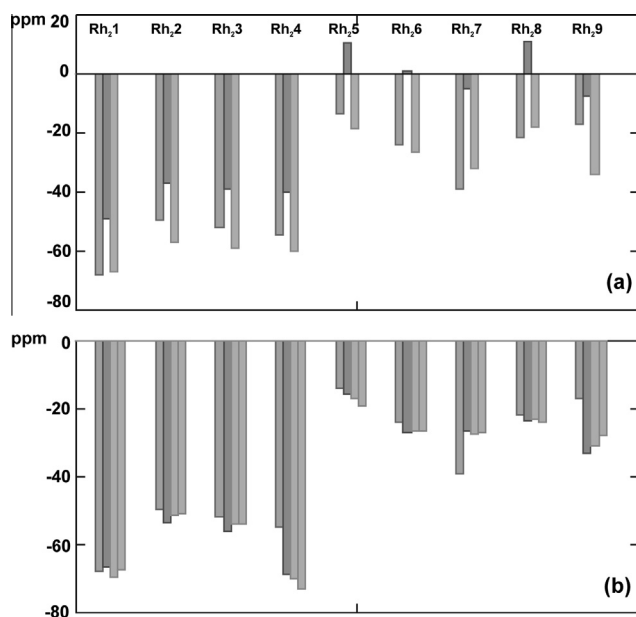


Fig. 4. A comparison between experimental and computed $\Delta\delta(^{15}\text{N})$. (a) The calculations of chemical shifts at the B3PW91/[6-311++G(2d,p), Stuttgart]//B3LYP/[6-31G(2d), LANL2DZ] theory level; the bars (from left to right) in each entry concern experimental $\Delta\delta(^{15}\text{N})$ and complexation shifts computed on the basis of non-scaled and scaled chemical shifts. (b) The calculation performed at the CGA-PBE/QZ4P theory level; the bars (from left to right) in each entry concern experimental complexation shifts and the values estimated from scaled chemical shifts computed by non-relativistic, scalar ZORA and spin-orbit ZORA methods.

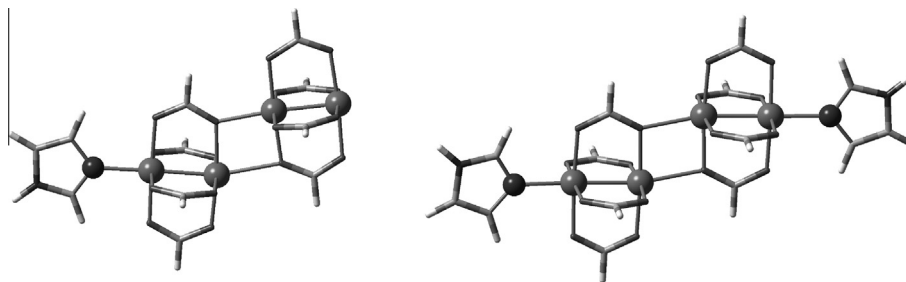


Fig. 5. Two examples of structure related to the 1:1 complex, $(\text{Rh}_2\text{form}_4-2)-\text{Rh}_2\text{form}_4$ and $(\text{Rh}_2\text{form}_4-2)_2$.

(Fig. 5). A ligand molecule can rotate around single Rh–N bond; thus, a set of rotamers should be considered in chemical shift calculations. Then, it is known that the prediction of ^{15}N chemical shift of a compound in solution requires a sophisticated solvation model which includes explicit solvent molecules. Concluding, the sum of several factors related to the limitations of assumed molecular model and experimental reference data appeared to be the main source of inaccuracies.

Conclusions

One can summarise this work as follows:

- (i) The calculations of ^{15}N NMR shielding constants for a set of nitrogenous ligands and their complexes with rhodium(II) tetracarboxylates have been performed using a few theory levels; both non-relativistic and relativistic (ZORA). Computed shielding constants correlated satisfactorily with the experimental chemical shifts (correlation coefficients over 0.99). Calculations at the non-relativistic level, namely at the B3PW91/[6-311++G(2d,p), Stuttgart]/[B3LYP/[6-31G(2d), LANL2DZ], provide the results comparable or slightly better than those obtained by the more expensive CGA-PBE/QZ4P ZORA (scalar and spin-orbit) methods.
- (ii) The conversion of the ^{15}N shielding scale to the chemical shift scale by the use of reference shielding constants (CH_3NO_2) resulted in very inaccurate values. Particularly, a large error occurred in the case of compounds containing a metal atom. In contrast, the application of correlation method, i.e. the use of the relationship $\delta_{\text{scal}} = a\sigma_{\text{calc}} + b$ improved the accuracy of the scale conversion. The parameters a and b for data sets computed at various theory levels have been determined and collected for further applications.
- (iii) Complexation shifts were calculated as the difference between computed ^{15}N chemical shifts of a complex and corresponding shift of a ligand. The use of scaled chemical shifts, i.e. the values obtained from shielding constants by the correlation method was essential in this case. Application of raw chemical shifts provided very inaccurate or erroneous complexation shifts. With some limitations, the experimental complexation shifts were reproduced qualitatively or semi-quantitatively.
- (iv) The analysis of correlation parameters indicated that errors in calculations arose from the limitations of assumed molecular model and quality of experimental reference data rather than an insufficient basis set and lack of relativistic corrections.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2014.11.034>.

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