Triple Resonance Experiments for the Rapid Detection of $^{103}$Rh NMR Shifts: A Combined Experimental and Theoretical Study into Dirhodium and Bismuth–Rhodium Paddlewheel Complexes

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ABSTRACT: A H(C)Rh triple resonance NMR experiment makes the rapid detection of $^{103}$Rh chemical shifts possible, which were previously beyond reach. It served to analyze a series of dirhodium and bismuth–rhodium paddlewheel complexes of the utmost importance for metal–carbene chemistry. The excellent match between the experimental and computed $^{103}$Rh shifts in combination with a detailed analysis of the pertinent shielding tensors forms a sound basis for a qualitative and quantitative interpretation of these otherwise (basically) inaccessible data. The observed trends clearly reflect the influence exerted by the equatorial ligands (carboxylate versus carboxamidate), the axial ligands (solvents), and the internal “metalloligand” (Rh versus Bi) on the electronic estate of the reactive Rh(II) center.

For a shift range on the order of 12,000 ppm, $^{103}$Rh NMR spectroscopy is, a priori, a cardinal tool to probe the electronic nature of a given rhodium complex. It allows even small electronic and geometric changes in the coordination sphere to be detected, which are difficult, if not even impossible, to assess otherwise. Its exceptional responsiveness to the chemical environment notwithstanding, $^{103}$Rh NMR is not nearly as routinely used by practitioners as one might assume. An extremely low gyromagnetic ratio in combination with often unduly long relaxation times offsets the inherent advantages of $^{103}$Rh as an $I = 1/2$ nucleus of 100% natural abundance. 2D inverse detection techniques based on polarization transfer, most notably HMOC experiments, are the currently best way to overcome this massive hurdle (Scheme 1); they mandate, however, that a sensitive nucleus (1H or 31P) is (directly) coupled to the Rh-center, which in turn limits the types of complexes that can be covered.

Scheme 1. Established and New Methods for the Determination of $^{103}$Rh Chemical Shifts

Because dirhodium tetracarboxylate complexes lack these requirements, such “paddlewheel” compounds have basically defied scrutiny by $^{103}$Rh NMR spectroscopy despite their paramount importance in (asymmetric) carbene chemistry and beyond. Not even the $^{103}$Rh chemical shifts of bare unquenched $[\text{Rh}_2\text{(OAc)}_4]$ (1) or $[\text{Rh}_2\text{(OTf)}_4]$ (6) are known, which are the parent members of this series and the starting points for the preparation of innumerable chiral variants by ligand exchange. Outlined below is a convenient NMR experiment that applies to these and other rhodium complexes that were previously beyond reach. A combined experimental and computational approach helps to interpret the now available shift data and in so doing provides insights into the electronic nature of these valuable catalysts.

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Scheme 1. Established and New Methods for the Determination of $^{103}$Rh Chemical Shifts
deemed remarkable in view of a T₁-relaxation time of 39 s (at 9.4 T and 310 K).5 The known temperature-dependence of the resonance (1.6 ppm/K) could be easily verified.1,37

The situation in [Rh₂(OAc)₄] is slightly more involved because the magnetization will be transferred from one C atom to two chemically equivalent Rh centers. In contrast to a mononuclear complex where the magnetization transfer efficiency of the HMQC step is Δ₂ = 1/(4 × Jₐₜₜ), the optimal delay for an IS₂ system is theoretically Δ₂ = 1/(8 × Jₐₜₜ).39 In our case, however, best results were obtained with Δ₂ = 1/(12 × Jₐₜₜ) (see the Supporting Information). Under these conditions, excellent spectra were recorded with 10⁻¹⁵ mM solutions of isotopically unlabeled [Rh₂(OAc)₄] in [D₃]-MeCN with a ≤15 min acquisition time regardless of whether the magnetization transfer pathway I or II was chosen (Figure 3).40 Once again, the strong temperature-dependence of the signal (1.33 ppm/K) was easily proven.41

Figure 1. H(C)Rh pulse sequence. The phase cycling scheme is as follows: x = pulses without a defined phase; Φ₁ = x, x, x, x, −x; Φ₂ = y; Φ₃ = x, −x, −x; Φ₄ = x, x, −x, −x; Φ₅ = x, −x, −x, −x. Gradient ratios are as follows: for concentrated samples, G₁ = 75%, G₂ = 32%, and G₃ = 14.2%; for diluted samples, G₁ = G₂ = 80%, G₃ = 5.1%; g_max = 51.3 G/cm, Δ₁ = 1/(4 × Jₐₜₜ); Δ₂ = 1/(4 × Jₐₜₜ) for monomeric Rh complexes, Δ₂ = 1/(12 × Jₐₜₜ) for dinuclear Rh(II) paddlewheel complexes.

Figure 2. (a) ¹³C{¹H} NMR signals of Rh(acac)₃. (b) H(C)Rh spectrum of Rh(acac)₃ (10 mM). (c) ¹⁰³Rh chemical shift of Rh(acac)₃ at temperatures between 223 and 323 K; the left axis shows the ¹⁰³Rh chemical shift referenced according to IUPAC recommendations (saturated Rh(acac)₃ in CDCl₃ (δ = 0 ppm), Ξ(¹⁰³Rh) = 3.186447%), and the right axis uses the commonly applied reference (Ξ(¹⁰³Rh) = 3.169).37

Figure 3. (a) ¹³C{¹H} NMR signals of [Rh₂(OAc)₄] (1) in CD₃CN. (b) Magnetization transfer pathways. (c) H(C)Rh spectra (15 mM) using pathway I or II.

Because acetonitrile acts as kinetically labile ligand to the axial coordination sites on the dimetallic cage of 1, the effect of different solvents was evaluated (Scheme 2A). The recorded data suggest that [D₈]-THF and [D₆]-acetone as supposedly weaker donors than MeCN cause a “deshielding” of the signal, whereas the analogous (catalytically inactive) adduct 1·PPh₃ has a notably lower shift.42−44

Next, the influence of the bridging carboxylate ligands was studied more systematically. To this end, all possible (heteroleptic) dirhodium acetate and trifluoroacetate complexes (1−6) were prepared and analyzed (Scheme 2B).45,46 The recorded data provide a dramatic illustration of the sensitivity of ¹⁰³Rh chemical shifts to changes in the periphery of the nucleus; remote fluorination entails incremental deshielding over a range of no less than 380 ppm. Qualitatively, increased electrophilicity at the rhodium seems to come along with higher δ¹⁰³Rh; to scrutinize this aspect, this particular set of complexes was chosen for a detailed computational analysis (see below).

Numerous other dirhodium tetracarboxylate complexes could be analyzed equally well (Figure 4). The recorded δ¹⁰³Rh
acids, \(^{47}\) which capture their donor strengths. Yet, all data fall into a fairly narrow shift window (especially if one disregards the highly fluorinated derivatives \(5\) and \(6\)), which indicates that the electronic character of the dirhodium core barely changes. One can hence safely conclude that peripheral modifications of the paddlewheels, as practiced in asymmetric catalysis, will hardly change the electronic nature of the catalyst and the selectivity-determining transition state.

The "modest" shift range of the tetracarboxylate complexes is best appreciated by a comparison with dirhodium paddlewheels comprised of one or more N-based ligands (Scheme 3A). \(^{46}\) The arguably most instructive example is the heteroleptic complex \(16\), since the incorporation of a single −NH group sets the signals of the now chemically different Rh sites >1000 ppm apart. This finding has implications for catalysis, as a chiral relative of \(16\) was recently shown to be uniquely effective in asymmetric cyclopropanation reactions of \(\alpha\)-stannylic(silyl) \(\alpha\)-diaoesters. \(^{49}\) Indirect evidence suggested that these reactions proceed at the rhodium face carrying the protic −NH group, which according to the shift data is the (much) less electrophilic site; this conclusion clearly mandates further scrutiny. In any case, \(^{103}\)Rh NMR makes it unambiguously clear that carboxylate- and carboxamidate-based paddlewheel complexes are very distinct types of catalysts in electronic terms. \(^{58}\)

A similar conclusion must be drawn for heterobimetallic [BiRh]−paddlewheel catalysts. \(^{50−53}\) They are known to afford much more electrophilic carbene complexes and perform particularly well in asymmetric cyclopropanation reactions. \(^{53−56}\) That the 4d orbitals of the Rh(+2) center will sense the incorporation of the sixth-row main group element unambiguously clear that carboxylate- and carboxamidate-based paddlewheel complexes are very distinct types of catalysts in electronic terms. \(^{58}\)

Case studies are known in the literature in which the shift of rhodium complexes (or derived reactive intermediates) could be correlated with catalytic performance, but the number is conspicuously small. \(^{2,57−63}\) With the technical problems in recording pertinent \(^{103}\)Rh NMR spectra come the challenges in interpreting the data, as many different parameters play roles that often prove difficult to disentangle \(^1−3\) even by computational means. \(^{64−66}\) Arguably, however, dirhodium tetracarboxylate complexes in general and the comprehensive subset 1−6 in particular are ideally suited for this type of analysis. They all are comprised of the same rigid "lantern" core and changes in the bite angles and the Rh−O distances are small and secondary interactions within the ligand sphere minute. Hence, the incremental shift changes when going from \([\text{Rh}_2(\text{OAc})_4]\) (1) to \([\text{Rh}_3(\text{OTfa})_4]\) (6) basically reflect electronic rather than geometric changes. A qualitative comparison was therefore deemed legitimate, and a quantitative analysis of the relevant shielding tensors was facilitated because the principal axes coincide in all cases.

Contingent upon the careful optimization of the geometries, the computed shift values reproduce the experimental values remarkably well (Table 1). \(^{55−57}\) Differences of no more than 0−36 ppm (on a scale of 12,000 ppm) imply that the chosen level of theory provides an accurate description of complexes.

Table 1. Comparison between Computed and Experimental \(^{103}\)Rh Chemical Shifts\(^a,b\)

| complex | \(\delta_{\text{exp}}\) | \(\delta_{\text{calc}}\) | \(\Delta\) | HOMO | LUMO | \(\Delta\) Homo−Lumo |
|---------|-----------------|-----------------|---------|------|------|-------------|
| 1       | 0.504           | -0.1882         | 0.6926  | 0.1281|
| 2       | 0.492           | -0.1953         | 0.6874  | 0.1244|
| 3       | 0.48            | -0.2053         | 0.6857  | 0.1263|
| 4       | 0.48            | -0.2030         | 0.6823  | 0.1202|
| 5       | 0.467           | -0.2133         | 0.6804  | 0.1227|
| 6       | 0.455           | -0.2238         | 0.6782  | 0.1244|

\(\Delta\)Homo−Lumo = \(\delta_{\text{exp}}−\delta_{\text{calc}}\). \(\delta_{\text{calc}}\) is the critical spin−spin coupling between the \(\alpha\)− and \(\beta\)-spin density at the Rh nucleus.

\(\delta_{\text{exp}}\) is the shift of compound \(0.0906\) ppm, referenced to \(\delta_{\text{exp}}\) (103Rh) = 3.16%) and correlation with the pKa of the parent carboxylic acids.\(^{47}\)
of this type. Based on this solid foundation, a more detailed analysis is possible and warranted.

As shown above, increasing the fluorination of the acetate ligands causes deshielding. The reduced donor ability of the fluorinated ligands renders the complexes increasingly electrophilic; indeed, the computed $^{103}$Rh chemical shifts can be correlated with the partial charge at Rh (Table 1). Although this picture is intuitive and may provide rough guidance for the practitioner, it is—at least—oversimplified. Note that the computed energy of the LUMO decreases when going from 1 to 6, as expected, but the energy of the HOMO drops to a similar extent such that $\Delta E$ remains essentially constant. The HOMO – LUMO gap alone does obviously not explain the observed results.

NMR shifts are neither primarily determined by the charge at the metal nor solely by the frontier orbitals. Rather, a chemical shift is an anisotropic property (even though solution NMR spectroscopy provides only the isotropic shift ($\delta_{iso}$)). Computational methods allow the individual components of the shielding tensor $\sigma$ ($\delta_i = \sigma_{iso,i} - \sigma_{ii}$) to be deconvoluted; it is the paramagnetic term ($\sigma = \sigma_{iso} + \sigma_{para}$) that largely determines the shift of a transition metal nucleus.

The paramagnetic contributions arise from magnetically induced admixture of electronically excited states into the electronic ground state by the angular momentum operator ($\hat{L}_i$) as described by the Ramsey equation (see the Supporting Information). Deshielding in the direction $\sigma_{para}$ depends on which orbitals $\phi_{loc}$ and $\phi_{lu}$ can be coupled via $L_i$ and on their relative energies: the smaller the energy gap, the larger the effect.

For complexes 1–6, the dominant contributions to $\sigma_{para}$ stem from interactions of the key frontier orbitals (Figure 5).

As expected, all MOs are delocalized over both Rh centers. Due to symmetry, the only nonzero contributions to the $\sigma_{para}$ component stem from the coupling of the virtual orbitals with the HOMO $- M$ (where $M$ is the difference of the HOMO and the LUMO), which is delocalized over the ligands on both axes. As a consequence, $\sigma_{para}$ is always affected by fluorination, irrespective of the position of the halogen atoms. The largest contributions to $\sigma_{para}$ originate from the coupling of the virtual orbitals with the HOMO $- 2$ ($d_{xy}$), which is delocalized over the ligands on both axes. As a consequence, $\sigma_{para}$ is always affected by fluorination, irrespective of the position of the halogen atoms. The largest contributions to $\sigma_{para}$ originate from the coupling of the virtual orbitals with the HOMO $- 2$ ($d_{xy}$), which is delocalized over the ligands on the $x$-axis. Similarly, the largest contributions to $\sigma_{para}$ originate from the coupling of the virtual orbitals with the HOMO $- 2$ ($d_{xy}$) orbital, which is mostly delocalized over the ligands on the $y$-axis. Hence, $\sigma_{para}$ and $\sigma_{para}$ mainly respond to fluorination on the perpendicular chemical shift and increases with the increasing fluorination; in contrast, $\delta_{para}$ is roughly constant for 1, 2, and 4, all of which are nonfluorinated along the $x$-axis, while $\delta_{para}$ is basically constant for complexes 4, 5, and 6, which are fully fluorinated along the $y$-axis. Analysis of a given shielding tensor hence provides information about the donor strength of the ligand at the perpendicular position of the lanthanum core.

The subtleties within this series notwithstanding, one will hardly go wrong in assuming that the $\approx 880$ ppm shift difference between $[\text{Rh}(\text{OAc})_4]$ (1) and $[\text{BiRh}(\text{OAc})_4]$ (21) bears witness of a drastically different electronic character (Scheme 3). An accurate assessment requires the same kind of analysis as outlined above for the (partly) fluorinated complexes; qualitatively, however, the massive upfield shift suggests that the Rh center, which is the catalytically relevant site of 21, is (much) less electrophilic. The situation in the heteroleptic species 16 is similarly intuitive; because of its relevance, however, a more detailed profiling is subject to ongoing studies. Likewise, we are using the H(C)Rh triple resonance experiment for investigations into other previously uncompliant rhodium complexes, including (highly) reactive intermediates. Pertinent results will be reported in due course.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c06414.

Experimental Section containing supporting NMR data and computational data (PDF)
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Notes
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(37) The strong temperature dependence disqualifies [Rh(acac)3] as the “standard” for referencing 103Rh NMR shifts; the consensus is to reference the 103Rh shifts to an absolute frequency related to the resonance frequency of the protons of tetramethyilsilane (δ(Rh103) = 3.16%), cf. ref 1.

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(41) For this reason, we expect 103Rh chemical shifts to vary by 5 ppm in different experiments, unless the temperature is very carefully controlled.

(42) The binding of an axial ligand involves the Rh–Rh B* orbital; raising the energy of this low-lying unoccupied orbital is expected to affect the shift according to the Ramsey equation (see below). For a general discussion of the three-center or four-electron bonding in dithiocarbamate paddlewheel complexes, see: Berry, J. F. The Role of Three-Center/Four-Electron Bonds in Superelectrophilic Dithiouronium Carbone and Nitrene Catalytic Intermediates. Dalton Trans. 2012, 41, 700–713.

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