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*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b12673 • Publication Date (Web): 14 Jan 2018

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# Structure and Reactivity of Half-Sandwich Rh(+3) and Ir(+3) Carbene Complexes. Catalytic Metathesis of Azobenzene Derivatives

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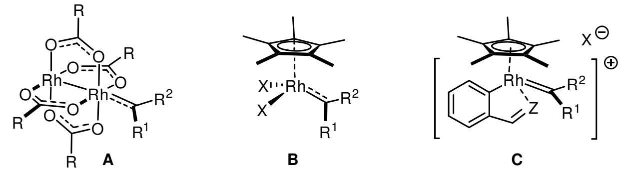
**ABSTRACT:** Traditional rhodium carbene chemistry relies on the controlled decomposition of diazo derivatives with [$Rh_2(OAc)_4$] or related dinuclear Rh(+2) complexes, whereas the use of other rhodium sources is much less developed. It is now shown that half-sandwich carbene species derived from [$Cp^*MX_2$]$_2$ (M = Rh, Ir; X = Cl, Br, I, Cp* = pentamethylcyclopentadienyl) also exhibit favorable application profiles. Interestingly, the anionic ligand X proved to be a critical determinant of reactivity in the case of cyclopropanation, epoxide formation and the previously unknown catalytic metathesis of azobenzene derivatives, whereas the nature of X does not play any significant role in -OH insertion reactions. This perplexing disparity can be explained on the basis of spectral and crystallographic data of a representative set of carbene complexes of this type, which could be isolated despite their pronounced electrophilicity. Specifically, the donor/acceptor carbene **10a** derived from ArC(=$N_2$)COOMe and [$Cp^*RhCl_2$]$_2$ undergoes spontaneous 1,2-migratory insertion of the emerging carbene unit into the Rh–Cl bond with formation of the C-metalated rhodium enolate **11**. In contrast, the analogous complexes **10b**,**c** derived from [$Cp^*RhX_2$]$_2$ (X = Br, I) as well as the iridium species **13** and **14** derived from [$Cp^*IrCl_2$]$_2$ are sufficiently stable and allow true carbene reactivity to be harnessed. These complexes are competent intermediates for the catalytic metathesis of azobenzene derivatives, which provides access to α-imino esters that would be difficult to make otherwise. Rather than involving metal nitrenes, the reaction proceeds via aza-ylides that evolve into diaziridines; a meta-stable compound of this type has been fully characterized.

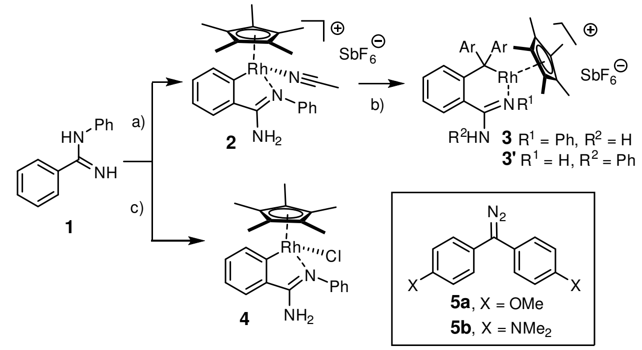
## INTRODUCTION

Dirhodium carbenes **A** formed in situ upon reaction of a diazo derivative with a (chiral) dinuclear Rh(II) tetracarboxylate complex are exceptionally versatile synthetic intermediates that power a host of transformations, including (asymmetric) cyclopropanations, C–H insertions, cycloaddition reactions and a myriad of ylide chemistry (Scheme 1).[1-7] Although the original report on the use of [$Rh_2(OAc)_4$] had indicated that a salt as simple as $RhCl_3 \cdot 3H_2O$ is also catalytically competent,[8a] mononuclear Rh(+3) carbene complexes in general and half-sandwich carbenes derived from [$Cp^*RhX_2$] precursors in particular have not been studied nearly as thoroughly.[8a,9] Only recently have intermediates of this type been implicated in directed C–H activation reactions, in which the precatalyst is first ionized e. g. with a soluble Ag(I) salt; the resulting electrophilic metal fragment [$Cp^*Rh$]$^{2+}$ then (cyclo)metalates the (arene) substrate *prior* to reaction with a diazo derivative to give a putative Rh(+3) carbene of type **C** which undergoes migratory insertion to give an *ortho*-substituted product.[10] This sequence has become quite popular: although most applications use transient carbenes **C** with at least one acceptor substituents ($R^1$ and/or $R^2$ = electron withdrawing group),[11] the example from our laboratory shown in Scheme 1 proves that even a donor/donor carbene is sufficiently electrophilic to give the meta-stable metallacycle **3** (Ar = $MeOC_6H_4$-) comprising a rare *tert*-alkyl rhodium unit, which could be characterized by crystallographic means (Figure 1).[12] The fact that complex **4** as the neutral analogue of the purported intermediate **2** could also be isolated in crystalline form (for its structure in the solid state, see Figure S1) lends credence to the proposed pathway.[12]

In contrast to the popularity of this type of directed C-H activation via cyclometalated rhodium carbenes **C**, proper pianostool Cp*Rh(+3) carbene complexes of type **B** have been studied much less extensively.[13] This situation, however, might be unjustified: During recent studies on structure and bonding in late-transition metal carbene complexes,[14-16] we found such species to be competent intermediates in catalytic cyclopropanation, alkoxyfuran formation, as well as RO–H and $R_3$Si–H insertion reactions.[17] Moreover, crystal structures of two reactive complexes of type **B** have been obtained.[17] We now follow up on these initial results and disclose a more comprehensive investigation into half-sandwich Cp*M carbene complexes of Rh(+3) and Ir(+3). Most notably, a striking correlation between the chosen counterion X and the stability and reactivity of the corresponding carbene was noticed that can be explained on the basis of the acquired structural data. Moreover, we now report that the new pianostool carbene complexes enable *catalytic* metathesis reactions of azo compounds which seem to be unprecedented in the literature.

**Scheme 1. Prototype Rhodium Carbene Complexes (top); Example of a "Donor/Donor" Carbene Participating in Directed CH-Activation/Carbene Insertion**[a]





[a] Reagents and Conditions: a) (i) $[Cp^*Rh(MeCN)_3][SbF_6]_2$, MeCN, reflux, see ref. 12; b) **5a**, $CH_2Cl_2$; c) $[Cp^*RhCl_2]_2$, NaOAc, toluene, reflux; Ar = 4-methoxyphenyl

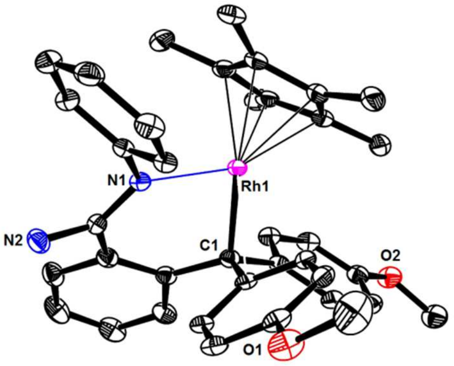


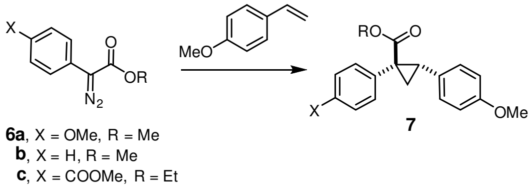
**Figure 1**. Structure of the cyclometalated product **3** formed by directed C–H activation followed by carbene insertion; the disordered $SbF_6^-$ counterion and solute $CH_2Cl_2$ are not shown for clarity

## RESULTS AND DISCUSSION

**Strong Effect of the Anionic Ligand on Reactivity**. The reaction of the diazo derivative **6a** with excess 4-methoxystyrene was chosen for an initial catalyst screening (Table 1). $[Cp^*RhCl_2]_2$ (1 mol%) afforded the expected cyclopropane **7**, but the yield remained low (≤ 46%) despite attempted optimization. Surprisingly, the result was improved when the chloride ligands on rhodium where replaced by iodide. Similarly, it was found that the formal substitution of Rh by Ir as the central metal furnished **7** in appreciable yield;[18] although the chosen anionic ligands still exert some influence, the effect seems to be less pronounced in the Ir series.

The same trend was observed in reactions with aromatic aldehydes, which are known to give epoxides when reacted with certain metal carbenes generated in situ.[19-22] Because the reaction is thought to commence with attack of the C=O heteronucleophile onto the carbene to give a carbonyl ylide intermediate, we conjectured that Rh(+3) half-sandwich carbenes might be particularly well suited because of their high oxidation state (Table 2). To our surprise, however, $[Cp^*RhCl_2]_2$ led to hardly any conversion (entry 1), whereas $[Cp^*RhI_2]_2$ afforded **8** in good yield as a single diastereomer (entry 2). The *cis*-disposition of the ester and the aryl substituent (see Figure S2) implies intervention of the ylide conformer **E** which is favored over **D** on steric grounds as it avoids the substituent R from clashing into the bulky ligand sphere about Rh comprising the Cp* and two chloride ligands. Epoxide formation proceeded without incident even if an electron-withdrawing substituent on the arene ring renders the aldehyde oxygen atom less nucleophilic and hence carbonyl ylide formation less favorable (entry 6).[23] Overall, $[Cp^*RhI_2]_2$ compares favorably with $Rh_2(OAc)_4$ previously used in the literature (compare entries 2/3 and 7/8), whereas $[Cp^*RhCl_2]_2$ is inadequate.[19] As previously communicated, $[Cp^*RhI_2]_2$ also performed well in a Si–H insertion reaction;[17] once again, use of the iodide-containing catalyst is necessary, whereas its chloride-based analogue basically fails to react.

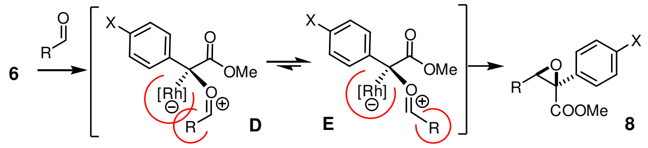
**Table 1. Catalyst Screening: Cyclopropanation**



| Entry | Substrate | Catalyst (1 mol%) | Solvent | T (°C) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | **6a** | $[Cp^*RhCl_2]_2$ | pentane | 22 | ≤ 46 |
| 2 | **6a** | $[Cp^*RhI_2]_2$ | pentane | 22 | 79 |
| 3 | **6a** | $[Cp^*IrCl_2]_2$ | $CH_2Cl_2$ | 40 | 63 |
| 4 | **6c** | $[Cp^*IrI_2]_2$ | $CH_2Cl_2$ | 22 | 58 |

[a] Yield of isolated product

**Table 2. Catalyst Screening: Darzens-type Epoxide Formation**[a]

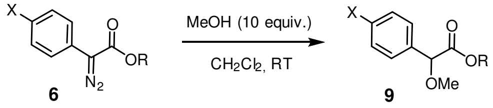


| Nr | Substrate | R | Catalyst (1 mol%) | Yield (%)[c] |
|---|---|---|---|---|
| 1 | **6b** | Ph | $[Cp^*RhCl_2]_2$ | 7 (GC) |
| 2 | **6b** | Ph | $[Cp^*RhI_2]_2$ | 61 |
| 3 | **6b** | Ph | $Rh_2(OAc)_4$ [b] | 66[19b] |
| 4 | **6b** | 4-$MeOC_6H_4$- | $[Cp^*RhI_2]_2$ | 96 |
| 5 | **6a** | 4-$MeOC_6H_4$- | $[Cp^*RhI_2]_2$ | 83 |
| 6 | **6b** | 4-$(MeOOC)C_6H_4$- | $[Cp^*RhI_2]_2$ | 85 |
| 7 | **6b** | PhCH=CH- | $[Cp^*RhI_2]_2$ | 88 |
| 8 | **6b** | PhCH=CH- | $Rh_2(OAc)_4$ [b] | 50[19b] |
| 10 | **6b** | EtCH=CH- | $[Cp^*RhI_2]_2$ | 98 |

[a] Unless stated otherwise, all reactions were carried out in $CH_2Cl_2$ at ambient temperature; [b] in refluxing $CH_2Cl_2$; [c] yield of isolated product, unless stated otherwise

The strong correlation between efficiency and the nature of the halide ligand X manifest in these examples stands in striking contrast to the results for the catalyzed insertion of **6** into the O–H bond of methanol (Table 3): all tested $Cp^*MX_2$ precatalysts – independent of their anionic ligand – afforded product **9** in good to excellent yield; even an Ir(I) complex proved effective.

**Table 3. Catalyst Screening: -OH Insertion Reaction**[a]



| Entry | X | Catalyst (1 mol%) | Yield (%)[b] |
|---|---|---|---|
| 1 | –OMe | $[Cp^*RhCl_2]_2$ | 83[c] |
| 2 | –OMe | $[Cp^*RhI_2]_2$ | 88 |
| 3 | –OMe | $[Cp^*IrCl_2]_2$ | 74 |
| 4 | –OMe | $[Cp^*IrI_2]_2$ | 76 |
| 5 | –COOMe | $[Cp^*IrI_2]_2$ | 90 |
| 6 | –OMe | $[(cod)IrCl]_2$ | 98[c] |

[a] All reactions were carried out in $CH_2Cl_2$ or pentane at ambient temperature; [b] yield of isolated product, unless stated otherwise; [c] NMR yield

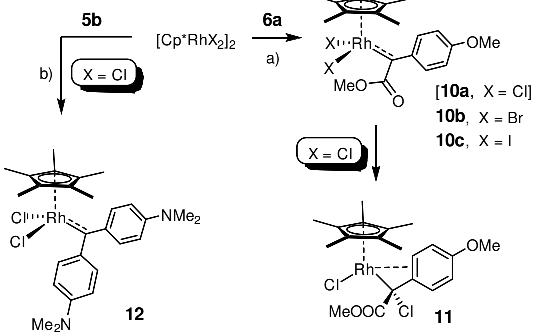
These strikingly different trends could not be reconciled at the outset of the project. Therefore it was deemed necessary to characterize the purported half-sandwich carbene intermediates of type **B** in more detail.

**Structures of Cp*M Carbene Complexes (M = Rh, Ir) in the Solid State**. Despite the tremendous preparative importance, carbene complexes **A** derived from dirhodium tetracarboxylate precatalysts had defied all attempts at experimental characterization for decades; only recently have spectral and crystallographic data of a representative set of reactive intermediates of this type been obtained.[15,17,24] In concord with computational results,[25] the gathered information suggests that the second rhodium atom exerts a stabilizing function as an integral part of the three center/four electron Rh(+2)–Rh(+2)–$CR_2$ core.[26] In recognition of the critical role of metal-metal bonding, it was expected that *mono*-nuclear complexes of type **B** might be even more fragile because such assistance by a neighboring metal center is missing and the oxidation state of rhodium is also higher (+3 in **B** versus +2 in **A**).

In fact, it required considerable experimentation until we managed to isolate the donor/acceptor carbene complexes **10** derived from the diazo ester derivative **6a** and $[Cp^*RhX_2]_2$ (X = Cl, Br, I) (Scheme 2). As previously reported, compounds **10b** (X = Br) and **10c** (X = I) represent the first true half-sandwich donor/acceptor carbene complexes of Rh(+3) to be fully characterized.[17] In contrast, the chloride analogue **10a** (X = Cl) escaped all attempts at isolation: although there is no doubt that this species is transiently formed, the nascent carbene unit inserts into one of the Rh–Cl bonds even at −50°C.[27,28] The structure of the resulting product **11** in the solid state shows a functionalized C-metalated rhodium enolate;[29] alternatively, this species can be viewed as a rhodium carbenoid because it comprises a C-atom carrying a metal atom and chloride as a potential leaving group.[17] The metalated center resonates at $\delta_C$ = 70.6 ppm ($CD_2Cl_2$, −50°C), whereas the true carbene complexes **10b**,**c** have the expected low-field NMR signatures ($\delta_C$ = 314.2 ppm (X = Br), 316.4 ppm (X = I)). Interestingly, these resonances are significantly downfield from those of all dirhodium carbene complexes of type **A** characterized so far (ca. 235-270 ppm).[17,24]

The spontaneous formation of **11** at cryogenic conditions suggests that the chloride ligands render the carbene center of transient **10a** so electrophilic that spontaneous 1,2-migratory insertion will ensue; in contrast, the somewhat less electronegative bromide or iodide ligands are incapable of triggering this process. Under this premise it seemed likely that formal replacement of the donor/acceptor entity of transient **10a** by an inherently less electrophilic donor/donor carbene[15a,30] would also prevent such a spontaneous insertion step from occurring. In fact, reaction of $[Cp^*RhCl_2]_2$ with **5b** furnished complex **12**, in which both chlorides remain bound to the Rh(+3) center and the carbene unit is fully intact (Scheme 2 and Figure 2). As one might expect, the Rh1–C1 distance (2.014(3) Å) of **12** is somewhat longer than that of **10c** (1.970(3) Å).[17]

**Scheme 2. Preparation of Half-Sandwich Rh(+3) Carbenes[a]**



[a] Reagents and conditions: (a) **6a**, $CH_2Cl_2/FC_6H_5$, 0°C → −20°C, see ref. 17; (b) **5b**, $CH_2Cl_2/FC_6H_5$, 0°C → −20°C

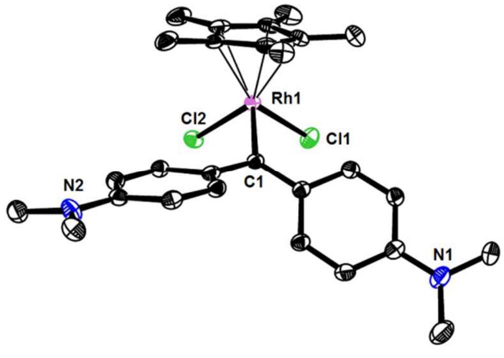
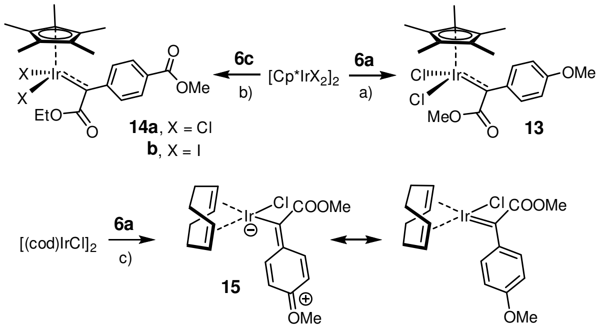


**Figure 2**. Structure of the donor/donor Cp*Rh(+3) carbene complex **12** in the solid state

**Scheme 3. Preparation of Iridium-Carbene Complexes[a]**



[a] Reagents and Conditions: a) **6a**, $CH_2Cl_2/FC_6H_5$, 0°C → −20°C; (b) **6c**, $CH_2Cl_2/FC_6H_5$, 0°C → −20°C; c) **6a**, $CH_2Cl_2/FC_6H_5$, 0°C → −20°C; cod = 1,5-cyclooctadiene

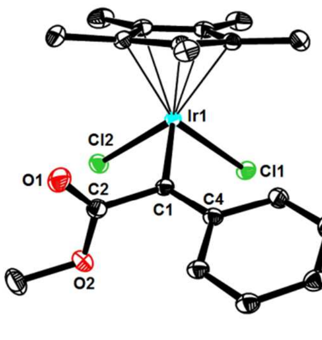


**Figure 3**. Structure of the Ir(+3) half-sandwich carbene complex **13** in the solid state; disordered fluorobenzene in the unit cell is not shown for clarity

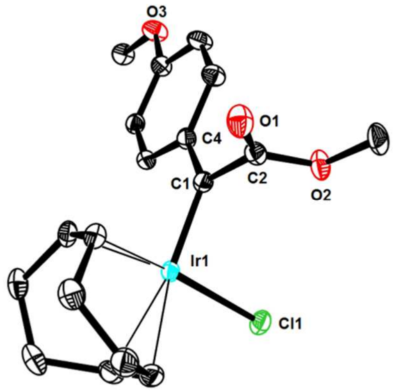


**Figure 4**. Structure of the Ir(+1) donor/acceptor carbene complex **15**

Formal replacement of Rh(+3) by Ir(+3) as the central metal also suppressed the ligand coupling (Scheme 3). Complex **13** is the iridium analogue of the transient rhodium carbene **10a** that had defied characterization (Figure 3).[31] Interestingly, the carbene center of **13** resonates at $\delta_C$ = 275.9 ppm ($CD_2Cl_2$) and is hence much less deshielded than those of the rhodium species **10b** (314.2 ppm) and **10c** (316.4 ppm). Moreover, the Ir1–C1 carbene bond (1.960(2) Å) is shorter than the Rh1–C1 bonds in **10c** (1.970(3) Å),[17] which speaks for stronger backbonding from Ir(+3) into the "empty" carbene orbital. The arene ring in **13** is aligned for maximal orbital overlap between the π-system and the carbene; as a consequence, the C1–C4 bond is markedly contracted to 1.429(3) Å. These structural attributes showcase that the donor substituent largely accounts for the stabilization of highly electrophilic species of this type. In contrast, the electron-withdrawing ester group is almost orthogonal to the carbene as to prevent any further destabilization of the already highly electron deficient site; the decoupling is also manifest in the rather long C1–C2 distance (1.510(3) Å).

We also managed to isolate the analogous Ir(+1) carbene **15**; the interest in this species was nurtured by the fact that $[(cod)IrCl]_2$ had proven competent in –OH insertion reactions (Table 3, entry 6).[32,33] The $^{13}C$ NMR spectrum of **15** shows four pairs of differently broadened lines for the cod ligand. This observation suggests twofold symmetry, whereby the broadening comes from the dynamic averaging about the symmetry axis. The resonances of the aromatic signals in the NMR spectra of **15** are also broad due to hindered rotation about the C1–C4 bond. The partial double bond character manifest in this spectral feature corresponds well to the crystallographic data, which show a short C1–C4 distance and an almost perfect alignment of the arene with the carbene "empty" orbital (Figure 4). As in **13**, it is largely the arene substituent that imparts (meta)stability onto this donor/acceptor carbene via delocalization of charge density within the aromatic π-cloud.[15,17] In line with the lower oxidation state of and hence higher electron density at the central metal, the Ir1–C1 carbene bond (1.912(3) Å) of **15** is shorter than that of the Ir(+3) species **13** (1.960(2) Å).[34] Yet, the dynamic behavior observed by NMR proves that even in **15** the carbene unit has little double bond character; the bond order of its Ir(+3) sibling **13** must therefore be even lower.

Not unexpectedly, the preparation of complexes **14a,b** was even more challenging as they carry an electron-withdrawing ester function (rather than a MeO- substituent) on the aryl ring (Figure 5).[35] The emerging "acceptor/acceptor" character is manifest in the structural data of **14a** in the solid state: as a deactivated arene is obviously less capable of compensating the electron deficiency of the adjacent carbene, the C1–C5 bond (1.460(4) Å) is markedly longer than that in the donor/acceptor carbene **13** (1.429(3) Å). As a consequence, back-donation from [Cp*Ir] is upregulated, which results in a significant contraction of the carbene Ir1–C1 bond to 1.914(3) Å in **14a** (versus 1.960(2) Å in **13**).

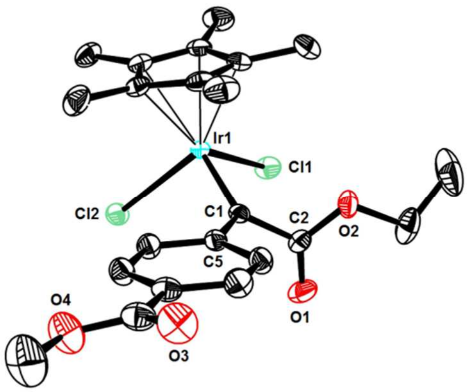


**Figure 5**. Structure of the half-sandwich "acceptor/acceptor" carbene **14a** in the solid state; $CH_2Cl_2$ in the unit cell is not shown for clarity

These insights into the subtle interplay between the central metal and the ligand framework allowed the reactivity trends to be rationalized that had surfaced during the initial screening. The striking correlation between the halide ligand X in the precatalyst and the efficiency of the cyclopropanation of olefins (Table 1) and the Darzens-type reactions of aromatic aldehydes (Table 2) likely has its origins in the distinct migratory aptitudes of X (Cl >> Br ≈ I) and hence the largely different stability of the carbene complexes of type **B**: the chloride-containing Cp*Rh(+3) carbene **10a** is only transiently formed: intramolecular carbene insertion into the Rh–Cl bond is evidently faster than the intermolecular attack of the C=O group of an aldehyde partner, which prevents carbonyl ylide **E** from forming and hence brings epoxidation to a halt. The resulting "carbenoid" **11** is also unlikely to cyclopropanate styrene, certainly not under mild conditions.[28] For **10b**,**c** (M = Rh, X = I, Br) as well as for all Cp*Ir(+3) complexes, in contrast, this migratory process has not been observed; such species are therefore competent partners in the cited transformations. The fact that the reaction with methanol seems largely unaffected by such changes in the precatalyst (Table 3) is understood if one considers that even a carbenoid such as **11** will react with an alcohol substrate.[17]

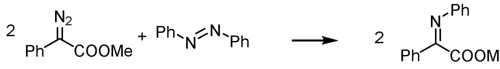
**Catalytic Azo-Metathesis**. The ability of certain Fischer carbene complexes to cleave the –N=N– bond of an azobenzene derivative has previously been demonstrated;[36-38] to the best of our knowledge, however, this transformation has never been translated into a *catalytic* process that would open a relevant new entry into α-imino esters. Compounds of this type find many different applications, which have recently been covered in a comprehensive review;[39] therefore it may suffice to mention that asymmetric reduction of α-imino esters provides rapid access to amino acid building blocks, whereas many organometallic reagents attack their imine entity at nitrogen (rather than at carbon) and, in doing so, lead to valuable N-substituted amino acid derivatives.[39,40]

Although condensation of an α-oxo-ester with the appropriate amine partner seems to be the obvious way for making α-imino esters such as **17**, numerous alternative methods have been developed in the past.[39] Especially when it comes to reacting poorly nucleophilic amines and/or sensitive α-oxo esters, recourse to a phosphine–mediated Staudinger ligation of an azide precursor with the carbonyl is often the method of choice, despite the poor atom economy of this process.[41] More recently, α-imino esters were prepared from donor/acceptor dirhodium carbenes upon reaction with aryl azides.[42,43]

Compared to azides, azoarenes have many obvious advantages as possible source of an [Ar–N=] fragment, because they are stable, safe, benign and readily available in functionalized form; for their role as classical dyes, a sizeable number of such compounds is available even in bulk quantities. Therefore it seemed warranted to investigate whether catalytic metathesis of azobenzene derivatives opens a potentially orthogonal gateway to α-imino esters that are difficult to make otherwise. To this end, however, –N=N– bond cleavage must outperform directed *ortho*-metalation of the azobenzene substrate.[44] This is a non-trivial task since the directing effect of the –N=N– bridge onto rhodium complexes is well established and has already served heterocycle synthesis in the past.[45]

Gratifyingly though, the reaction of diazo derivative **6b** with azobenzene **16** in the presence of catalytic $[Cp^*RhI_2]_2$ in toluene furnished traces of the desired α-imino ester **17** (Table 4, entry 3; for the product structure, see Figure S3); although a better yield was obtained at reflux temperature, the outcome proved erratic upon attempted scale-up (entry 4). We surmised that light might play a role in triggering isomerization of the largely *E*-configured azo derivative **16** to the potentially more nucleophilic and sterically less hindered *Z*-isomer.[46,47] This assumption proved correct in that essentially quantitative conversion was reached when the diazo derivative was added over the course of 2 h to the mixture irradiated with light emitted by a commercial blue LED; the 91% yield of pure **17** obtained under these conditions proved well reproducible (entry 8). As no other product derived from the azobenzene substrate was detected in the crude material, both halves of **16** must have ended up in the product. A control experiment using an unsymmetrical azobenzene derivative confirmed this conclusion (see below, Scheme 4).

**Table 4**. Catalytic Metathesis of Azobenzene



**6b** **16** **17**

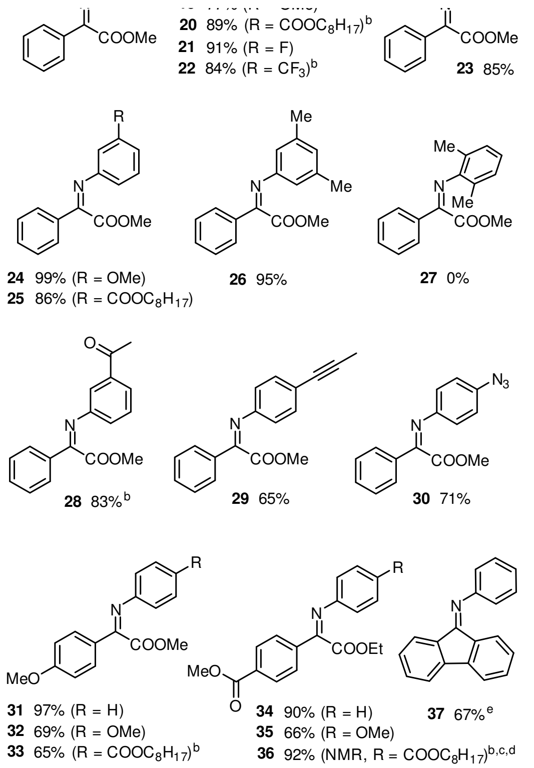
| Nr | Catalyst (2 mol%) | solvent | T | LED[a] | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $[Cp^*RhCl_2]_2$ | toluene | RT | – | < 1 |
| 2 | | toluene | RT[c] | + | 13 |
| 3 | $[Cp^*RhI_2]_2$ | toluene | RT | – | 8 |
| 4 | | toluene | 80°C | o | ≤ 69[d] |
| 5 | | THF | 80°C | o | < 1 |
| 6 | | MeCN | 80°C | o | 14 |
| 7 | | DCE | 80°C | o | 48 |
| 8 | | toluene | RT[c] | + | 98 (91) |
| 9 | $[Cp^*RhBr_2]_2$ | toluene | RT[c] | + | 98 |
| 10 | $[Rh_2(OAc)_4]$ | toluene | RT[c] | + | 72 |
| 11 | $[Cp^*IrCl_2]_2$ | toluene | RT[c] | + | 93 |
| 12 | $[Cp^*IrI_2]_2$ | toluene | RT[c] | + | 96 |
| 13 | $[(cod)IrCl]_2$ | toluene | RT[c] | + | 16 |
| 14 | $[Cu(MeCN)_4]PF_6$ | toluene | RT[c] | + | 16 |

[a] +: irradiation with light emitted by commercial blue LED; –: the reaction was carried out in the dark; o: daylight; [b] NMR yield (isolated yield); [c] despite irradiation, the internal temperature was only slightly above RT when the reaction was carried out in toluene; [d] poor reproducibility on scale up, see Text

A brief screening showed once again a striking correlation between catalytic activity and the nature of the anionic ligands (I ≈ Br >> Cl) when working with half-sandwich rhodium precatalysts of type $[Cp^*MX_2]_2$; this effect basically vanished for M = Ir(+3) (Table 4). In view of the structural data outlined above, these trends suggest the intervention of true carbene intermediates. In line with this notion, $[Rh_2(OAc)_4]$ was also found effective (entry 10), although the yield was lower and the functional group tolerance definitely inferior (see below); in contrast, Ir(+1) as well as Cu(+1) proved inadequate (entries 13, 14).

Under the optimized conditions, the reaction shows a broad scope and appreciable compatibility with polar and apolar substituents; moreover, it was found to scale well. As can be seen from Table 5, the azobenzene derivative to be metathesized can be electron rich or electron poor, even though the latter usually require higher temperatures. The need for more forcing conditions suggests that the reaction commences with attack of an N-atom of the azo-bridge onto the electrophilic carbene center, which is obviously less favorable for electron deficient substrates. In any case, the new methods allows α-imino esters such as **20**-**22**, **25**, **28**, **33** and **36** to be made, which are difficult to access by conventional carbonyl condensation since the required aniline derivatives are poorly nucleophilic and therefore do not react well with an α-oxo-ester. The substituents can be placed *ortho*, *meta* or *para* to the azo bridge with little change in efficiency; only the 2,6-disubstituted derivative **27** did not form, most likely because the –N=N– unit is too shielded for attack onto the rhodium intermediate. Donor/acceptor carbenes of the structural type discussed in the previous sections of this paper gave the best results; electron donating or withdrawing substituents on their aryl rings do not matter much. The more stabilized donor/donor carbenes react reluctantly (see product **37**): their carbene center is less electrophilic and hence less susceptible to attack by the –N=N– bridge. In contrast, diazo derivatives with only electron withdrawing substituents such as diazomalonate are not decomposed by $[Cp^*MX_2]_2$ and therefore cannot be used at the current stage of development. Moreover, an attempt at using this reaction for the ring opening of pyridazine, a heteroaromatic "azo"-derivative, met with failure, because this and related substrates form stable adducts with the $[Cp^*RhCl_2]$ fragment.[48]

**Table 5**. **Selection of imines formed by azobenzene metathesis**[a]

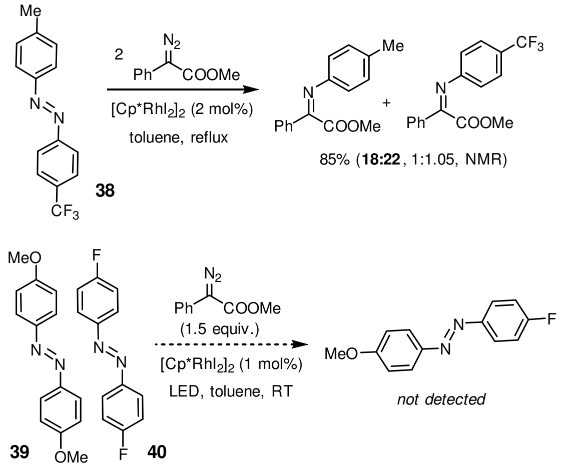


[a] unless stated otherwise, all compounds were made using $[Cp^*RhI_2]_2$ (1 mol%) in toluene at ambient temperature under irradiation with light emitted by blue LED's; [b] at 90°C; [c] using $[Cp^*IrI_2]_2$ as the catalyst; [d] the product is subject to partial hydrolysis during flash chromatography; [e] addition of the diazo derivative over 5 h

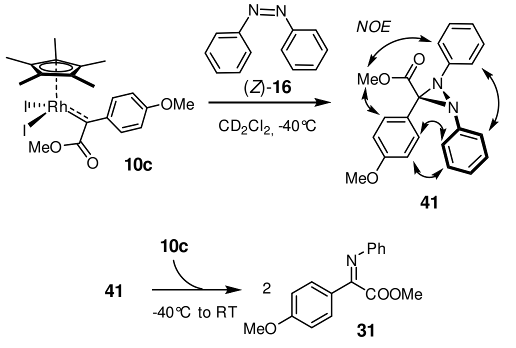
Compounds **28**-**30** nicely illustrate the favorable chemoselectivity profile of this new transformation. An imine such as **28** bearing an unprotected ketone on its backbone is neither accessible from an α-oxo-ester by ordinary condensation chemistry nor by Staudinger ligation. Furthermore, the intact alkyne in compound **29** shows that catalytic –N=N– cleavage is faster than cyclopropene formation.[17] Arguably most notable, however, is the synthesis of product **30**: the fact that $[Cp^*RhI_2]_2$ cleaved the azo bridge while leaving the azide intact sets this catalyst apart from many other metal complexes (including $[Rh_2(OAc)_4]$ and other dirhodium tetracarboxylate complexes), which readily react with azides to form highly reactive metal nitrene intermediates.[49,50]

**Mechanistic Studies**. The stoichiometric reactions of Fischer carbene complexes of tungsten or chromium with azo derivatives reported in the literature had been explained in analogy to canonical olefin metathesis by invoking metal-nitrenes and metallacyclic intermediates.[36,37] Although rhodium nitrene complexes could not be excluded as the propagating species at the outset of our investigation, the lack of any scrambling of the azobenzene derivatives **39** and **40** in the control experiment shown in Scheme 4 argued against such a scenario.

**Scheme 4. Control Experiments**



**Scheme 5. Formation and Evolution of a Diaziridine Intermediate**



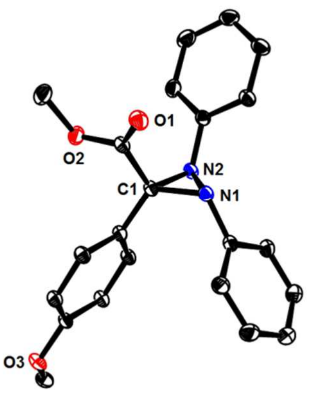


**Figure 6**. Structure of diaziridine **41** in the solid state

We conjectured that the new catalytic metathesis reaction of azobenzene derivatives described herein might commence by attack of an N-atom of the –N=N– bridge onto the half-sandwich rhodium (iridium) carbene to form an ylide intermediate in the first place. With samples of pure crystalline carbenes in hand, we were in a positon to test this hypothesis.

To this end, a sample of (*Z*)-**16** was prepared according to the literature,[51] as the preparative results had clearly indicated that only this geometric isomer engages in metathetic N=N bond cleavage. Slow warming of a 1:1 mixture of (*Z*)-**16** and complex **10c** in $CD_2Cl_2$ solution in the dark from −78°C to ambient temperature afforded the expected α-imino ester **31** and unreacted azobenzene in a ≈ 2.9:1 ratio (NMR) (Scheme 5); importantly, recovered **16** had completely isomerized to the thermodynamically more stable (*E*)-isomer. This outcome shows that the reaction pathway involves a reversible step generating the unreactive azobenzene isomer and hence explains why constant light-driven $E\rightarrow Z$ isomerization is necessary for full conversion in a catalytic set-up. Treatment of (*Z*)-**16** with two equivalents of **10c** led to clean formation of **31** as the only product detected by NMR. This experiment proved that both halves of the azobenzene convert into product; the use of the unsymmetrical substrate **38** confirmed this conclusion (Scheme 4).

Monitoring of the 1:1 mixture of **10c** and **16** by NMR showed the build-up of an intermediate, which reached maximum concentration at −40°C; it proved stable enough for full characterization when kept cold. This compound was unambiguously assigned the diaziridine structure **41** based on extensive 1D and 2D NMR analyses; the *trans*-disposition of the two phenyl rings derived from the azobenzene was evident from the NOESY data and the presence of two signals in the $^{15}N$ NMR spectrum. This stereochemical setting implies that *cis/trans*-isomerization must have taken place *prior* to formation of the three-membered ring; the cyclization is therefore almost certainly a stepwise rather than concerted process. The assignment was confirmed when crystals of this metastable intermediate suitable for X-ray diffraction could be grown. The structure of **41** in the solid state (Figure 6) features an almost isosceles trianglar core, in which the N1–N2 single bond (1.481(2) Å) is only slightly longer than C1–N1 (1.459(2) Å) and C1–N2 (1.463(3) Å) bonds and all three angles are very close to 60°.

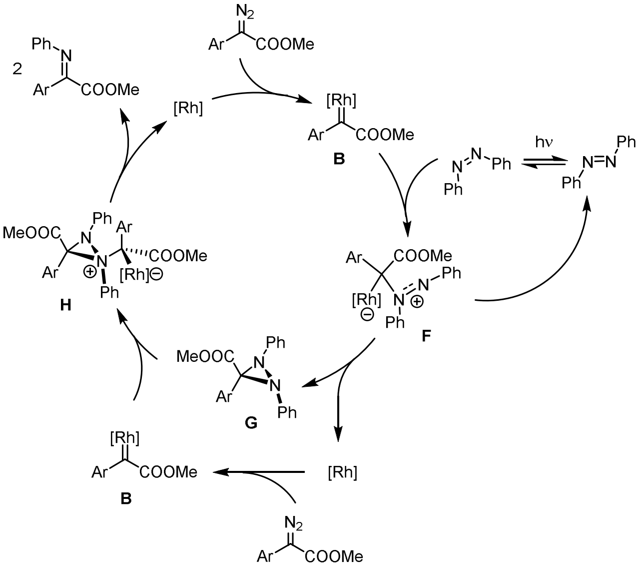
Diaziridine **41** reacts with a second equivalent of the rhodium half-sandwich carbene complex **10c** to yield two equivalents of **3** (Scheme 5). This result suggests that the N-atoms of **41** are sufficiently nucleophilic to attack the carbene center.

Diaziridines had been formed in modest yields in some of the stoichiometric reactions of Fischer tungsten carbenes with (electron deficient) azo compounds, when carried out in polar solvents such as MeCN.[37a,52] Although a possible role in the stoichiometric metathesis of azobenzene had not been excluded, the –N=N– cleavage was explained in a canonical fashion via metal-nitrene complexes and diazametallacyclobutane derivatives in analogy to the Chauvin cycle of regular olefin metathesis.[37a] Actually, it was insinuated at one point that diaziridine formation and metathesis might be competing reaction channels.[52]

In striking contrast to the literature, all available experimental data suggest that the rhodium catalyzed cleavage of azobenzenes described herein passes through a diaziridine as the key intermediate. We confidently propose that the reaction proceeds as shown in Scheme 6: the electrophilic rhodium carbene **B** primarily formed succumbs to attack by an N-atom of azobenzene, provided the latter is (*Z*)-configured. This step is likely reversible even at low temperature and leads to isomerization of the substrate, which therefore constantly needs to be photo-isomerized back to the active form to ensure complete conversion in the catalytic set-up. The resulting ylide **F** evolves into diaziridine **G**, such that the transannular interactions between the aryl substituents are minimized. Attack by a second carbene **B** affords an intermediate of type **H** which breaks down, presumably via a cheletropic process, to give two equivalents of the α-imino ester product.[53]

Overall, the stepwise scission of the –N=N– bond of azobenzene by a metal carbene described herein is reminiscent of the equally stepwise metathetic cleavage of the –N≡N triple bond of aryldiazonium salts by metal alkylidynes recently described by our group.[54] Though certainly overshadowed by the immense success of alkene[55,56] and alkyne metathesis,[57] these and other unorthodox manifestations showcase that metathesis in general continues to provide many opportunities for methodological innovation.[58]

**Scheme 6. Proposed Catalytic Cycle; [Rh] = $Cp^*RhI_2$**



## CONCLUSIONS

Although the net outcome of the reaction between a rhodium carbene and the hetero-double bond of azobenzene formally represents a “metathesis” reaction, the underlying mechanism is distinct from the principles governing alkene metathesis, which became immensely popular and versatile with the advent of the well-defined Schrock- and Grubbs-type catalysts.[55] In any case, the new manifold increases the portfolio of multiple-bonded substrates amenable to metathesis and provides access to synthetically valuable α-imino esters, some of which would be difficult to make otherwise.

The most effective and tolerant precatalysts are half-sandwich complexes of type $[Cp^*MX_2]_2$ (M = Rh, Ir), which perform better than the popular dirhodium tetracarboxylate complexes that dominate contemporary rhodium carbene chemistry. A representative set of pertinent half-sandwich Cp*M carbene complexes has been isolated and fully characterized, despite their sensitivity. The acquired data explain why the reactivity of this previously unexplored class of intermediates is strongly correlated with the nature of the halide ligands X; most notably, the complex derived from $[Cp^*RhCl_2]_2$ undergoes spontaneous migratory insertion of the incipient carbene unit into the Rh–Cl bond before true carbene reactivity can be harnessed. This and related results allow a host of preparative data to be rationalized, and should provide guidance for further explorations of the field.

## ASSOCIATED CONTENT

**Supporting Information**. Experimental part including characterization data, NMR spectra of new compounds, and supporting crystallographic information (PDF)

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## ACKNOWLEDGMENT

We thank Mr. S. Größl and Dr. J. Murphy for valuable discussions and the analytical departments of our Institute for excellent support. Generous financial support by the MPG is gratefully acknowledged.

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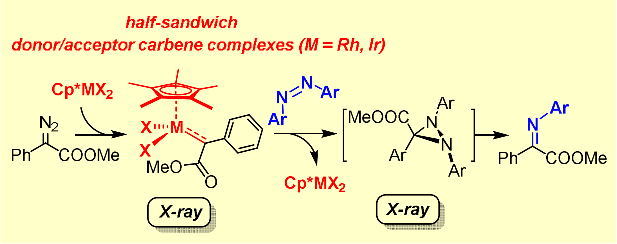
half-sandwich
donor/acceptor carbene complexes (M = Rh, Ir)
Cp*MX2
N2
Ph
COOMe
X
M
X
MeO
O
X-ray
N
N
Ar
Ar
Cp*MX2
MeOOC
N
Ar
Ar
N
Ar
X-ray
N
Ar
Ph
COOMe