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The Structures of Reactive Donor/Acceptor and Donor/Donor Rhodium Carbenes in the Solid State and their Implications for Catalysis

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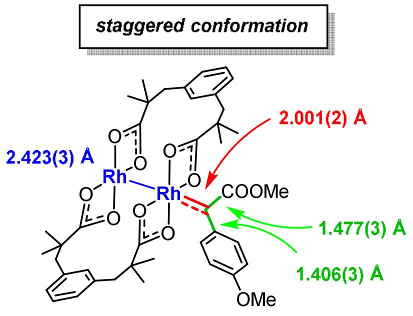
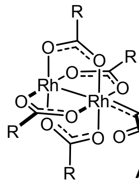
ABSTRACT: Owing to its tremendous preparative importance, rhodium carbene chemistry has been studied extensively during past decades. The invoked intermediates have, however, so far proved too reactive for direct inspection and reliable experimental information has been extremely limited. A series of X-ray structures of pertinent intermediates of this type, together with supporting spectroscopic data, now closes this gap and provides a detailed picture of the constitution and conformation of such species. All complexes were prepared by decomposition of a diazoalkane precursor with an appropriate rhodium source; they belong either to the dirhodium(II) tetracarboxylate carbene series that enjoys widespread preparative use, or to the class of mononuclear half-sandwich carbenes of Rh(III), which show considerable potential. The experimental data correct or refine previous computational studies, but corroborate the currently favored model for the prediction of the stereochemical course of rhodium catalyzed cyclopropanations (which is likely applicable to other reactions too). Emphasis is put on stereoelectronic rather than steric arguments, with the dipole of the acceptor substituent flanking the carbene center being the major selectivity determining factor. Moreover, the very subtle influence exerted by the anionic ligands on a Rh(III) center on the chemical character of the resulting carbenes species is documented by the structures of a homologous series of halide complexes. Finally, the isolation of an N-bonded Rh(II) diazoalkane complex showcases that steric hindrance represents an inherent limitation of the chosen methodology.



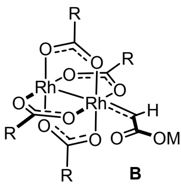
INTRODUCTION

Since the first controlled decomposition of a diazo compound with catalytic amounts of Rh$_2$(OAc)$_4$,[1,2] this methodology has gained considerable importance. The resulting carbenes power a host of intra- and intermolecular bond forming reactions or reaction cascades: For example, they engage in cyclopropanations, cyclopropenations, [4+3] cycloadditions, insertions into E–H (E = C, Si, O, NR, S) and carbon-heteroatom bonds, as well as in a myriad of ylide chemistry.[3-10] Many of these transformations are distinguished by impressively high turn-over numbers and -frequencies as well as truly remarkable levels of chemo-, regio-, diastereo- and enantioselectivity.[3-10] This is particularly true for reactions of carbenes of type **C** with a donor/acceptor substitution pattern that slightly tempers the "superelectrophilic" character of the pure acceptor analogues **A** and **B**.

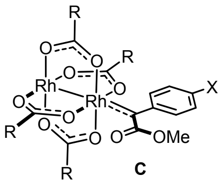
The extensive body of preparative work on rhodium carbenes in general has led to a good qualitative understanding of their reactivity profiles. Based on this knowledge it was possible to conclude, for example, that olefin cyclopropanation proceeds via a concerted but highly asynchronous mechanism.[11,12] This scenario puts emphasis on the resonance extreme **D** in which the reactive species is represented as a metal-stabilized carbocation.[13] Yet, even this consensus model has witnessed a striking evolution: Specifically, it had originally been assumed that an alkene approaches a donor/acceptor carbene **C** in a "side-on" manner while passing over the acceptor (e. g. ester) group.[14,15] Today, however, the opposite trajectory is considered more plausible, invoking an "end-on" oriented olefin traversing alongside the donor (e. g. arene) substituent (Autschbach/Davies model).[12] Moreover, the computed barriers along the reaction coordinate have been considerably revised over the years.[16]



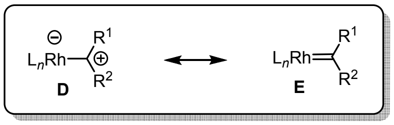
A



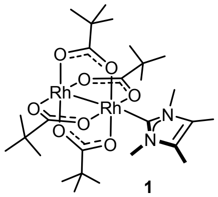
B



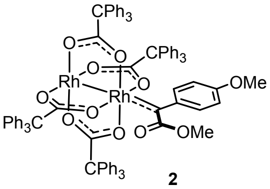
C



While these amendments certainly reflect advances in computational chemistry,[11,12,17] they also emphasize the lack of experimental calibration points. Relevant dirhodium carbenes largely defied direct inspection. Only the X-ray structures of various NHC adducts such as **1** are known.[18,19] Although **1** misses the prototypical reactivity of electrophilic carbenes, the lengthening of the Rh–Rh bond concurs with a three center/four electron bonding mode that is currently thought to be the best description of the dimetallic core.[20,21] Only very recently have Davies, Berry and coworkers managed to observe the prototype push/pull dirhodium carbene **2** in solution.[22] The characteristic signal at δ_C = 242 ppm showcases the electrophilic nature of this species, whereas the recorded EXAFS data suggest a linear Rh–Rh–C array and an elongated Rh–Rh bond (2.43 Å). The averaged Rh–C and Rh–O distances derived from the EXAFS spectra were deconvoluted by DFT to individual bond lengths of 1.972 Å and 2.041 Å, respectively.[22] Relevant conformational details, however, could not be deduced.



1



2

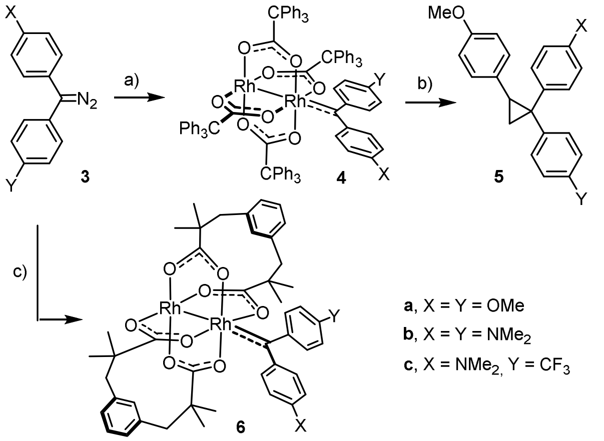
Outlined below is a series of crystal structures of reactive carbenes of the Rh(II) tetracarboxylate as well as of the Rh(III) half-sandwich type with different substitution patterns. This includes the donor/acceptor complex **10**, which differs from **2** only in that it carries a α,α,α′,α′-tetramethyl-1,3-benzenedipropionate (esp)[23] rather than triphenylacetate (tpa)[24] ligand set; esp ligands have an impressive track record in rhodium catalysis.[23,25] Collectively, our data provide a detailed picture of the constitution, conformation and bonding of these important reactive intermediates; they allow the published computational data to be validated and the predictive models to be checked.[26]

RESULTS AND DISCUSSION

The Donor/Donor Series. Since donor substituents are known to tame an adjacent electrophilic carbene center, it seemed reasonable to start our structural investigations by targeting dirhodium carbenes bearing *two* donor groups.[27] The bis(*p*-methoxyphenyl)carbene backbone was deemed a good candidate, not least because this particular motif had allowed us to isolate the first reactive gold carbenes in crystalline form.[28,29] Our efforts were invigorated by a control experiment, which showed that the reaction of the readily prepared and safe-to-handle bis(4-methoxyphenyl)-diazomethane **3a**[30,31] with 4-methoxystyrene in the presence of $[Rh_2(tpa)_4]\cdot CH_2Cl_2$ (0.5 mol%) cleanly furnished the desired cyclopropane derivative **5a** (Scheme 1). This result proves that the putative carbene **4a** generated in situ shows the prototype chemical behavior of this class of reactive intermediates;[32,33] its structure is therefore undoubtedly relevant for mechanistic discussions.

Treatment of a cold solution of $[Rh_2(tpa)_4]\cdot CH_2Cl_2$ in CH_2Cl_2 with a solution of **3a** in the same solvent resulted in an instantaneous color change from purple to dark turquoise and the vigorous evolution of N_2. The resulting species **4a** turned out to be sufficiently stable at −20°C for characterization by NMR, UV, IR and even HRMS (ESI+). The resonance at δ_C = 268.9 ppm bears witness for its carbene character; somewhat counterintuitively though, this signal is downfield from that of the push/pull complex **2** (δ_C = 242 ppm) observed by Davies, Berry and coworkers.[22]

Scheme 1. Preparation of dirhodium tetracarboxylate complexes and their use in olefin cyclopropanation.[a]



[a] Reagents and conditions: (a) $[Rh_2(tpa)_4]\cdot CH_2Cl_2$, CH_2Cl_2, −10°C; b) *p*-methoxystyrene, pentane, see Text; c) $[Rh_2(esp)_2]$, CH_2Cl_2, −10°C

After numerous attempts, we managed to grow crystals of **4a** suitable for X-ray diffraction. Major difficulties arose from the fact that even the pure crystalline material decomposes in less than 12 h at −20°C; solute CH_2Cl_2 and toluene are necessary to ensure meta-stability, yet tend to be highly disordered within the unit cell. Considerable experimentation was necessary to find that crystals grown from the ternary mixture CH_2Cl_2/toluene/fluorobenzene were of better quality, allowing all atoms of the complex to be refined anisotropically (R = 5.9%).

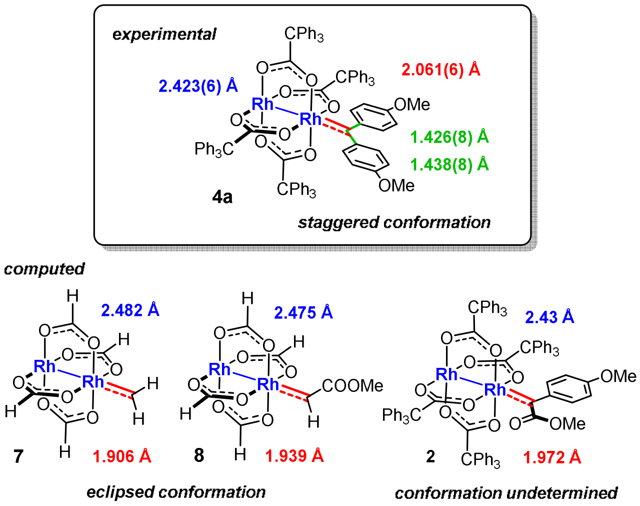


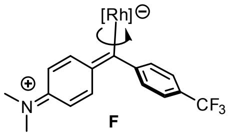
Figure 1. Comparison of important structural features of complex **4a** with in silico data

As the structure of **4a** in the solid state has been published in a recent Communication,[26] it suffices to briefly summarize the relevant attributes (Figure 1). As expected, the carbene ligand occupies an axial coordination site on the dirhodium cage and the Rh2-Rh1–C1 axis is almost linear (176.9°). The

Rh1–C1 bond distance (2.061(6) Å) is substantially longer than that computed for the model compounds **7** (1.906 Å)[20] and **8** (1.939 Å)[20] and even the hemi-stabilized carbene **2** (1.972 Å).[22] This fact suggests that back-donation of electron density from the metal into the carbene center is low. To compensate, C1 strongly engages with the flanking arenes, one of which is coplanar to ensure maximum orbital overlap. This tight interaction leads to a significant contraction of the bonds between C1 and the C_{ipso} atoms (1.426(8)/1.438(8) Å). The entire carbene substituent adopts a staggered conformation relative to the O–Rh–O unit, an aspect to be discussed in more detail below, whereas **7** and **8** were computed to prefer the eclipsing orientation.[20]

The analogous complexes **4b** and **6b** have also been obtained in crystalline form, which carry $-NMe_2$ rather than –OMe groups on the arene rings and differ from each other in the ancillary tetracarboxylate ligand set (tpa in **4** versus esp in **6**). Their basic structural attributes are largely similar to those of **4a**, with a staggered conformation of the carbene entities relative to the dimetallic core and a strong participation of the electron rich arenes in the stabilization of the carbene center (X-ray structures of **4b** and **6b** are displayed in the Supporting Information). A subtle and as yet unexplained difference, however, relates to the fact that **4a** and **6b** crystallize as coordination polymers, in which the –OMe ($-NMe_2$) group of one monomer unit ligates Rh2 of the next unit, whereas **4b** is monomeric in the unit cell.

The Donor/Acceptor Series. Next, we prepared complex **4c** in which one electron-rich and one electron-deficient phenyl ring flank the carbene center. The structure of this particular push/pull dirhodium carbene in the solid state is informative (Figure 2). As one might expect, the phenyl ring with the $-NMe_2$ substituent carries the burden of stabilizing the carbene center; it adopts an almost perfectly coplanar orientation (Θ = 0.9°) to maximize overlap of the π-cloud of the phenyl ring with the (empty) carbene p-orbital representing the major lobe of the LUMO. With only 1.389(3) Å, the C1-C2 distance is even shorter than the already very tight C1-C_{ipso} bonds in **4a** (Figure 1). The $F_3CC_6H_4$- ring as the acceptor substituent, in contrast, lies orthogonal to the carbene center (Θ = –94.7°) to largely cut-off any destabilizing electronic communication. As a consequence, the C1-C10 bond (1.473(4) Å) is significantly longer than C1-C2. Once again, the carbene entity adopts a staggered orientation relative to the dinuclear core. The structural features of the analogous complex **6c** endowed with esp rather than tpa ligands are largely similar (for details, see the Supporting Information). This comparison confirms that the choice of ancillary ligands exerts only a small effect on the structure of such dirhodium species.



F

The NMR data suggest that the structure of these complexes in solution must be very similar. Most notably, the rotation about the C1–C2 bond in **4c** and **6c** is largely frozen out at –10°C and the species are best depicted by the quinoid resonance extreme **F**. In addition to the inequivalent protons of the $Me_2NC_6H_4$- ring, the characteristic ^{15}N NMR shift of the Me_2N- group (δ_N = –282.6 ppm) is in excellent agreement with this description.[34] On the other hand, the rotation about the Rh1–C1 bond is unrestricted on the NMR time scale, which confirms the low bond order of the "carbene" unit deduced from the crystallographic data.

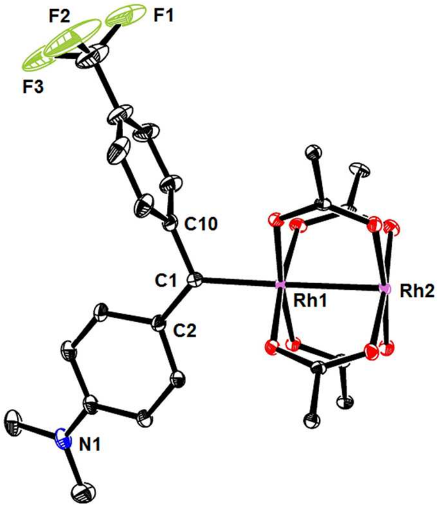
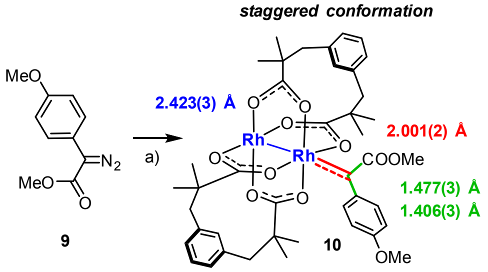


Figure 2. Structure of the donor/acceptor dirhodium carbene **4c** in the solid state; the lateral phenyl rings of the tpa ligands on the dimetallic cage are removed for clarity (for the complete structure and further details, see the Supporting Information).

Particularly noteworthy is the structure of complex **10** in the solid state, which represents a prototype donor/acceptor carbene of the type that has been most widely studied in the past (Scheme 2).[6,7,35] **10** is the esp-analogue of the tpa complex **2** which could previously only be characterized by spectroscopic means.[22] As the data outlined above suggest that the change of the ancillary ligand set has little structural bearing, the high-quality X-ray data (R = 3.18%) of this very labile intermediate are considered an important reference point (Figure 3). This notion is supported by the fact that the carbene centers of **10** (δ_C = 237.1 ppm) and of **2** (δ_C = 242 ppm)[22] resonate at very similar field.

Scheme 2. Preparation of the prototypical donor/acceptor dirhodium tetracarboxylate complex 10 and summary of relevant structural data.[a]



[a] Reagents and conditions: $[Rh_2(esp)_2]$, FC_6H_5/CH_2Cl_2, 0°C → –20°C

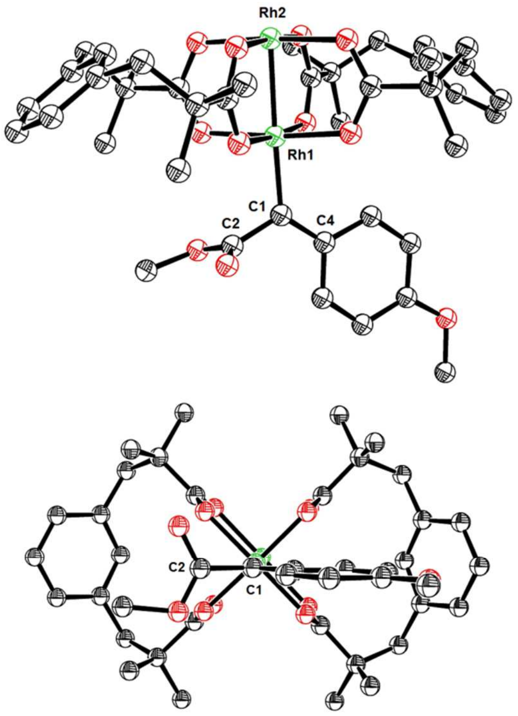


Figure 3. Structure of the donor/acceptor dirhodium carbene **10** in the solid state in two different orientations; for details, see the Supporting Information

The donor substituent is perfectly coplanar with the carbene center (Θ = 0°); accordingly, the C1-C4 bond is very short (1.406(3) Å). The fact that all protons on the arene ring are inequivalent in the ^{1}H NMR spectrum recorded at −50°C suggests that this structure-determining motif is retained in solution (whereas the rotation about the Rh1-C1 "carbene" bond is unrestricted at this temperature). In contrast, the ester is orthogonally oriented, such that the C1-C2 distance is not contracted (1.477(3) Å).

With regard to the carbene ligand itself, it is noteworthy that the Rh1-C1 bond in **10** (2.001(2) Å) clearly exceeds the 1.972 Å computed for **2**, whereas the Rh2−Rh1 distance (2.4226(3) Å) is somewhat shorter than the 2.43 Å proposed for **2** based on EXAFS/DFT.[22] The mutual compensation of the bond lengths within the core is readily understood on the basis of a 3-center/4-electron for the Rh–Rh–C unit.[20,21] Another interesting and as yet undescribed aspect concerns the asymmetry of the bond angles about the carbene center: While the arene ring is visibly bent away from the cage (Rh1-C1-C4, 127.6(1)°), likely to avoid a clash with the tetracarboxylate ligand framework, the orthogonally disposed ester group is sterically hardly inflicting as evident from the small Rh1-C1-C2 angle (113.7(2)°).

The two esp ligands orient their *meta*-disubstituted benzene rings in a *syn*-fashion, such that the dimetallic core adopts C_s symmetry; it is noteworthy that this conformation is different from that of [$Rh_2(esp)_2$](acetone)$_2$, which is C_2 symmetric.[23] Once again, the carbene entity is staggered relative to the O−Rh−O unit, formally bisecting the binding pocket created by the ancillary ligands (Figure 3, bottom). Provided this orientation is retained in solution, it is safe to predict that an olefin (or other nucleophilic reaction partner) will hardly be able to approach the (empty) carbene lobe by passing over the ester (Figure 4). Though sterically unhindered, trajectory (a) is stereoelectronically unfavorable and does not lead to efficient orbital overlap. The seemingly most open trajectory (b) is equally unlikely on stereoelectronic grounds because of massive dipole-dipole repulsion between the ester carbonyl and the incoming nucleophile. Therefore it is probable that the reaction partner approaches the carbene center in a Bürgi-Dunitz-type trajectory by gliding alongside the arene, which itself is no obstacle in the orientation that it adopts. The structure of **10** in the solid state therefore lends credence to the Autschbach-Davies model currently favored in predicting the stereochemical course of reactions involving dirhodium tetracarboxylate carbenes derived from aryldiazoacetates, which generally provide excellent diasteroselectivities in reactions with olefins or other partners.[12,36]

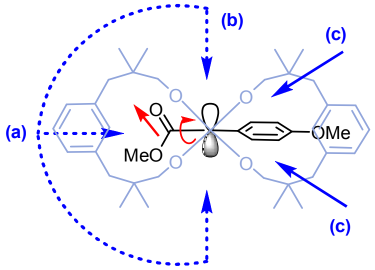
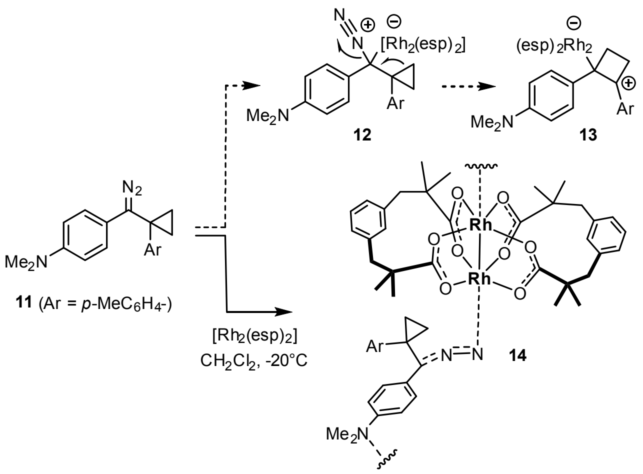


Figure 4. Newman-type projection of complex **10** along the C1−Rh1−Rh2 bond; the blue arrows show possible trajectories for an incoming nucleophile, the straight red arrow indicates the dipole of the acceptor group. For the unhindered rotation of the ester (curved red arrow), any backside attack will face the same stereoelectronic demands.

As outlined above, the structure of the donor/acceptor carbenes **4c** and **6c** bearing two aryl groups of different electronic character are largely similar to that of **10**. Even though the dipole of the $F_3CC_6H_4$- ring acting as the acceptor substituent in lieu of the ester is orthogonal rather than parallel to the carbene p-orbital, trajectories (a) and (b) remain stereoelectronically disfavored. Therefore one can expect the reaction of *p*-methoxystyrene with the diaryl diazomethane **3c** catalyzed by Rh_2[(esp)]$_2$ to provide cyclopropane **5c** with excellent selectivity (Scheme 1); this is indeed the case (dr > 98:2, NMR).[37]

Limitation. The diazomethane derivative **11** was conceived as an appropriate substrate in an attempt to probe the chemical character of the resulting rhodium carbene. Any strong contribution of a bipolar resonance extreme **D** would impart "non-classical" carbocation character onto the derived carbene.[38,39] If so, ring opening of the cyclopropyl unit or, more likely, ring expansion is expected to occur, because the cyclobutyl cation resonance form **13** seems most favored for the extra benzylic stabilization (Scheme 3).

Scheme 3. Attempted formation of a rhodium carbene with "non-classical" carbocation character led to the isolation of a diazo adduct.



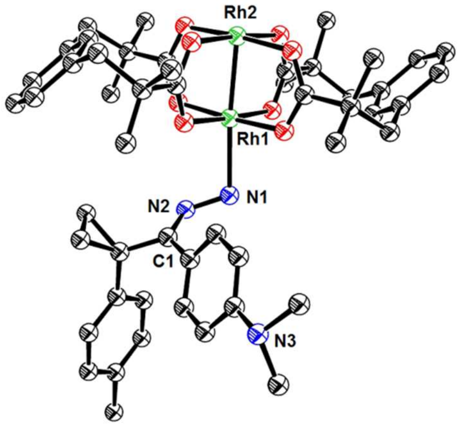
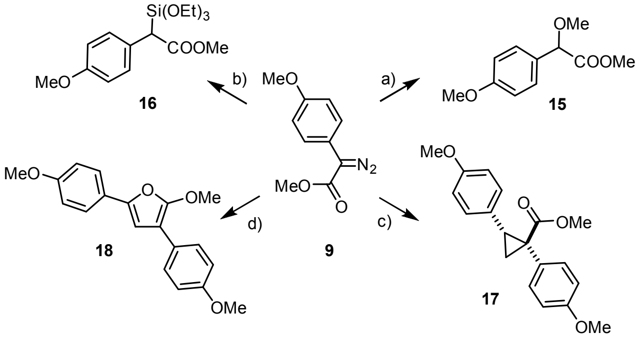


Figure 5. Structure of the diazo adduct **14** in the solid state; for details, see the Supporting Information

Yet, the attempted formation of a carbene complex failed; rather, adduct **14** was isolated (as a coordination polymer in the solid state), in which the intact diazo group is ligated end-on to the dirhodium fragment (Figure 5).[40] The doubly-bent coordination geometry positions the substituents on the N-atoms quasi orthogonal to each other (Rh1-N1-N2-C1 108.2°).[41] The failure to form a rhodium carbene is ascribed to steric hindrance, which prevents bulky $[Rh_2(esp)_2]$ from reaching the negatively polarized C-atom of **11** with formation of **12** as the necessary first step en route to a metallocarbene.[42] Under more forcing conditions, substrate **11** decomposed; therefore the envisaged chemical interrogation of rhodium carbenes with the help of suitable reporter groups must await future studies.

Rhodium(III) Half-Sandwich Carbene Complexes. Although the use of the dinuclear Rh(II) tetracarboxylate carbenes **A**-**C** dominates the field, not least because they are easily rendered chiral, it is well established that various Rh(I) as well as Rh(III) sources also lead to carbenes with useful reactivity profiles.[1,2,43,44] A potentially interesting class are Rh(III) carbenes of the half-sandwich type, which are invoked in a large body of (directed) C–H activation chemistry for the (late-stage) functionalization of various heterocyclic scaffolds.[45-47] They are usually prepared from $[Cp^*RhX_2]_2$ and an appropriate diazo precursor (frequently in combination with a soluble Ag(I) salt to abstract the chloride ligands from the active species). It is believed, however, that the highly electrophilc metal fragment (cyclo)metalates the chosen arene substrate before it actually reacts with the diazo derivative.[45-47] This very large and rapidly growing body of work contrast to the lack of information about proper piano-stool Rh(III) carbenes devoid of a cyclometalated backbone. Yet, such species exhibit excellent reactivity (Scheme 4). An unoptimized loading of 1 mol% sufficed for typical O–H or Si–H insertions to proceed in excellent yield. The cyclopropanation of 4-methoxystyrene also worked well, provided that $[Cp^*RhI_2]_2$ was chosen as the precatalyst, whereas $[Cp^*RhCl_2]_2$ proved markedly less efficient (see below for a possible explanation of this different behavior). Particularly noteworthy is the direct formation of the alkoxyfuran **18** on reaction of **9** with (4-methoxyphenyl)acetylene; in judging the outcome, one has to keep in mind that this particular product is prone to hydrolysis on work up. In any case, terminal alkynes usually afford cyclopropenes in the first place, which can be rearranged to (alkoxy)furan derivatives in a separate step.[4-9,48] While this reactivity pattern has ample precedent in the acceptor/acceptor series, the few recorded examples for donor/acceptor carbenes tend to be low-yielding.[49] Therefore the direct formation of **18** is an interesting lead, not least because such electron rich furan derivatives have promising follow-up chemistry.[50]

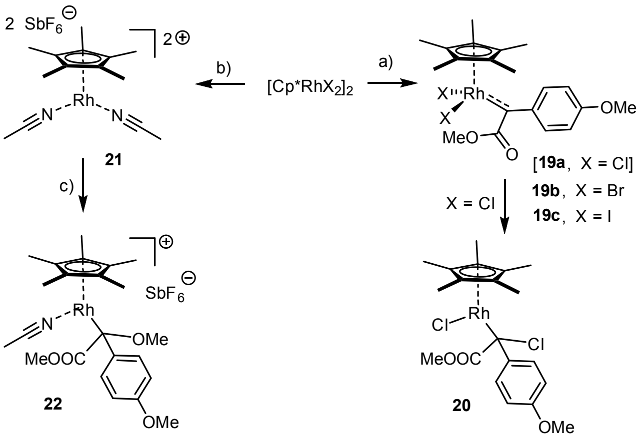
Scheme 4.



[a] Reagents and conditions: a) $[Cp^*RhI_2]_2$ (1 mol%), CH_2Cl_2, MeOH, 88%; b) $[Cp^*RhI_2]_2$ (1 mol%), $(EtO)_3SiH$, CH_2Cl_2, 81%; c) *p*-methoxystyrene, pentane, 69% (with $[Cp^*RhI_2]_2$ (1 mol%)); 46% (with $[Cp^*RhCl_2]_2$ (1 mol%)); d) $[Cp^*RhI_2]_2$ (1 mol%), (*p*-methoxyphenyl)acetylene, CH_2Cl_2, 65%

Secured structural information about any type of half-sandwich Rh(III) carbene is missing. The higher oxidation state of the central rhodium atom and the lack of an adjuvant second metal center, as present in **A**-**C**, suggest that the resulting mononuclear carbenes might be even less stable. In line with this notion, no carbene signal was detected by ^{13}C NMR in the reaction of $[Cp^*RhCl_2]_2$ with the aryldiazoester **9** (Scheme 5), but a new resonance appeared at 70.6 ppm. It was not clear at the outset whether this observation reflected inherent chemical issues or was simply caused by the instability of the complex, which decomposes in solution in < 1.5 h at −50°C. An X-ray structure clarified the point: As can be seen from Figure 6, the push/pull carbene **19a** generated in situ has inserted into one of the Rh–Cl bonds, resulting in the formation of the chloroalkyl species **20**. This species can be viewed as a functionalized C-metalated rhodium enolate, chiral at metal and at the metalated C atom; it is formed as a single diastereomer.[51,52] To compensate for the loss of an anionic ligand, the now formally 16e Rh(III) center engages with the aromatic ring, as evident from the short contacts to the *ipso*- and one of the *ortho*-C atoms. This interaction likely persists in solution as suggested by the high-field shift of the corresponding C-atoms (broad signals at ≈ 94 and ≈116 ppm). The comparatively long Rh1–C1 (2.1226(12) Å) and C1–C4 (1.4666(17) Å) bonds clearly reflect the loss of true "carbene" character (note that **20** is still "carbenoid" in the sense that it contains a carbon atom carrying at the same time a metal and a leaving group).

Scheme 5. Preparation of Rh(III) half-sandwich carbene complexes.[a]



[a] Reagents and conditions: a) **9**, FC_6H_5/CH_2Cl_2, 0°C → –20°C; b) 2 $AgSbF_6$, MeCN; c) **9**, MeOH, 0°C → –20°C

The formation of **20** is thought to illustrate the exceptional electron demand of the transient Rh(III) carbene **19a**, which engenders the halide shift at low temperature. This "internal quenching" mechanism might well explain why the majority of catalytic transformations based on the decomposition of a diazoester derivative with $[Cp^*RhCl_2]_2$ uses silver salts as additives, which likely prevent such halide shifts from occurring and allows nucleophilic partners to react with the carbene center.[45-47] This hypothesis is corroborated by the outcome of the reaction of aryldiazoacetate **9** with the cationic rhodium precursor **21** (Scheme 5). In line with our expectations, the clean formation of the corresponding cationic methyl ether derivative **22** was observed, which proves that the transient rhodium carbene devoid of the potentially interfering chloride ligands is trapped by the external nucleophile MeOH chosen as the reaction medium. Complex **22** also represents a functionalized, C-metalated and chiral Rh(III) enolate; its structure is similar to the chloroalkyl species **20** even with regard to the interaction of the metal center with the electron rich arene (Figure 7).

In this context it is also noteworthy that a complex related to the chloroalkyl species **20** has previously been inferred from spectroscopic data. Thus, reaction of *iodo*-rhodium(III) tetra-*p*-tolylporphyrin with ethyl diazoacetate was proposed to afford an *iodo*alkyl complex that failed to cyclopropanate styrene.[53,54] In view of this precedent, it seemed reasonable to assume that the reaction of **9** with $[Cp^*RhX_2]_2$ (X = Br, I) in lieu of $[Cp^*RhCl_2]_2$ should also result in halide migration with formation of the corresponding haloalkyl species. Surprisingly, however, the corresponding carbene complexes **19b,c** were the major species (Scheme 5). Of note it their highly deshielded carbene center (δ_C = 314.2 ppm, X = Br; 316.4 ppm, X = I), which resonates downfield from that in the dirhodium(II) donor/acceptor carbene **10** (δ_C = 237.1 ppm).

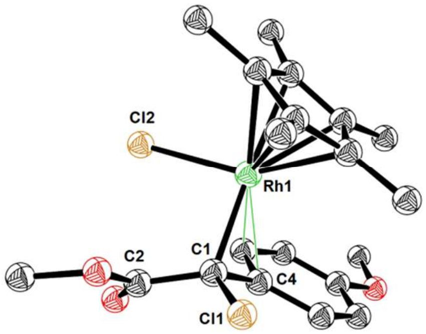


Figure 6. Structure of the chloroalkyl complex **20** in the solid state

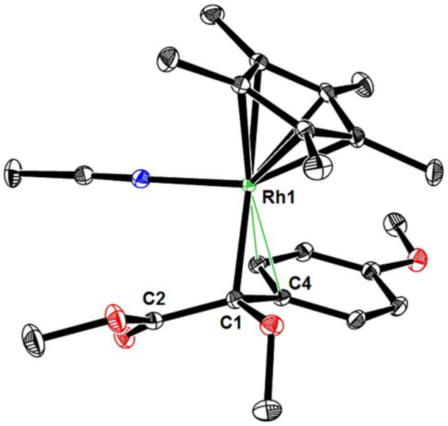


Figure 7. Structure of the methanol adduct **22** in the solid state; only the complex cation is shown for clarity

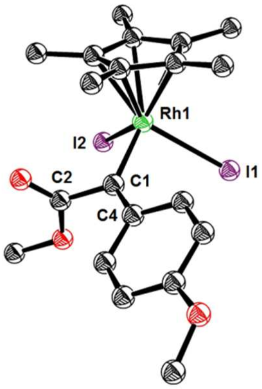


Figure 8. Structure of the half-sandwich donor/acceptor Rh(III) carbene **19c** in the solid state

The constitution of **19b,c** was unambiguously established by X-ray diffraction (Figure 8; for the dibromo complex **19b**, see the Supporting Information). As expected, the arene as the donor substituent is coplanar with the carbene center (Θ = 0.5°) to maximize orbital overlap, whereas the plane of the ester is essentially perpendicular to it (Θ = 104.5°). Along with this come a contracted C1-C4 (1.414(2) Å) but a long C1-C2 (1.497(2) Å) bond; with only 1.9671(1) Å, the Rh1-C1 bond is visibly shorter than the analogous carbene distances in the dirhodium(II) tetracarboxylate complexes outlined above. The fact that the nature of the anionic ligand determines whether a true carbene (**19b**,**c**) or a "carbenoid" (**20**) is passed through illustrates an as yet hardly recognized way to control rhodium catalyzed reactions of diazo compounds. The better performance of $[Cp^*RhI_2]_2$ as compared to $[Cp^*RhCl_2]_2$ in the cyclopropanation shown in Scheme 4 likely reflects this aspect.

CONCLUSION

The tremendous importance of rhodium carbene chemistry in general stands in striking contrast to the lack of experimental data concerning the structure of the relevant intermediates. For their pronounced electrophilicity, such species are highly unstable and therefore largely defied direct inspection by spectroscopic or crystallographic means. This difficulty notwithstanding, we are able to present a series of crystal structures of dinuclear tetracarboxylate complexes of Rh(II) as well as mononuclear half-sandwich complexes of Rh(III), which are by far the most commonly used intermediates in this field. They provide an unprecedentedly close look at representative members of these families and reveals many conformational details which could hitherto only be inferred from indirect evidence and/or in silico data. The experimental results refine the understanding of their gross structural attributes and correct pertinent bond lengths, which had previously been deduced from computational studies at different levels of theory. A recurrent theme in these X-ray structures is the staggered orientation of the carbene unit relative to the dirhodium tetracarboxlyate core carrying the ancillary ligands. This trait is critically important for the understanding of the diastereo- and enantioselective course of rhodium catalyzed reactions of diazoalkanes. While our data suggest that stereoelectronic (rather than purely steric) factors play a decisive role, the basic concept of the currently favored predictive model is validated.[12] Finally, it is shown how the anionic ligands present in half-sandwich Rh(III) carbenes regulate the electrophilicity of reactive intermediates of this type. Thus, the seemingly subtle change from bromide (or iodide) to chloride dramatically alters the chemical nature of the resulting complexes from a prototype carbene to a chloroalkyl species. This insight allows the common use of silver additives in reactions of diazoesters catalyzed by $[Cp^*RhCl_2]_2$ to be rationalized.

ASSOCIATED CONTENT

Supporting Information

Experimental part including characterization data and copies of NMR spectra of new compounds, as well as supporting crystallographic information concerning the structures of complexes **4b**, **4c**, **6b**, **6c**, **10**, **14**, **19b**, **19c**, **20** and **22** in the solid state.

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Notes

The authors declare no competing financial interests.

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